LOCATION OF GUEST SPECIES IN ZEOLITES
BY SOLID-STATE NMR

by

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ABSTRACT

Zeolites and related microporous materials are exploited in many commercial applications because of the size and shape selectivity conferred by the molecular dimensions of their channel and cage systems. However, at present there is little direct information regarding the exact location of guest species within these materials; it is difficult to determine the structures of the host-guest complexes by X-ray diffraction techniques due to the limited availability of suitable crystals, and theoretical calculations are not always in agreement with one another.

This thesis describes the application and evaluation of cross polarization (CP), rotational echo double resonance (REDOR), and transferred echo double resonance (TEDOR) solid-state NMR experiments for determining the complete three-dimensional structures of zeolite frameworks containing guests such as ions or sorbed organic molecules. In principle, these techniques permit accurate internuclear distances between spin-1/2 nuclei to be determined from measurements of the heteronuclear dipolar coupling.

The viability and reliability of $^{19}$F-$^{29}$Si CP, REDOR and TEDOR NMR experiments was demonstrated by locating the fluoride ions within the octadecasil framework. The experimental methods were optimized and appropriate mathematical data analysis strategies developed. A comprehensive description of the mathematical methods is included. Accurate Si-F distances were determined which were in excellent agreement with those known from the single crystal structure.

A series of calculations provided insight into the likelihood of being able to obtain reliable distances from REDOR and TEDOR data in cases where information regarding the number of spins, and the geometrical arrangement of these, is not known a priori.
Preliminary investigations to locate $p$-difluorobenzene molecules within the channels of purely siliceous ZSM-5 were undertaken using these techniques. Apparatus which permitted the extended low temperature operation was developed. Powder X-ray diffraction experiments confirmed the sorbate- and temperature-induced phase changes observed for this system.

Using a specially designed piece of equipment, a single crystal of ZSM-5 was loaded with a precisely controlled amount of $p$-xylene and the structure successfully refined from X-ray diffraction data collected at 180 K. This represents the most accurate determination of the ZSM-5 framework to date.
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SYMBOLS AND ABBREVIATIONS

\[ a, b, c \] crystallographic unit cell dimensions (lattice constants)
\[ b_i \] orientation dependent dipolar coupling \((i = 0, 1,2)\)
\[ B_0 \] static magnetic field of an NMR spectrometer
\[ B_{1I} \] radiofrequency magnetic field applied to the \(I\) nuclei
\[ B_{1N} \] radiofrequency magnetic field applied to the \(S\) nuclei
\[ c \] number of combinations of possible spin states
CP Cross Polarization
\[ D \] dipolar coupling
\[ f \] Hartmann-Hahn matching condition
FID Free Induction Decay
FT Fourier Transform
\[ h \] Planck’s constant
HHCP Hartmann-Hahn Cross Polarization
\[ I \] magnetic quantum number associated with \(I\) spins; unobserved nucleus
INADEQUATE Incredible Natural Abundance Double Quantum Transfer Experiment
\[ J_i \] Bessel functions of the first kind
\[ n \] number of rotor periods in REDOR experiment
\[ N \] number of rotor periods before coherence transfer in TEDOR experiment
\[ N \] number of spin pairs; number of \(I\) spins
NMR Nuclear Magnetic Resonance
\[ m \] number of rotor periods after coherence transfer in TEDOR experiment
\[ M \] macroscopic magnetization of a spin system in the presence of \(B_0\)
\[ M_0 \] equilibrium macroscopic magnetization of a spin system in the presence of \(B_0\)
\[ M_{2}(II) \] \(I-I\) homonuclear second moment
\[ M_{2}(IS) \] \(I-S\) heteronuclear second moment
\[ M_{2}(SS) \] \(S-S\) homonuclear second moment
MAS Magic Angle Spinning
\[ p \] probability that a given site is occupied
\[ P_i \] Binomial probability of that \(i\) sites are occupied
\[ r \] internuclear distance
r.f. radio frequency
REDOR Rotational Echo Double Resonance
\[ S \] magnetic quantum number associated with \(S\) spins; observed nucleus
Si-1, Si-2, etc. crystallographically inequivalent T-sites (silicons) in a zeolite framework
\[ S_0 \] signal intensity in REDOR experiment with no dephasing pulses applied
\[ S_f \] signal intensity in REDOR experiment with dephasing pulses applied
\[ S_T \] signal intensity in TEDOR experiment
\[ t \] time
\[ t_i, t_f \] position of dephasing pulses during rotor cycle as fraction of rotor period \(\tau\)
T-1, T-2 crystallographically inequivalent T-sites in octadecasil framework
\[ T_1 \] spin-lattice or longitudinal relaxation time
$T_{1p}$ spin-lattice relaxation time in the rotating frame

$T_2$ spin-spin or transverse relaxation time

TEDOR Transferred Echo Double resonance

TGA Thermal Gravimetric Analysis

u.c. unit cell

v $I$-$S$ internuclear vector $\{v_1, v_2, v_3\}$ (unit length)

x $\{1, 0, 0\}$, unit vector parallel to x-axis

XRD X-ray Diffraction

y $\{0, 1, 0\}$, unit vector parallel to y-axis

z $\{0, 0, 1\}$, unit vector parallel to z-axis

$\alpha, \beta$ polar angles describing orientation of $I$-$S$ vector in a powder sample

$\alpha, \beta, \gamma$ crystallographic unit cell angles (lattice constants)

$\alpha_{av}$ average Si(OSi)$_4$ angle

$\alpha_1, \beta_1, \gamma_1$ angles describing orientation of aromatic ring in zeolite channels

$\alpha_2, \beta_2, \gamma_2$ angles describing orientation of aromatic ring in zeolite channels

$\gamma_I, \gamma_S$ gyromagnetic ratios of $I$ and $S$ spins

$\delta$ chemical shift

$\zeta$ $I$-$S$-$I$ angle in a 3-spin system

$\lambda$ $nD\tau_r$ dimensionless parameter (REDOR)

$\lambda_n$ $nD\tau_r$ dimensionless parameter (TEDOR)

$\lambda_m$ $mD\tau_r$ dimensionless parameter (TEDOR)

$\tau$ contact time in cross polarization experiment

$\tau_r$ rotor period (time for one complete rotor cycle)

$v_r$ spinning speed (s$^{-1}$)

$\omega_r$ rotor frequency (rad s$^{-1}$)

$\omega_{0l}$ Larmor frequency of the $I$ spins

$\omega_{0s}$ Larmor frequency of the $S$ spins

$\omega_{1l}$ amplitude of the radiofrequency field applied to the $I$ spins

$\omega_{1s}$ amplitude of the radiofrequency field applied to the $S$ spins

$\Delta \Phi_R$ accumulated dephasing during REDOR experiment

$\Delta S$ $S_0 - S_r$ REDOR difference

$\Delta \Phi_{T,n}$ dephasing in $n$ rotor cycles before coherence transfer in TEDOR experiment

$\Delta \Phi_{T,m}$ dephasing in $m$ rotor cycles after coherence transfer in TEDOR experiment

$\theta$ angle between $I$-$S$ internuclear vector and static magnetic field $B_0$

$\theta, \phi, \psi$ Euler angles used to describe orientation of $I$-$S$ vectors

$\theta_m$ the “Magic Angle”, 54.74°
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Dedicated to the memory of my Father
CHAPTER 1

AN INTRODUCTION TO ZEOLITES
AND SOLID-STATE NMR SPECTROSCOPY

This chapter introduces the structures and physical properties of zeolites and related microporous materials, then briefly discusses some concepts and techniques used in solid-state nuclear magnetic resonance (NMR) spectroscopy. An overview of previous investigations of microporous materials and guest species by solid-state NMR is also presented.

1.1 ZEOLITES AND RELATED MATERIALS

1.1.1 General Introduction

Zeolites are crystalline open framework aluminosilicates which play important roles as rock-forming materials (minerals) and as synthetic products of considerable industrial and scientific interest. They have many large scale industrial applications as catalysts, ion exchangers, molecular sieves, and absorbents. The name “zeolite” is derived from the Swedish word zeolit coined by Cronstedt in 1756 from the Greek words ζείν (zein = to boil) and λίθος (lithos = stone) to describe the apparent “boiling” he observed as the water frothed out of the mineral stilbite upon heating with a flame. Traditionally, the term zeolite was only considered to describe porous aluminosilicates, however in recent years its usage has been expanded to include crystalline inorganic materials containing elements other than silicon and aluminium which have zeolite-like frameworks. These zeolite-like materials encompass completely siliceous analogues
of zeolites and clathrates (zeosils and clathrasils respectively), porous aluminophosphates (AlPO₄₅), and materials such as GaPO₅ which contain gallium or other elements. Several comprehensive books have been written about these materials including those by Barrer, Breck, and the more recent compilations from the International Zeolite Association Summer Schools.

1.1.2 Synthesis

Although natural mineral zeolites have been known for more than 200 years, there was relatively little interest in them until McBain demonstrated their ability to selectively absorb organic molecules and coined the term “molecular sieve” in 1932. In the 1940s, Barrer began the first systematic studies of zeolite synthesis, demonstrating not only their molecular sieving properties, but also producing the hydrogen forms of these materials, which act as strong acid catalysts. Within a relatively short period following the synthesis of the naturally occurring zeolites chazabite, and mordenite, the first synthetic zeolite not found in nature, zeolite A, was prepared by Milton. The early synthetic methods were based on hydrothermal treatments of alkaline silicate and aluminate gels and produced samples with relatively low (< 6) Si/Al ratios similar to those found in naturally occurring zeolites. Kerr pioneered the use of quaternary ammonium organic cations R₄N⁺ as “templating” or structure directing species, which allowed the direct synthesis of materials with larger Si/Al ratios and this gave rise to a whole new generation of materials, many with previously unknown structures.

Zeolite compositions may be described using a simple empirical oxide formula (Eq. 1.1), where the Mⁿ⁺ represents the exchangeable cations, the part within brackets the framework, and z H₂O the water of hydration.

\[ M_{x/n}^{n+} [(SiO₂)ₓ (AlO₂)ₙ] · z H₂O \]  

The silicon to aluminium ratio (Si/Al = y/x) may vary from 1 to infinity, and the cations are usually metal ions or quaternary organic ammonium cations incorporated during crystallization. These cations are required to balance the net negative charges introduced by the aluminium.
atoms in the framework. Often the large organic cations block the pores and channels and need to be removed before the materials can be used. In many cases this is simply achieved by heating the material at about 550 °C in air (oxygen) to combust the organic matter. Other species such as ammonium ions and transition metal complexes may be introduced after synthesis by ion exchange, however protons are by far the most important cations because they generate strongly acidic catalytic sites within the zeolite voids.

Once it became apparent that properties such as the catalytic activity and thermal stability were related to the Si/Al ratio, other methods involving thermochemical modification, chemical treatments, and acid extraction, were developed to increase the Si/Al ratio. Where a framework can’t be directly synthesized in a high Si/Al ratio (e.g. zeolite Y) steaming of the hydrogen form can be used to remove aluminium from the framework. Heating (usually above 700 °C) in the presence of steam drives a fraction of the hydrogen ions from the zeolite crystals and causes an equal number of aluminium atoms to leave the framework. The vacancies created are somehow filled by silicon atoms, thereby increasing the Si/Al ratio. Some aluminium species may remain in the pores as octahedrally coordinated cations and can act as catalytic sites. Zeolites synthesized with boron rather aluminium can also be steamed, and the boron is much easier to remove from the framework. A direct isomorphous substitution of Si for Al can be achieved by treating the sample with SiCl₄.

In the 1980s a new class of materials, the AlPO₄s, whose frameworks contain aluminium and phosphorus were discovered. AlPO₄s have frameworks with Al/P ratios of unity and rigorous alternation of Al and P sites within their structures which means there is no net charge on the framework. However it is principally the charge balancing cations which create the catalytic sites in zeolites so the synthetic techniques were quickly extended to permit isomorphous substitution (e.g. of P by Si or Al by Ga) and thereby introduce net framework charges in these materials.

A new synthetic route involving the use of non-alkaline, fluoride-containing media was introduced by Flanigen and Patton, and has been extended by Guth and co-workers, and
others. This method allows the direct synthesis of purely siliceous materials, AlPO₄s and isomorphously substituted and many novel materials have been prepared using this approach. A wide variety of treatments have also been successfully used to modify the as-synthesized materials.

1.1.3 Structural Topologies and Nomenclature

1.1.3.1 Framework Topologies and Structures

Zeolites and their non-aluminosilicate analogues are microporous materials, having pore sizes and channel dimensions in the range 3-13 Å, and as such are distinct from the mesoporous materials which have much larger void dimensions (up to 100 Å). Some common frameworks, showing the channel systems which can be one, two, or three-dimensional in nature, are depicted in Figure 1.1. It is the dimensions of these channels which confers the size and shape selectivities.

These frameworks contain only corner-sharing tetrahedra, allowing them to be distinguished from layered materials such as clays, which share many of their useful physical properties (e.g. cation exchange abilities, voids of molecular dimensions and very similar elemental compositions), but also have edge-sharing octahedra. A further, though less clear-cut distinction can be made between zeolites, which contain true “channels”, and clathrates whose structures consist of assemblies of cage-like units with intraframework cavities connected through the cage openings.

The basic building blocks of zeolite-like structures are TO₄ units, where T represents elements such as silicon, aluminium, or phosphorus, tetrahedrally coordinated to four oxygen atoms. These positions in the framework structure are usually referred to as “T-sites”, even when, as is the case of Al in some AlPO₄s, up to two water molecules can be absorbed to yield five- or six-coordinated atoms. These are linked together by sharing oxygen atoms into larger finite units known as Secondary Building Units (SBUs) which contain up to 16 T-sites (Figure
Figure 1.1 Representations of the framework structures of some selected zeolites. (a) Sodalite, (b) Zeolite A, (c) faujasite, (d) ZSM-5, (e) mordenite, and (f) VPI-5. The 3-letter codes designating the structure types are also given.
Figure 1.2 The secondary building units (SBU’s). All of the known zeolite topologies can be built from combinations of these. In these figures, each vertex or termination represents a T-site. The oxygens (omitted for clarity) lie approximately midway between the vertices, but not on the line joining them because the T-O-T angles are not 180°. After reference 17.
1.2). The assembly of these SBUs into three-dimensional structures through oxygen-bridges produces the familiar frameworks containing regular systems of molecular-sized, interconnected channels and cavities. The cations necessary to balance the negative charge of the framework, and other guest species including water molecules, non-silicate anions (e.g. fluoride and chloride ions), organic cations, or organic molecules may be located in the voids.

An alternative method of visualizing zeolite topologies is to consider the frameworks as being constructed from stacks of polyhedral cages. These cages, which must share faces with other polyhedra, can be either different or all alike. Some of the common polyhedra found in zeolites are depicted in Figure 1.3. These are useful for describing many structure types, especially the clathrates, but also for some of the common zeolites such as sodalite, zeolite A, and the faujasite structure of zeolites X and Y. The frameworks structures of these four materials contain the truncated octahedron (β-cage or [4^6_6^8] unit), sharing 4-ring faces in the case of sodalite, or linked through double 4-ring (D4R) units (zeolite A), or double 6-ring (D6R) units (faujasite) as shown in Figure 1.1. Representations of three other common zeolites (ZSM-5, mordenite and VPI-5), whose frameworks are better described as being built up from chains of SBUs are shown in Figure 1.1. The channels present in many zeolites are clearly seen in the latter two examples. Variations in the framework composition (e.g. by isomorphous substitution), coupled with large number of possibilities for connecting the sub-units into 3-dimensional networks, yield an essentially infinite conceivable number of structures. At present several hundred naturally occurring zeolites and related synthetic materials are known, with more than a hundred distinct structure types confirmed.16

Microporous materials such as zeolites and AlPO₄s can have many different types of channels and intrastructural cavities.16 The sizes are determined by the number of T- or O-atoms that form the rings (often circular or elliptical) and control diffusion through the channels. Generally, only those apertures which are more open than regular six-membered rings are
Figure 1.3 Compilation of the cage-like polyhedra observed in clathrasils and high silica clathrates. The topological code descriptor, and the free volume for the different units are indicated. After reference 18.
considered to be channels, and the smaller openings are described as windows which connect larger cavities. One, two, and three-dimensional systems of channels are known, and in many cases (but not always), these are interconnected. Table 1.1 summarizes information about the nature and free diameters of the channel systems for some common structures. The void volumes of these polyhedra are given in Figure 1.3. It must be emphasized that the frameworks are not completely rigid: the T-O bond lengths and particularly T-O-T angles can change with temperature and in the presence of sorbed or occluded species.

1.1.3.2 Nomenclature

The conventions for naming zeolites and related materials are quite diverse, principally because many groups have synthesized materials and given them “in-house” names, but also because of the many naturally occurring mineral analogues which have their own established nomenclature. There are cases where identical materials have been synthesized by several research groups and given different names, and also of materials containing different elements but having the same framework topology. Recently however, an IUPAC Commission on Zeolite Nomenclature ruled that names consisting of three capital letters will be assigned to designate the structure types of porous framework materials. The mnemonic codes (which are generally derived from one of the established names of the material type) represent the structures and connectivities within the frameworks and a complete listing of these codes is given in the current on-line edition of the International Zeolite Associations’ publication “Atlas of Zeolite Structure Types”. These structure types do not depend on composition, distribution of the various possible atoms, cell dimensions or symmetry, and should not be confused or equated with actual materials. For example the faujasite framework type is denoted by FAU and describes the framework structure of faujasite, zeolite X, Y and others. Several more examples are given in Table 1.1.
Table 1.1 Pore dimensions and dimensionalities of selected zeotype structures (compiled from data listed in reference 17.)

<table>
<thead>
<tr>
<th>Structure Type</th>
<th>Materials</th>
<th>Pore System Dimensionality</th>
<th>Channel Diameters [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTA</td>
<td>zeolite A, Gallophosphate-A, SAPO-42</td>
<td>3</td>
<td>4.1</td>
</tr>
<tr>
<td>MFI</td>
<td>ZSM-5, Silicate-1, TS-1, VS-1</td>
<td>3</td>
<td>5.3 x 5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.1 x 5.5</td>
</tr>
<tr>
<td>MEL</td>
<td>ZSM-11, Silicate-2, TS-2, VS-2</td>
<td>3</td>
<td>5.3 x 5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.3 x 5.4</td>
</tr>
<tr>
<td>MTT</td>
<td>ZSM-23, KZ-1, EU-13</td>
<td>1</td>
<td>4.5 x 5.2</td>
</tr>
<tr>
<td>AEL</td>
<td>AIPO₄-11, SAPO-11</td>
<td>1</td>
<td>3.9 x 6.3</td>
</tr>
<tr>
<td>MTW</td>
<td>ZSM-12, NU-13, Theta-3</td>
<td>1</td>
<td>5.5 x 6.2</td>
</tr>
<tr>
<td>TON</td>
<td>Theta-1, ZSM-22, KZ-2, NU-10</td>
<td>1</td>
<td>4.4 x 5.5</td>
</tr>
<tr>
<td>MOR</td>
<td>Mordenite, Zeolon</td>
<td>1</td>
<td>6.5 x 7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>2.6 x 5.7</td>
</tr>
<tr>
<td>BEA</td>
<td>zeolite β</td>
<td>1</td>
<td>7.6 x 6.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>5.5 x 5.5</td>
</tr>
<tr>
<td>AFI</td>
<td>AIPO₄-5, SAPO-5</td>
<td>1</td>
<td>7.3</td>
</tr>
<tr>
<td>FAU</td>
<td>Faujasite, zeolite X, zeolite Y, SAPO-37</td>
<td>3</td>
<td>7.4</td>
</tr>
<tr>
<td>AET</td>
<td>AIPO₄-8, MCM-37</td>
<td>1</td>
<td>7.9 x 8.7</td>
</tr>
<tr>
<td>CLO</td>
<td>Cloverite</td>
<td>3</td>
<td>13.2 x 4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.8</td>
</tr>
<tr>
<td>VFI</td>
<td>VPI-5, AIPO₄-54, MCM-9</td>
<td>1</td>
<td>12.1</td>
</tr>
</tbody>
</table>

† In certain structures, the different channels may be interconnected to yield 2- or 3-dimensional pore systems.
Aluminosilicate materials are generally referred to as zeolites or clathrates, while their purely siliceous analogues are known as zeosils and clathrasils respectively. Aluminophosphate molecular sieves are denoted as $\text{AlPO}_4$s (or sometimes $\text{AlPO}_4$-n, where n denotes a specific structure type, but other names are also used) and the materials formed by isomorphous substitution into $\text{AlPO}_4$s are called MeAPOs or ElAPLOs. Here Me and El denote the metals or elements (e.g. Fe, Ti, Si, Ge, B etc.) which have been introduced into tetrahedral framework positions. $\text{GaPO}_4$s (Ga and P) and $\text{SAPO}_4$s (Si, Al, and P) are examples of such materials.

### 1.1.4 Structural Characterization Methods

The main physical techniques used to characterize the structures and properties of crystalline microporous materials are diffraction, microscopy, and spectroscopy. Other methods such as thermal analysis and adsorption studies also provide valuable information about thermal stability, pore sizes, channel structure, and surface area. In recent years progress has been made in the development of computer modelling software (e.g. packages such as Cerius$^2$) for calculating the energies of framework structures, and properties related to the interactions between guest species and the host framework, such as their preferred locations and diffusion rates. These methods involve predicting the minimum energy configuration of the system being investigated, and the limiting factor at present is the availability of reliable potential energy functions.

Diffraction remains by far the most important technique for determining the atomic arrangements in these crystalline materials. Single crystal diffraction studies using X-rays, electrons, and neutrons are capable of yielding accurate positions for the constituent atoms, but these require single crystals of adequate quality and size, and this can often present a major obstacle because it is extremely difficult to synthesize such large zeolite crystals of sufficient quality. However, the recent availability of area detectors and increased source beam intensities (e.g. synchrotron beam lines) now means, in principle at least, that smaller crystals may be
analyzed. In most cases, recourse must be made to the use of X-ray and neutron diffraction from microcrystalline or powder samples, which yield only limited information. However, Rietveld refinement and more recently, the use of so-called "Direct Methods" have proven to be effective means for structure elucidations. Rietveld refinement requires that a model structure is proposed (based on information such as elemental composition, symmetry, and unit cell dimensions derived from NMR and X-ray diffraction experiments) and then refined, usually with geometric restraints such as acceptable ranges for bond lengths and angles.

Notable advances for probing the microstructure of these materials have been achieved in the last few years through the use of Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). In a few cases these techniques have provided images at close to atomic resolution showing the pore openings and channels, as well as crystal defects such as dislocations, site vacancies and stacking faults. These have been reviewed by Thomas.

Spectroscopic techniques can be used to probe local structural properties such as site symmetries, coordination numbers, and to detect the presence of crystal imperfections, variations in local order, and impurities. Spectroscopic measurements generally provide details about the short-range or local order, which is complimentary to the information concerning long-range ordering obtained from microscopic and diffraction techniques. Some important methods include vibrational spectroscopy (infrared and Raman), X-ray spectroscopy (X-ray fluorescence (XRF), absorption edge fine structure (AEFS), extended X-ray absorption edge fine structure (EXAFS)), and electron spectroscopy (X-ray photoelectron spectroscopy (XPS or ESCA). The most useful and important spectroscopic technique for characterizing microporous crystalline materials is solid-state nuclear magnetic resonance spectroscopy, since it is capable of providing unique information about both the frameworks and guest species within the void spaces of these materials. In addition it is a non-destructive technique that requires relatively small samples (ca. 100-500 mg) in the form of powders. A review of previous NMR investigations of microporous materials is presented in Section 1.3.2.
1.1.5 Structure Related Properties and Applications

Molecular sieves have industrially important applications as catalysts, ion exchangers, adsorbents, and in gas separations. The wide range of applications is directly related to their unique structures, and the key to a better understanding of the chemical and physical properties of crystalline microporous materials such as zeolites lies in detailed knowledge of their framework structures, and the locations of guest species within the channels and cavities. This is the principal goal of many current research efforts, including the investigations reported in this thesis.

Each aluminium atom present in a zeolite framework introduces a net negative charge, which is balanced by cations. These cations are exchangeable, and this property is exploited in many of the industrial processes which use zeolites. By far the largest use of zeolites is as water softeners: the propensity of zeolites A and P to effectively remove Ca\(^{2+}\) and Mg\(^{2+}\) cations from “hard” water and replace them with Na\(^+\) ions means these materials have replaced the potentially environmentally damaging phosphates in many detergents. The application of zeolites as adsorbents, desiccants, and in gas separations stem from their regular arrays of molecular-sized pores and channels. For example, the 4 Å openings in the sodium form of zeolite A make it highly efficient desiccant that is used to dry solvents and gases in almost every laboratory in the world, while the Ca\(^{2+}\) exchanged form has 5 Å openings and is utilized as a molecular sieve to separate nitrogen and oxygen gas. The hydrophobicity of zeolites increases with the Si/Al ratio, and materials with high silicon contents have been used to selectively adsorb organic molecules from aqueous media.

Probably the most important property of these microporous materials after their pore size, is their acidity. Both Brønsted and Lewis acid sites may be present in zeolites, and very often these are the active catalytic sites. The acid or hydrogen form of a zeolite (often written HZ, where Z represents the zeolite framework) is obtained by ammonium ion exchange, followed by calcination in air at 500 °C to drive off ammonia gas (Eqs. 1.2 and 1.3):
\[
\begin{align*}
\text{NaZ}_6(s) + \text{NH}_4^+(aq) & \leftrightarrow \text{NH}_4\text{Z}_6(s) + \text{Na}^+(aq) \\
\text{NH}_4\text{Z}_6(s) & \xrightarrow{500^\circ \text{C AIR}} \text{HZ}_6(s) + \text{NH}_3(g)
\end{align*}
\]

For zeolites crystallized using a quaternary ammonium cation as template, calcination of the "as-synthesized" material produces the acid form directly. The proton associates with an oxygen connected to a trivalent framework aluminium, thus producing a Brønsted acid site whose proton donor ability greatly exceeds that of amorphous silica-alumina catalysts. Further heating at 550 °C may result in the formation of Lewis acid aluminium sites.

There is an extraordinary range of chemistries possible when organic reactants are in contact with zeolites and related materials.\(^1,26\) Although small pore (8-ring) zeolites were the first to be exploited as catalysts, it was the medium pore (10-ring) zeolites such as ZSM-5 which provided the size- and shape-selectivity that revolutionized the oil industry. The shape selectivity means that only molecules smaller than the aperture of the zeolite pores can reach the internal catalytic sites, and only those reactions with intermediate transition states having geometries capable of being accommodated in the cavities or pores can be formed and diffuse out. These materials are still extremely important in petroleum refining, aromatics processing, and in the production of synthetic fuels and petrochemicals. More recently applications of the larger pore (12 rings and above) molecular sieves such as the AlPO\(_4\), SAPO and MeAPO types have begun to appear. Isomorphous substitution has also provided new chemical applications including the use of titanium-containing MFI in the presence of hydrogen peroxide to achieve shape-selective oxidation.\(^3\)

The ability to tailor the reactivity and selectivity of zeolites and related materials to specific reactions and their characteristic physical properties make them attractive as catalysts. Additional benefits are gained from their heterogeneous nature, which means they may be used with a variety of reactor designs and are easily separated from liquid or gaseous reaction...
products. Environmental advantages arise because they are reusable (although they may need to be regenerated), non-corrosive, and generally non-toxic.

1.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY OF SOLIDS

1.2.1 Nuclear Magnetic Resonance Spectroscopy

Over the last 50 years, high-resolution NMR has developed into one of the most powerful and useful techniques available to chemists for the investigation and elucidation of molecular structures, particularly with the availability of superconducting high field magnets and pulse Fourier transform (FT) spectrometers. The introduction of two-dimensional techniques in the 1970s greatly expanded the kind of information available from NMR studies.

Four main features characterize a high-resolution NMR spectrum of the liquid state (i.e., solutions and isotropic liquids) and provide chemical information. These are:

(i) the exact resonance frequencies of the signals (also called the "chemical shift"). These are dependent on the particular nucleus, the strength of the magnetic field, and are characteristic of the magnetic, and therefore the chemical, environment of the different individual nuclei.

(ii) the relative signal intensity of each resonance which is directly proportional to the total number of nuclei undergoing resonance.

(iii) the multiplet structure arising from spin-spin scalar coupling. This provides information about the numbers of closely bonded nuclei and on the geometric relationship between them.

(iv) the width and line shape of the resonance. This can provide insight into molecular motions.

Many of the magnetic spin interactions are averaged to zero or to their isotropic values by the rapid random molecular motions in the liquid state. In the solid-state these interactions can cause severely broadened, relatively featureless, absorption spectra. However, although additional chemical information compared to that available from liquid state spectra is present, it is usually obscured. The primary objective of high-resolution NMR spectroscopy of solid
samples is usually to reduce or average these interactions, thereby simplifying the spectra to recover information about the chemical shifts, intensities, and couplings. For structural investigations it is possible to recover the three-dimensional anisotropic information. The following sections provide a brief overview of the nuclear spin interactions which are important in the solid-state, and also of some techniques useful for obtaining "liquid-like" NMR spectra of solids. For more detailed treatments of the theory and practice of solid-state NMR the reader is directed to the texts by Abragam, Ernst et al., Slichter, Engelhardt and Michel, Mehring, and Fyfe. Other useful NMR theory and background can be found in references 33-39.

1.2.2 Nuclear Spin Interactions in the Solid State

The interactions for nuclear spins in an applied magnetic field may be divided into five main categories:

(a) the Zeeman interaction of the nucleus with the applied magnetic field.
(b) the chemical shift interaction caused by magnetic shielding from the surrounding electrons.
(c) dipolar interactions with other nuclei.
(d) scalar coupling with other nuclei.
(e) quadrupolar interactions which are present for nuclei with spins greater than 1/2.

In the liquid state, rapid molecular tumbling averages these interactions to their isotropic values. However in solids, molecular motions are generally more restricted, and because these interactions are orientation dependent (anisotropic), they usually have significantly larger effects. In Table 1.2 typical magnitudes of the various interactions for $^{13}$C nuclei in solids and liquids are compared.

A general Hamiltonian, $H$ may be written (Eq. 1.4) which describes the total nuclear spin interactions as the sum of the individual interaction Hamiltonians. The subscripts $Z$, $CS$, $D$, $SC$, $Q$ and $K$ refer to the Zeeman, chemical shift, dipolar, scalar coupling, quadrupolar, and Knight interactions respectively.
\[ H = H_z + H_{CS} + H_D + H_{SC} + H_Q + H_K \]  \hspace{1cm} 1.4

With the exception of \( H_z \), the individual Hamiltonians in Eq. 1.4 can be generalized:

\[ H_i = C_i \mathbf{I} \cdot \mathbf{\hat{T}} \cdot \mathbf{K} \]  \hspace{1cm} 1.5

Here \( C_i \) is a constant which varies for different interactions, \( \mathbf{I} \) is a quantum mechanical operator (with components \( I_x, I_y \), and \( I_z \)) with the eigenvalues of \( \mathbf{I}^2 \) being \( I(I+1) \). \( I \) is the spin quantum number which is often referred to as spin. The angular momentum and thus the spin is proportional to the magnetic moment \( \mu \) of the nucleus, \( \mu = \gamma \frac{h}{2\pi} \mathbf{I} \), where \( h \) is Planck’s constant. This equation defines the gyromagnetic ratio \( \gamma \). \( \mathbf{K} \) is either an external magnetic field or a nuclear spin vector. \( \mathbf{\hat{T}} \) is a second rank tensor which characterizes the magnitude and directional characteristics of the interaction. Tensors representing the chemical shift, dipolar, scalar coupling and quadrupolar interactions are denoted by \( \mathbf{\hat{\sigma}}, \mathbf{\hat{D}}, \mathbf{\hat{J}}, \) and \( \mathbf{\hat{Q}} \) respectively. The interaction of a spin 1/2 nucleus with its local electronic environment is incorporated in the chemical shift interaction, and in cases where the spin quantum number \( I \) is greater than 1/2, in the quadrupolar interaction. Spin-spin couplings may be either through-bond or through-space interactions, and these are represented by the scalar and dipolar coupling interactions respectively. Because quadrupolar nuclei and metals were not investigated in the present work the discussion below will not include the quadrupolar and Knight interactions.

1.2.2.1 The Zeeman Interaction

The Zeeman interaction is the basis of NMR spectroscopy, and occurs for all nuclei possessing a non-zero spin-quantum number. As seen from Table 1.2 it is usually far larger than the other interactions (except for some quadrupolar nuclei). This interaction determines both the frequency of observation in a given magnetic field, and via the Boltzmann distribution, the
Table 1.2 Typical magnitudes of nuclear spin interactions for $^{13}$C in a 4.7 Tesla magnetic field (After reference 42).

<table>
<thead>
<tr>
<th>Spin Interaction</th>
<th>Magnitude in Solids</th>
<th>Magnitude in Liquids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeeman</td>
<td>50 MHz</td>
<td>50 MHz</td>
</tr>
<tr>
<td>Chemical Shielding</td>
<td>up to 1 kHz</td>
<td>isotropic value</td>
</tr>
<tr>
<td>Dipolar</td>
<td>~ 15 kHz</td>
<td>0</td>
</tr>
<tr>
<td>Scalar</td>
<td>~ 200 Hz</td>
<td>~ 200 Hz</td>
</tr>
<tr>
<td>Quadrupolar Coupling</td>
<td>up to ~ 100 MHz</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 1.3 Important NMR parameters of selected nuclei. (Data from reference 33).

<table>
<thead>
<tr>
<th>Nuclear Isotope</th>
<th>Spin</th>
<th>Gyromagnetic Ratio $\gamma / 10^7$ rad T$^{-1}$ s$^{-1}$</th>
<th>NMR Frequency at 9.4 T / MHz</th>
<th>Natural Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>1/2</td>
<td>26.7520</td>
<td>400.22</td>
<td>99.985</td>
</tr>
<tr>
<td>$^2$H</td>
<td>1</td>
<td>4.1066</td>
<td>61.40</td>
<td>0.015</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>1/2</td>
<td>6.7283</td>
<td>100.58</td>
<td>1.108</td>
</tr>
<tr>
<td>$^{15}$N</td>
<td>1/2</td>
<td>-2.7120</td>
<td>40.54</td>
<td>0.37</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>1/2</td>
<td>25.1810</td>
<td>376.30</td>
<td>100</td>
</tr>
<tr>
<td>$^{27}$Al</td>
<td>5/2</td>
<td>6.9760</td>
<td>104.22</td>
<td>100</td>
</tr>
<tr>
<td>$^{29}$Si</td>
<td>1/2</td>
<td>-5.3188</td>
<td>79.46</td>
<td>4.70</td>
</tr>
<tr>
<td>$^{31}$P</td>
<td>1/2</td>
<td>10.8410</td>
<td>161.92</td>
<td>100</td>
</tr>
<tr>
<td>$^{79}$Br</td>
<td>3/2</td>
<td>6.7228</td>
<td>100.22</td>
<td>50.54</td>
</tr>
<tr>
<td>$^{127}$I</td>
<td>5/2</td>
<td>5.3817</td>
<td>80.02</td>
<td>100</td>
</tr>
</tbody>
</table>
fundamental detection sensitivity for a particular magnetically active isotope. The interaction of a spin with a static external magnetic field \( B_0 \) can be described by Eq. 1.6:

\[
H_z = -\gamma I \cdot B_0
\]

1.6

The Zeeman interaction is linear with the applied magnetic field, with larger separations of the quantized energy levels and correspondingly larger population differences occurring at higher fields, giving increased sensitivity. Different magnetically active isotopes have characteristic gyromagnetic ratios and corresponding resonance frequencies in a given magnetic field strength. Table 1.3 lists some important NMR parameters of selected nuclei of interest in the present work. Because of their high natural abundances and large gyromagnetic ratios, \(^1\text{H}, ^{19}\text{F}, \) and \(^{31}\text{P} \) are the most sensitive common nuclei. Isotopic enrichment is often used to enhance the sensitivity of other commonly investigated nuclei such as \(^{13}\text{C} \) and \(^{15}\text{N} \) which are of low natural abundance as well as having lower gyromagnetic ratios.

In the presence of a static magnetic field \( B_0 \) the spins will align themselves either parallel or antiparallel with the direction of \( B_0 \). A population difference (defined by the Boltzmann populations of these two levels) creates a net macroscopic magnetization \( M \) aligned with \( B_0 \). If this magnetization is tilted by some means so as to make an angle \( \theta \) with \( B_0 \), it will precess around \( B_0 \) at a frequency \( \omega_0 = |\gamma| B_0 \text{ rad s}^{-1} \). This frequency is called the Larmor frequency, and is in the range \( 10^7 \text{ - } 10^9 \text{ Hz} \), which falls in the radio-frequency (r.f.) domain.

The practical method for tilting the magnetization away from its equilibrium orientation is to apply an r.f. field \( B_1 \ll B_0 \), which is perpendicular to \( B_0 \) and rotates around \( B_0 \) with frequency \( \omega_o \). To simplify the discussion of these effects, a change of reference frame from a static Cartesian axes system \((x, y, z)\) to one that rotates about \( B_0 \) at the frequency of the applied r.f. field (denoted by \( x', y', z' \)) is used. In this rotating frame of reference, the magnetization will precess around \( B_1 \) at frequency \( \omega_1 = |\gamma| B_1 \text{, and if } B_1 \text{ is applied for a time } t, \) the magnetization will be tipped away from the direction of \( B_0 \) by an angle \( \theta = \omega_1 t \). After \( B_1 \) is switched off, the
magnetization will precess around $B_0$. In practice the sample is surrounded with a coil (connected to an appropriately tuned r.f. circuit) which can produce an r.f. field $B_1$ (a "pulse"). The coil also detects the induced electromagnetic field following a pulse, which is then amplified and observed as the free-induction decay (FID) of the NMR signal. Fourier transformation of the FID yields the NMR spectrum (Figure 1.4).

The rotation of the net magnetization by the pulse can be controlled by varying either the power or the time for which it is applied, and a pulse which causes the orientation of the magnetization to change by 90 degrees is called a $\pi/2$ pulse. The relative phase of the applied field, which determines the direction that the magnetization is tipped can also be controlled, and the usual convention is that a $\pi/2$ pulse applied along the positive $x'$ axis is denoted as $(\pi/2)_x$ and rotates the magnetization so that it lies along $y'$ (Figure 1.5(a)). The relationship between the time and frequency domains, coupled with the relatively broad frequency ranges that need to be excited by a pulse in solid-state NMR, means that the strength of $B_1$ must be quite high so that typical $\pi/2$ pulses are less than 15 $\mu$s. The field strength of a pulse can be deduced from the frequency at which the magnetization is rotated. For example a pulse which takes 20 $\mu$s to rotate the magnetization of spin 1/2 nuclei through 360 degrees corresponds to an r.f. field strength of 50 kHz. The ability to control the phases and amplitudes of the pulses, as well as the phase of the receiver, is crucial for the successful implementation of many NMR experiments, and schemes that cycle these phases are used to suppress instrumental artifacts and to select specific coherence pathways.

1.2.2.2 The Chemical Shift Interaction

The chemical shift interaction is related to the screening or shielding of the applied magnetic field by the fields induced from the motions of the electrons surrounding the nucleus. The Hamiltonian which describes this interaction is given in Eq. 1.7.
Figure 1.4 Free induction decay (FID) signal and resulting spectrum (real part only) following Fourier transformation.

Figure 1.5 Illustration of the phase shift of the net magnetization induced by application of: (a) $\pi/2_x$, and (b) $\pi/2_y$ r.f. pulses. The direction of the external magnetic field ($B_0$) and the r.f. pulse ($B_1$) are shown.
In a suitable axis frame (the principal axis system), $\hat{\sigma}$ becomes diagonal, with principal (diagonal) elements $\sigma_{xx}$, $\sigma_{yy}$, and $\sigma_{zz}$. Because rapid molecular motions occur in liquids, the three-dimensional nature of the interaction (which potentially contains diagnostic structural information) is averaged to its isotropic value $\sigma_{iso} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) / 3$, and a single NMR resonance is observed at the isotropic chemical shift $\delta_{iso}$. Generally in solids, molecular motions do not completely average the chemical shift anisotropy (CSA). For single crystals, sharp lines will be observed whose resonance frequencies depend on the orientation of the crystal (and therefore the nucleus in the molecular coordinate system) relative to the applied static magnetic field. In the case of microcrystalline (powder) samples, every crystallite orientation is possible, and each has its own resonance frequency. The resulting spectrum is the sum of all of these resonances, and is thus very significantly broadened. However this may not be the only interaction responsible for broadening the spectra (see below). The exact shape of the absorption observed in the spectrum will depend on the principal elements of the chemical shift tensor. 

The chemical shift interaction has a linear dependence on the strength of the applied magnetic field, and will thus make a larger contribution relative to the dipolar interaction (which has no field dependence) at higher fields. The range of frequencies covered by the chemical shift broadening of a single resonance in solids is similar to, or larger than, the whole range of isotropic chemical shifts values found for liquids.

### 1.2.2.3 The Dipolar Interaction

The dipolar interaction is the interaction between the magnetic moments of nuclear spins; spin $I$ experiences the magnetic field of spin $S$ with the Hamiltonian given by:

$$H_D = \frac{h}{\pi} I \cdot \hat{D} \cdot S$$
In liquids the fast random molecular motions yield an isotropic value of zero for the dipolar couplings (because \( \hat{D} \) is a traceless tensor). In solids, however, molecular motions are more restricted, and so the dipolar interactions are usually not averaged to zero. The dipole-dipole interaction is an entirely through-space coupling, and can be either homonuclear (e.g. \( ^1\text{H}-^1\text{H} \)) or heteronuclear (e.g. \( ^1\text{H}-^{13}\text{C} \)) in nature. The magnitude of the dipolar coupling is dependent on the gyromagnetic ratios, the distance between the spins, and the orientation of the internuclear vector with respect to the applied static magnetic field. Unlike the chemical shift interaction, the magnitude of the dipolar interaction is independent of the strength of the applied magnetic field.

For a pair of heteronuclear nuclei \( I \) and \( S \) the Hamiltonian can be written as:

\[
H_D^{\text{HETERO}} = \frac{D h}{4\pi} (3\cos^2 \theta - 1) I_z S_z
\]

where \( D \) is the dipolar coupling constant (in Hz) defined by:

\[
D = \frac{\mu_0 \gamma_I \gamma_S h}{16\pi^3 r^3}
\]

\( \mu_0 = 4\pi \times 10^{-7} \text{ kg m s}^{-2} \text{ A}^{-2} \) is the permittivity of free space, \( r \) is the distance between the two nuclei (in metres), the gyromagnetic ratios \( \gamma_I \) and \( \gamma_S \) have units of \( \text{rad s}^{-1} \text{T}^{-1} \), and \( \theta \) is the angle between the internuclear vector and the direction of the applied static magnetic field.

The strong inverse dependence of the dipolar coupling on the internuclear distance (\( D \propto \frac{1}{r^3} \)) means that the magnitude of the dipole-dipole interaction decreases rapidly with increasing separation of the nuclei, and thus only neighbouring nuclei will experience a strong coupling. This distance dependence can be used to accurately determine distances between pairs of nuclei. Because dipole-dipole interactions are directly proportional to the gyromagnetic ratios of the two nuclei, dipolar couplings will be more important for systems containing nuclei with large gyromagnetic moments such as \( ^1\text{H} \) and \( ^19\text{F} \). Conversely, exchange of abundant spins having
large gyromagnetic ratios by an isotope with a lower $\gamma$ (e.g. replacement of $^1\text{H}$ by $^2\text{H}$) can be a very effective method for reducing dipolar broadening.

1.2.2.4 The Scalar Coupling Interaction

Scalar coupling, also called $J$-coupling, arises from indirect coupling between spins, and is mediated by the bonding electrons. Like the dipolar interaction, the scalar interaction can be either homo- or heteronuclear in nature, but it is a through-bond, rather than a through-space, spin-spin coupling. The multiplet structure arising from $J$-couplings between two or more spins, and the magnitudes of these couplings, often provide very useful information about the conformations and structures of molecules. The Hamiltonian for the heteronuclear scalar interaction between spins $I$ and $S$ can be written as:

$$H_{sc} = \frac{h}{2\pi} \mathbf{I} \cdot \mathbf{J} \cdot \mathbf{S}$$

Scalar couplings are independent of the magnitude of the applied magnetic field, and are usually smaller than the other interactions in solids (see Table 1.2), by which they are often overshadowed in the solid-state. The magnitude of the scalar coupling drops rapidly as the number of intervening bonds increases, but is very similar in liquids and solids, only differing if the molecular geometry is altered with the change of state.

1.2.2.5 Summary of Interactions

The relative importance of the different nuclear spin interactions which contribute to NMR spectroscopy in the solid state will depend on the nucleus being observed, the static magnetic field strength, and the particular system being studied. The critical feature of these interactions is their orientational dependence, and the relatively restricted motions in solids means they are usually not averaged to their isotropic values. Although the NMR spectra of
solids may have linewidths of up to several thousand hertz, they potentially contain more information than solution spectra because the individual principal components of the various tensors may be determined, and these describe the three-dimensional character of the interactions. Usually however, NMR spectra of solids must be simplified by obtaining higher resolution if structural information is to be readily extracted, and the next section introduces techniques developed for this purpose.

1.2.3 Techniques for Obtaining “High-Resolution” NMR Spectra from Solids

The orientation dependence of nuclear spin interactions in the solid state means that NMR spectra of powdered solids can have linewidths of several kHz. Two main approaches are used to average or reduce these in order to obtain high resolution spectra of powders. The first kind involves the use of mechanical reorientations or rotations of the sample, and this includes the techniques of Magic Angle Spinning (MAS), Dynamic Angle Spinning (DAS) and DOuble angle Rotation (DOR). These techniques work by averaging the spatial parts of the spin Hamiltonians, and have recently been reviewed by Chemlka and Zwanziger. DAS and DOR are specifically used for quadrupolar nuclei, where the second order terms need to be averaged.

The second approach is to reduce or average the spin part of the Hamiltonian through the use of r.f. pulses. This may be further divided into techniques used for decoupling hetero- and homonuclear interactions, which may be achieved by using high power decoupling and multiple pulse schemes, respectively. Multiple pulse sequences including WAHUHA, MREV-8, and BR-24, rely on carefully chosen cycles of pulses (and the phases of these) to average the dipolar interactions to zero. The chemical shift anisotropy is scaled but not removed by these multiple pulse techniques. Combinations of mechanical reorientation and pulse techniques can be used for homonuclear decoupling (e.g. Combined Rotation and Multiple Pulse Scheme or CRAMPS. MAS with high power decoupling is by far the most common technique for
heteronuclear decoupling. The following discussion will be restricted to high power
deheteronuclear decoupling and MAS as these were the techniques employed in this research.

1.2.3.1 High Power Decoupling

For most dilute spin-1/2 systems (e.g. those having a low concentration of magnetically
active nuclei such as $^{13}$C and $^{29}$Si which are of low isotopic abundance), the major source of
linebroadening in the solid-state NMR spectrum is heteronuclear dipolar coupling to other
abundant spins such as $^1$H and $^{19}$F. It is possible to eliminate these heteronuclear interactions by
applying a strong r.f. field at the Larmor frequency of the abundant spins. This resonant
irradiation causes rapid transitions of the abundant nuclei between their two spin states, with the
result that their average contribution to the effective local field is zero, and so no net
heteronuclear coupling interactions are observed for the dilute nuclei. To be effective, the
strength of the applied r.f. field must be such that the frequency of the abundant nuclei spin-flips
is comparable to (or preferably exceeds) the heteronuclear coupling frequency. In typical systems
this requires r.f. fields of the order of gauss, requiring amplifier powers in the range of hundreds
of Watts compared to the ca. 50 W decoupling fields used in liquid state spectroscopy. Another
consideration is that these decoupling fields often need to be applied throughout the entire pulse
sequence and the data acquisition, meaning that the amplifiers must be capable of providing
stable r.f. fields for hundreds of milliseconds.

1.2.3.2 Magic Angle Spinning

As discussed above, chemical shift anisotropy, dipolar and quadrupolar interactions can
result in linebroadening for solids. These interactions have a first-order orientational dependence
which contains the term $(3 \cos^2 \phi - 1)$, where $\phi$ is the angle between a specific molecule-fixed
vector and the applied static magnetic field $B_0$. For the dipole-dipole interactions it is convenient
to use the internuclear vector $r$. In solution, fast, random molecular tumbling averages the value
of \((3 \cos^2 \theta - 1)\) to zero. Independently, both Andrew\(^{37}\) and Lowe\(^{39}\) realized that time-dependent motions could be imposed on a solid to mimic or approximate the isotropic molecular motions in liquids. As an example we will consider the dipolar interaction. Rotation of a solid sample about an axis at an angle \(\theta_m\) with respect to \(B_0\) causes the vector \(r\) to trace out a conical path described by the angles \(\alpha\) and \(\beta\) as shown in Figure 1.6. The average value of \((3 \cos^2 \theta - 1)\) over the conical path is given by Eq. 1.12, where \(\omega_r\) is the angular velocity of the rotation (sample spinning), and the brackets \(<\>\) indicate that it is an average over the rotation.\(^{51}\)

\[
<3 \cos^2 \theta - 1> = \frac{1}{2} (3 \cos^2 \theta_m -1) (3 \cos^2 \beta -1) \\
+ \frac{3}{2} \left[ \sin 2 \theta_m \sin 2 \beta \cos (\omega_r t + \alpha) + \sin^2 \theta_m \sin^2 \beta \cos (2 \omega_r t + \alpha) \right]  
\]  

1.12

In a rigid solid \(\beta\) will be constant for a given crystal in the spinner. However for a powder sample each individual crystallite can be at a different (random) orientation with respect to \(B_0\) and so \(\beta \in [0, \pi]\). A sufficiently high value of \(\omega_r\) (i.e. “fast” spinning compared to the frequency of the interaction) will average the time dependent parts \(\cos (2 \omega_r t)\) and \(\cos (\omega_r t)\) to zero.\(^{51}\) The \(\frac{1}{2} (3 \cos^2 \theta_m -1)\) term acts as a scaling factor, and the angle \(\theta_m\) is under the control of the experimentalist. If \(\theta_m = \cos^{-1} \frac{1}{\sqrt{3}} \approx 54.74^\circ\), then \((3 \cos^2 \theta_m -1) = 0\), and so \(<3 \cos^2 \theta -1> = 0\) for all crystallite orientations (all values of \(\beta\)). This improves the resolution in the NMR spectrum by eliminating broadening arising from the chemical shift anisotropy as well as homo- and heteronuclear dipole-dipole interactions. The angle 54.74° is called the “Magic Angle”, and spinning samples about an axis inclined at the magic angle to the static magnetic field is referred to as Magic Angle Spinning or MAS.\(^{51}\) However, the sample rotation rate required must be greater than the frequency of the dipolar couplings which need to be averaged to zero so spinning speeds of the order tens of kHz are usually required. At present speeds of 2-15 kHz are routinely
Figure 1.6 Definitions of the angles used to describe the orientation of the $I$-$S$ internuclear vector in a powder sample undergoing magic angle spinning. $\theta_m$ is the "Magic Angle", $r$ is the $I$-$S$ distance, and $\theta$ is the angle between the $I$-$S$ vector and the external magnetic field $B_0$. 

$\theta_m = 54.74^\circ$
available, and for small diameter spinners (< 5 mm), frequencies in excess of 30 kHz can be attained.

The problem of homonuclear broadening is eliminated if the nucleus being studied is of low natural abundance (e.g. $^{13}$C, $^{29}$Si, see Table 1.3) since the NMR active nuclei are dilute in the sample. For nuclei of high isotopic abundance it is possible that physical dilution is achieved due to the nature of the sample, or that it can be introduced through isotopic exchange as is often done for hydrogen nuclei (i.e. exchange of $^1$H by $^2$H).

For dilute nuclei where homonuclear interactions are weak, fast MAS and high power decoupling can be used to average the dipole-dipole interactions to their isotropic value. Spinning the sample at frequencies lower than the frequency width of the chemical shift anisotropy powder pattern does not completely average the time dependent parts of Eq. 1.12. This produces a series of "spinning sidebands" in the spectrum, centered at the isotropic chemical shift, and spaced at multiples of the spinning speed. The intensity envelope of these spinning sidebands mimics the chemical shift anisotropy observed in the spectrum of the static sample (the "powder pattern"). Figure 1.7 illustrates these effects. Since the chemical shift anisotropy is proportional to the strength of the applied magnetic field, the sideband pattern will be larger at higher magnetic fields for a given spinning rate. Information about the full anisotropy (averaged by MAS) is retained in the sideband pattern, and appropriate analysis of the sidebands can be used to determine the principal tensor components, but not their orientation.\textsuperscript{32} Methods for suppressing these sidebands under MAS have also been reported.\textsuperscript{33,34}

As discussed above, MAS is capable of averaging some of the anisotropic interactions to their isotropic values. This is a time-average over each complete rotation of the sample, and the magnitude of a given interaction is not equal to the isotropic value at every instant during the rotor cycle. The anisotropic parts are still present and result in dephasing of the spins immediately following the application of an r.f. pulse. However, at the end of each rotor period following the pulse, all of the spins will be back in their original positions. This refocusing of the
Figure 1.7 $^{13}\text{C}$ ($^1\text{H}$ decoupled) spectra obtained for a powder sample of ferrocene, $(\text{C}_5\text{H}_5)_2\text{Fe}$

The spectra were recorded: (a) for a stationary sample, and (b)-(e) using MAS at the rotation speeds $v_r$ indicated. Adapted from reference 56.
spins after each rotor cycle is often referred to as a "rotational echo".\textsuperscript{55}

Because the majority of the experiments used in the research reported here were performed under MAS conditions and relied upon the dipolar interactions or involved the determination of the dipolar coupling, the effects of MAS on the dipole-dipole interactions will now be discussed.

Spinning the sample sufficiently fast about an axis inclined at the magic angle averages the dipolar coupling to zero over a complete rotor cycle. However the dipole-dipole interaction does not vanish - in fact only those spin pairs whose internuclear vectors are parallel to the spinning axis will have a dipolar coupling of zero at all times during a rotor cycle. For all other orientations the dipolar coupling is still present and changes continuously during the rotor period. Eq. 1.13 gives the time dependency for the dipolar coupling under MAS.\textsuperscript{57}

\[
\omega_D(\alpha, \beta, t) = \frac{1}{2} D \left[ \sin^2 \beta \cos 2(\omega, t + \alpha) - \sqrt{2} \sin \beta \cos (\omega, t + \alpha) \right]
\]

Here $\alpha$ and $\beta$ are the azimuthal and polar angles respectively, and define the position of the internuclear vector as shown in Figure 1.6. The value of the dipolar coupling has a periodic dependence on the rotor cycle, and since only the time average of the dipole-dipole interactions over each cycle are zero, the dipolar coupling can still be utilized to investigate connectivities and measure distances between nuclei. Solid-state NMR techniques specifically designed for this purpose (\textit{e.g.} REDOR and TEDOR) are discussed in detail in Chapter 3.

1.2.3.3 Cross Polarization

For dilute spin-1/2 nuclei, direct one-pulse NMR experiments often suffer from two disadvantages: inherently low sensitivity and the requirement of long recycle delays due to the relatively long $T_1$ relaxation times. The cross polarization (CP) technique, first introduced by
Pines, Gibby and Waugh,\textsuperscript{38} can often eliminate these disadvantages. During the CP experiment spin polarization, and thus net magnetization, is transferred via dipolar interactions from abundant \textit{I} spins (usually \textsuperscript{1}H) to the dilute \textit{S} spins (e.g. \textsuperscript{13}C, \textsuperscript{15}N, or \textsuperscript{29}Si), which are then observed.

The CP experiment provides enhancement of the \textit{S} spins magnetization up to a theoretical maximum factor given by the ratio of the gyromagnetic ratios of the two spins, $\gamma_I / \gamma_S$, which can be as large as 4 for \textsuperscript{1}H-\textsuperscript{13}C, and 5 for \textsuperscript{1}H-\textsuperscript{29}Si. The recycle delay for the CP experiment is determined by the $T_1$ of the (abundant) \textit{I} spins, and these are often much shorter than those of the observed (dilute) nuclei. This means that more FIDs can be accumulated in a given time period, resulting in improved signal to noise in the final CP spectrum compared to a one-pulse experiment.

Figure 1.8 shows the pulse sequence used to accomplish the magnetization transfer from \textit{I} to \textit{S} spins and a representation of the behaviour of the magnetization vectors during the CP experiment. Initially both \textit{I} and \textit{S} spins are at their equilibrium magnetization distributions. A $\pi/2$ pulse along $x'$ is applied to the \textit{I} spins, rotating the magnetization along the $y'$ axis in the rotating frame. The application of an on-resonance r.f. field with strength $B_{1I}$ along $y'$ spin-locks the \textit{I} spin magnetization along this axis, which it precesses about with frequency $\omega_{1I} = \gamma_I B_{1I}$. During this spin-locking pulse, an r.f field $B_{1S}$ is applied (along the $x'$ axis) to the \textit{S}-spins, causing them to rotate about the $y'$ axis with angular frequency $\omega_{1S} = \gamma_S B_{1S}$. The time period for which both r.f. fields are applied is known as the "contact time". During this contact time, $\tau$, net \textit{S} spin magnetization builds up along the direction of the applied $B_{1S}$ field. Following the contact time, the $B_{1S}$ r.f. field is switched off and the \textit{S} spin FID signal is recorded. The \textit{I} spin r.f. field is left on during the acquisition and acts as a decoupling field. The process is repeated after an appropriate recycle delay, with suitable phase cycling of the pulses to remove instrumental and phenomenological effects.

For efficient magnetization transfer to occur during the contact time, the amplitudes of the r.f. fields applied to the \textit{I} and \textit{S} spins must be adjusted so that the Hartmann-Hahn matching
Figure 1.8 (a) Pulse sequence for the Hartmann-Hahn spin-locked cross polarization experiment. (b) Vector representation showing the spin locking of the I spins and the build-up of the S spin magnetization during the contact time $\tau$. 

(a) Pulse sequence for the Hartmann-Hahn spin-locked cross polarization experiment.

(b) Vector representation showing the spin locking of the I spins and the build-up of the S spin magnetization during the contact time $\tau$. 

Figure 1.8
condition is met.\textsuperscript{59} For spin-1/2 nuclei undergoing MAS, the Hartmann-Hahn match is described by Eq. 1.14:\textsuperscript{60}

\[ \gamma_s B_{1S} = \gamma_I B_{1I} \pm f \omega_r \]  

where \( \omega_r \) is the spinning frequency and \( f = 1 \) or \( 2 \). If the Hartmann-Hahn condition is satisfied then the Zeeman level separation in the rotating frame are equal for both the \( I \) and \( S \) spins, and therefore mutual spin-flips can occur. The mutual spin-flipping allows the transfer of polarization between the two spin systems via \( I-S \) dipolar interactions. The spin-locking method described above is not the only means for establishing cross polarization, and some other techniques are discussed by Slichter,\textsuperscript{29} Pines \textit{et al.},\textsuperscript{18} and others.\textsuperscript{60}

Historically, CP has been used to transfer spin polarization from abundant spins to dilute spins, with protons being used almost exclusively as the abundant spins. There have been some examples where other nuclei, particularly \( ^{19} \text{F} \), have been used.\textsuperscript{61-63} Schaefer and co-workers\textsuperscript{64} reported magnetization transfer between \( ^{13} \text{C} \) and \( ^{15} \text{N} \) in isotopically enriched materials and successfully demonstrated elegant triple-resonance "Double Cross Polarization" experiments involving initial polarization transfer from \( ^1 \text{H} \) to \( ^{13} \text{C} \) followed by a second magnetization transfer to \( ^{15} \text{N} \). Recently Fyfe \textit{et al.} demonstrated the first CP experiments involving polarization transfer from quadrupolar nuclei (\( ^{27} \text{Al} \)) to spin-1/2 nuclei (\( ^{29} \text{Si} \) and \( ^{31} \text{P} \)).\textsuperscript{65,66} Several reviews of CP experiments involving less common pairs of nuclei have been published.\textsuperscript{57-69} Further details of the cross polarization experiment are discussed Chapter 3 and reference \textsuperscript{70}.

1.2.4 NMR Relaxation Processes

The presence of molecular motions causes a fluctuation of the anisotropic magnetic interactions that provides a well-defined relaxation mechanism for the nuclei via modulations of the spin interactions.\textsuperscript{71} Shielding anisotropy, scalar and spin rotation interactions, dipole-dipole interactions and interactions with unpaired electrons can all provide relaxation pathways under
the appropriate conditions. The most important relaxation mechanism in both homo- and heteronuclear spin systems in the majority of situations is via dipole-dipole interactions between the nuclei. The measurement of relaxation times is a powerful technique for the detection and quantification of molecular motions. The three relaxation times which are commonly measured will be briefly discussed below.

1.2.4.1 Spin-Lattice Relaxation Time ($T_1$)

Spin lattice relaxation is the process by which a population difference between two spin states returns to its equilibrium value after a perturbation. This is assumed to be a first order kinetic process which is exponential in nature and is described by Eq. 1.15. $M_0$ is the equilibrium magnetization, and $T_1$ (units of seconds) is the reciprocal of the kinetic rate constant which is referred to as the spin-lattice relaxation time.

\[
\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1}
\]

The name spin-lattice relaxation is derived from the fact that the process involves a transfer of Zeeman energy from the “excited” spins to the surrounding environment or “lattice.” Because spin-lattice relaxation involves the restoration of magnetization along the z-axis it is sometimes referred to as “longitudinal” relaxation. Five times $T_1$ after a perturbation more than 99% of the magnetization is recovered.

The Inversion-Recovery experiment is commonly used to measuring $T_1$ is (pulse sequence: $\pi - \tau - \pi/2 -$ acquire - recycle delay). $T_1$ is determined from the variation of the signal intensity as a function of the delay $\tau$. A disadvantage of the Inversion-Recovery experiment is that some prior knowledge of the approximate $T_1$ values is required to ensure that the recycle delay between successive scans is long enough to permit the magnetization to recover.
sufficiently for a quantitative determination. For solids $T_1$ can be of the order of seconds to hours which can mean very long recycle delays are needed.

The use of cross polarization can dramatically improve the efficiency of the Inversion Recovery experiment through increased sensitivity (up to 4 in the case of $^1\text{H}-^{13}\text{C}$), and because the recycle delay during a CP experiment will be determined by the (usually) much shorter $T_1$ of the abundant spins.$^{72}$

1.2.4.2 Spin-Spin Relaxation Time ($T_2$)

When a $\pi/2$ pulse is applied to an ensemble of spins initially at equilibrium in a static magnetic field, the net $z$-magnetization is rotated into the $x$-$y$ plane. Following this perturbation, spin-spin relaxation occurs via the exchange of spin energy brought about by mutual spin-flipping of the spin-states of different nuclei, and by dephasing that occurs due to inhomogeneities in the magnetic field. These spin-flips change the net magnetization along the $x$- and $y$-axes ($M_x$ and $M_y$ respectively), but do not change the total Zeeman energy of the spin system. Because this relaxation occurs in the $x$-$y$ plane it is sometimes also called “transverse” relaxation. Assuming that we can describe this process as exponential, we can define a time constant $T_2$ which is the reciprocal of the first order kinetic rate constant governing the spin-spin relaxation in a perfectly homogeneous magnetic field (Eq. 1.16). A similar expression can also be written for $M_y$.

$$\frac{dM_x}{dt} = -\frac{M_x}{T_2} \tag{1.16}$$

Any inhomogeneity in the magnetic field will cause the relaxation to proceed more rapidly, and the time constant $T_2^* < T_2$ is used to denote the relaxation time in the presence of such inhomogeneities.
A spin-echo experiment ($\pi/2 - \tau - \pi - \tau$ - acquire - recycle delay, Figure 1.9(a)) can be used to measure $T_2$. The initial $\pi/2$ pulse tips the magnetization into the x-y plane, then after a time $\tau$, a $\pi$ pulse is applied which inverts the direction of the dephasing. This causes the spin-coherence to be refocussed, producing an “echo” at time $2\tau$ (Figure 1.9(c)). The $\pi$-pulse also refocusses the chemical shifts and the effects of any inhomogeneities in the applied static magnetic field $B_0$. In practice $T_2$ is usually determined using the Carr-Purcell-Meiboom-Gill (CPMG) sequence which generates a train of echoes separated by $2\tau$, whose peak intensities decay with time constant $T_2$. The decay of the individual FIDs is determined by $T_2^*$ (Figure 1.9(b)).

For solid samples under MAS conditions, it is desirable to chose the delays between $\pi$ pulses to be integral multiples of the rotor period $\tau_r = 1/v_r$ ($v_r$ is the spinning frequency of the sample in Hz) to ensure that the dipolar interactions and chemical shift anisotropy are properly averaged to zero for each experiment. Cross polarization can also be used to improve the efficiency of the Spin-Echo experiment.

1.2.4.3 Spin-Lattice Relaxation Time in the Rotating Frame ($T_{1p}$)

As described above, spin-spin relaxation as described by $T_2$ normally occurs following a $\pi/2$-pulse; however if another r.f. pulse which has its phase changed by 90° is applied immediately after the initial pulse, a different situation arises. In the rotating frame an initial $\pi/2$ pulse applied along $x'$ will rotate the magnetization from $z'$ and generate a net magnetization along $y'$. If a second pulse is applied along $y'$ (i.e. the phase of the applied r.f. field $B_1$ is shifted by 90°) then the magnetization will precess about $B_1$ (in the rotating frame) rather than decay due to $T_2^*$. Because this second phase-shifted pulse effectively “locks” the magnetization along the axis parallel to $B_1$ it is called a “spin-locking” pulse, and while this $B_1$ r.f. field is applied the spins are said to be “spin-locked”. However this spin-locking $B_1$ field also acts as a static magnetic field in the rotating frame, and relaxation analogous to conventional spin-lattice
Figure 1.9 The spin-echo pulse sequence showing: (a) the timing of the pulses, and (b) the decay and formation of the echo of the free-induction decay (FID) signal. The FID decays with a time constant $T_2^*$ ($< T_2$), while the echo amplitude decays with a time constant $T_2$ (the true spin-spin relaxation time). (c) A vector representation showing the progressive dephasing and the refocussing of the transverse magnetization spin isochromats during the spin-echo sequence.
relaxation occurs, with characteristic time constant $T_{lp}$.

Spin-locking is an essential component of the CP technique used for solid-state NMR, and thus $T_{lp}$ is an important parameter in the analysis of CP experiments. To measure $T_{lp}$ the spin locking pulse is applied for a variable time $\tau$ after which the FID is detected. The variation of the observed signal intensity $I$ with $\tau$ allows $T_{lp}$ to be determined from Eq. 1.17 where $I_0$ is the full signal obtained when $\tau = 0$.

$$I = I_0 \exp \left( -\frac{\tau}{T_{lp}} \right) \quad 1.17$$

### 1.2.5 Internuclear Distance Measurements by Solid-State NMR

The combination of high power decoupling and MAS usually provides the necessary resolution to obtain chemical and structural information from dilute spins in solids. However during MAS the heteronuclear dipolar interaction is averaged to zero during each complete rotor cycle$^{57,73}$ and thus in its simplest form, the use of MAS precludes a direct measurement of $D$.

Several techniques for measuring heteronuclear distances from determinations of the heteronuclear dipolar coupling have been reported. These include Spin-Echo DOuble Resonance (SEDOR),$^{74}$ Rotational Echo Triple ResOnance (RETRO),$^{75}$ Rotational-Echo DOuble Resonance (REDOR),$^{57}$ Transferred Echo DOuble Resonance (TEDOR),$^{76}$ and others.$^{77}$ Techniques which utilize the homonuclear dipolar interaction to obtain information about internuclear distances between spins in solids possessing the same gyromagnetic ratio have been devised. These include RF Driven Dipolar Recoupling (RFDR),$^{78}$ Dipolar Recovery at the Magic Angle (DRAMA),$^{79}$ Simple Echo Excitation for Dephasing of Rotational Echo Amplitudes (SEDRA),$^{80}$ Dipolar Recoupling with a Windowless Sequence (DRAWS),$^{81}$ and others.$^{82-84}$ These have been recently reviewed by Bennett et al.$^{85}$
With the exception of SEDOR, all of the techniques listed above were explicitly designed to function under MAS conditions, and with appropriate analysis to allow the magnitude of the dipolar coupling, \( D \) to be measured. Because \( D \) is inversely proportional to the third power of the heteronuclear distance, \( r \) (Eq. 1.10), these experiments are capable of providing considerable insight into molecular structures. Moderately accurate values of dipolar couplings can yield very accurate values for the corresponding internuclear distances. While the most unambiguous distance measurements will come from experimental systems where the heteronuclei \( I \) and \( S \) interact as isolated spin pairs, these techniques also permit the discrimination between different structural models for complex systems.

To date the most successful techniques for determining reliable (and accurate) measurements of the heteronuclear dipolar coupling for isolated spin pairs seem to be REDOR and TEDOR. Cross polarization also depends on the heteronuclear dipolar interaction, and can in principle be used to obtain heteronuclear distances. These three methods were used extensively in the research presented in this thesis, and the reader is referred to Chapter 3 for detailed descriptions of the theory, pulse sequences and calculations used to extract distance information.

1.3 INVESTIGATIONS OF ZEOLITE FRAMEWORKS AND GUEST SPECIES

The use of diffraction techniques, solid-state NMR, and computer modelling to determine framework structures and investigate the guest species within the channels and cages of molecular sieve materials will be outlined in the following sections. Potential problems related to the application, and reliability of the various methods will also be discussed.

1.3.1 Structure Determinations by Diffraction Techniques

As discussed in Section 1.1, there is considerable interest in investigating the detailed three-dimensional lattice structures of zeolites and related materials, and locating guest species
within them. Although these materials are normally highly crystalline, the structural information obtainable from X-ray diffraction measurements is often severely limited for the reasons outlined in Section 1.1.4. In light of these difficulties, it is remarkable that several hundred framework structures have been solved. However, there is relatively little direct experimental information regarding the exact location of the various guest species within the channels and cages of the microporous frameworks. A few structures have been solved for as-synthesized microporous materials where the location of the organic template has been determined: however this is not always possible, and sometimes the results are ambiguous.

In general, even in cases where the framework structure is known, it is usually not possible to locate the occluded guest species. To date, there have only been six detailed single crystal structures which locate sorbed organic guest molecules (other than templating species) in the framework, all involving the MFI (ZSM-5) framework. There have been some powder X-ray and neutron diffraction investigations which have tried to locate ionic templating species or sorbed organic species, but often there is disagreement between the various studies. For example, the structures of the host-guest complexes formed by benzene in zeolite Y, and pyridine in zeolite L have been determined from neutron powder diffraction studies, and several groups have attempted to locate p-xylene or p-dichlorobenzene in ZSM-5. However in the case of the p-dichlorobenzene in ZSM-5, the location proposed from the powder data was not the same as found later by a more reliable single crystal study.

Structural determinations of such host-guest systems can also be complicated by the fact that the structure can depend on both the temperature and the number of the guest molecules sorbed per unit cell. The sorbed species may be disordered or quite mobile at ambient temperature. Furthermore, sorbates of a similar size and shape may show powder diffraction patterns with peaks at virtually the same 2θ values, but large differences in the peak intensities. Such a case was observed by Fyfe et al. for several organic sorbates in ZSM-5. The observation of intensity differences in the X-ray powder patterns implied that the sorbates are
more or less ordered (i.e. they are located at specific sites within the framework), since disordered guest molecules would only contribute to diffuse scattering, and this was later confirmed by single crystal structure determinations.19,20,89

Recent advances in the use of computer modelling methods have meant that these techniques are beginning to correctly predict both the framework structures and the locations of guest species (see Section 1.3.3). At present however, these calculations are not always reliable, and other techniques capable of providing detailed structural information need to be developed. As will be outlined in the next section, solid-state NMR is capable of providing information which is extremely helpful in structure elucidations of microporous materials and their complexes with guest species.

1.3.2 NMR Studies of Zeolite Frameworks and Guest Species

Several reviews which discuss the application of solid-state NMR to microporous materials have been published including the comprehensive book by Engelhardt and Michel,30 and shorter reviews by Fyfe et al.,104,105 and others.106,107 Virtually all of the atoms making up the frameworks of zeolites and related microporous materials have NMR-active nuclei, and can thus be studied by solid-state NMR. These include, among others, $^{11}$B, $^{17}$O, $^{27}$Al, $^{29}$Si, $^{31}$P, and $^{71}$Ga. In addition, $^1$H nuclei may be present in the framework structure as hydroxy groups. Many of the guest species which can occupy the channels and cages in molecular sieves are also amenable to investigation by NMR. For instance, the templating species and sorbed organic molecules contain $^1$H, $^{13}$C and sometimes $^{15}$N, and the majority of the exchangeable charge-compensating cations have NMR active isotopes (e.g. $^7$Li, $^{23}$Na and $^{133}$Cs). This section will briefly review the information that can be obtained from one and two-dimensional solid-state NMR investigations of the frameworks and the guest species.
1.3.2.1 One-Dimensional NMR Studies of Zeolite Frameworks

The important nuclei that are commonly present in the framework structures of microporous materials (and their natural abundances) are: $^1$H (100%), $^{17}$O (0.04%), $^{27}$Al (100%), $^{29}$Si (4.7%), and $^{31}$P (100%). Other nuclei such as boron, gallium, germanium, titanium, cobalt, and vanadium, which have NMR-active isotopes may also be present in certain cases. MAS usually yields particularly simple NMR spectra for the spin-1/2 nuclei such as $^{29}$Si and $^{31}$P. The NMR spectra of the quadrupolar nuclei are much more complex, but are capable of providing additional information regarding their local environments. The use of high magnetic fields, ultrafast spinning, and techniques such as Dynamic Angle Spinning and Double-Angle Rotation simplifies the NMR spectra of these quadrupolar nuclei.\textsuperscript{43,108} Although oxygen is a very important component of the framework, its extremely low natural abundance means that isotopic enrichment must be used if it is to be profitably studied by NMR, and thus relatively little research has been done on it. In a few cases, DAS NMR of $^{17}$O-enriched samples has been able to resolve crystallographically distinct framework oxygen sites.\textsuperscript{109} The overwhelming majority of solid-state NMR studies of molecular sieve frameworks have been devoted to $^1$H, $^{27}$Al, $^{29}$Si, and $^{31}$P and these will be discussed below.

The $^{27}$Al MAS NMR spectra of aluminosilicates generally show two types of resonances related to the usual tetrahedral and octahedral coordination geometries of Al within these materials. The tetrahedrally coordinated Al is actually in the framework, and has a chemical shift in the range 50-65 ppm (referenced to aqueous [Al(H$_2$O)$_6$]$^{3+}$). In virtually all cases, only a single resonance is observed for these tetrahedral aluminiums, and so crystallographically inequivalent Al-sites are not distinguishable. Only in the case of zeolite omega have crystallographically inequivalent Al-sites been resolved.\textsuperscript{110} The octahedrally coordinated Al (which usually gives rise to a peak at about 0 ppm) is due to “extra-framework” aluminium, that is, aluminum species within the pores, and not part of the framework. The high sensitivity of $^{27}$Al NMR, and the ability to readily distinguish the two types of Al, have meant that $^{27}$Al NMR has been extensively used
to study the dealumination of zeolite lattices, and to investigate the efficiency of various treatments designed to remove any extra-framework Al species following dealumination.\textsuperscript{32,105}

The $^{27}$Al MAS NMR spectra of AlPO$_4$s often show single resonances due to tetrahedrally-coordinated (to four P atoms because there is strict Al/P lattice alternation in these materials), Upon hydration, some framework Al in AlPO$_4$s may also coordinate two molecules of water, changing its coordination from 4-fold to 6-fold, and this is readily detected by $^{27}$Al MAS NMR. The $^{31}$P nuclei in these materials are always tetrahedrally coordinated, and often only a single signal is observed in the $^{31}$P MAS NMR spectrum. However, for AlPO$_4$-8 and VPI-5 and others which have complex unit cells, several well-resolved resonances corresponding to the different T-sites have been observed.\textsuperscript{65}

$^{29}$Si MAS NMR spectra have yielded a wealth of information about the framework structures of zeolites, and the temperature and sorbate induced changes they sometimes undergo. For low Si/Al ratio zeolites, the $^{29}$Si MAS spectra of the simplest systems show five resonances which could be assigned to the five possible distributions of Si and Al atoms about a silicon nucleus at the center of an SiO$_4$ tetrahedron: Si[4Al], Si[3Al,1Si], Si[2Al,2Si], Si[1Al,3Si], and Si[4Si]. The chemical shift ranges for these resonances are reasonably characteristic, (Figure 1.10) although they overlap and care must be taken in their use. The Si/Al ratio of the framework may be calculated from the $^{29}$Si MAS spectra under the assumption that Loewenstein's rule\textsuperscript{111} (which postulates that Al-O-Al linkages in the framework should be avoided if possible) holds. Because this yields the Si/Al ratio for the framework, it is complementary to that provided by bulk chemical analysis, which determines the total Al content of the sample (\textit{i.e.} elemental analysis also includes any Al-containing species occluded within the pores).

The resonances in the $^{29}$Si MAS NMR spectra of low Si/Al ratio zeolites are quite broad (5 ppm), however if the aluminium is removed (\textit{e.g.} by hydrothermal or chemical treatments), then highly siliceous frameworks can be obtained. If the lattice structures of these highly siliceous zeolites are also well ordered (\textit{i.e.} highly crystalline), then the spectra will show narrow
Figure 1.10 (a) The five possible local environments of a Si atom in a zeolite framework and the corresponding chemical shift ranges.
(b) $^{29}$Si MAS NMR spectrum of a NaY zeolite (Si/Al ratio of 2.6) with the resonances for the five different silicon environments resolved. After reference 112.
resonances due only to Si[4Si]. With careful optimization of the experimental variables and instrumentation, ultra high resolution NMR spectra with peak widths of ca. 0.1 ppm can be obtained in the best cases as depicted in Figure 1.11.

The excellent resolution of these spectra can be exploited to obtain very useful structural information that is not readily obtainable by other techniques. Fyfe et al. and others have reported high resolution $^{29}$Si MAS NMR spectra for a number of highly siliceous zeolites and related materials including ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-39, DD3R, decadecasil, offretite, and mordenite. In these spectra, the individual resonances correspond to crystallographically inequivalent T-sites. With appropriate care, quantitative spectra can be obtained wherein the relative peak intensities reflect the populations of the different T-sites. This allows a direct link to be made between the NMR spectra and the information provided by diffraction methods. While NMR is sensitive to the local (short range) ordering, diffraction methods reflect the long range ordering in the lattice, and the complementary nature of the two techniques has been exploited to elucidate the detailed structures of several microporous materials.

In a few cases the number of resonances and relative intensities may provide sufficient information to allow the individual peaks to be unambiguously assigned to specific T-sites in the lattice (e.g. zeolite offretite). In other cases there may be accidental degeneracies (e.g. mordenite), or several resonances with equal intensities, which means that the assignments cannot be obtained from the 1-D spectra, and the use of two-dimensional NMR techniques such as INADEQUATE and COSY is required. These 2-D methods are discussed in Section 1.3.2.2.

Several empirical correlations have been proposed which relate $^{29}$Si chemical shifts to various aspects of the local geometry of the Si nuclei in the lattice. These include relationships based on the mean Si-O-Si bond angle and the average Si-Si distance. Unfortunately, these methods are not accurate enough to provide rigorously correct assignments of the resonances to specific T-sites, especially in cases where the chemical shift differences are small, and thus
Figure 1.11  (a) $^{29}\text{Si}$ MAS NMR spectrum of calcined, highly siliceous zeolite ZSM-5 at 79.495 MHz. (b) $^{29}\text{Si}$ MAS NMR spectrum obtained of a very crystalline, completely siliceous sample of ZSM-5 after careful optimization of all experimental variables. (c) Deconvolution of spectrum (b) in terms of Lorentzian curves corresponding to the 24 individual T-sites. After reference 105.
should only be used as a general guide. This is mainly due to the uncertainties in the exact Si-O-Si bond angles and Si-Si distances found from X-ray structure determinations.

The assignment of the $^{29}\text{Si}$ resonances to specific T-sites is further complicated by the chemical shift variations observed as the temperature is changed, or in the presence of guest molecules within the channels, since both may induce subtle changes in the local geometry. For example, the $^{29}\text{Si}$ MAS spectra of calcined (empty) ZSM-5 at 293K contains 21 resonances which may be assigned (using 2-D INADEQUATE) to the 24 T-sites determined from the crystal structure at the same temperature. At this temperature the framework has monoclinic ($P2_1/n,1.1$) symmetry, but this changes to orthorhombic ($Pnma$) if the temperature is raised above 357 K. In the orthorhombic phase, there are only 12 T-sites. These changes are accurately reflected in the $^{29}\text{Si}$ MAS spectra and are completely reversible. Similar changes have been observed for ZSM-11 and ZSM-39.

The introduction of organic species into the channels can sometimes result in dramatic changes in the $^{29}\text{Si}$ spectra, again reflecting the slight modifications which can occur in the local environments of the T-sites. Several groups have reported $^{29}\text{Si}$ MAS NMR of ZSM-5 and ZSM-11 containing various organic sorbates which illustrate these changes. The spectra show a dependence on the actual number of molecules per unit cell that are present, and the nature of the adsorbed molecule. The combined effects of sorbate and temperature have also been investigated. These effects are discussed in more detail in Chapter 6.

There have been a few studies where distances between framework atoms were determined from NMR experiments. Van Eck and Veeman used SEDOR to estimate average $^{27}\text{Al}$-$^{31}\text{P}$ distances in AlPO$_4$-5 and SAPO-11. They measured mean $^{27}\text{Al}$-$^{31}\text{P}$ distances of 3.15 Å and 3.17 Å for the two materials respectively, by observing $^{27}\text{Al}$ while dephasing $^{31}\text{P}$. These distances are in good agreement with those determined from refinements of X-ray and neutron powder diffraction data. Fyfe and co-workers have reported 1-D REDOR and TEDOR experiments on several zeolites and the AlPO$_4$ VPI-5. However because these techniques
were designed to measure the dipolar coupling between spin-1/2 nuclei and they used $^{27}\text{Al}$ as one of the nuclei in their experiments, Fyfe et al. were unable to determine Al-P distances.

$^1\text{H}$ nuclei are often present in the framework structures of zeolites, most commonly at the Bronsted acid sites or in hydroxyl groups at lattice defect sites. Extensive $^1\text{H}$ MAS NMR studies have led to the assignments of the various proton resonances which are observed, and these have been reviewed by Pfeifer et al. $^{133}$ Freude et al. $^{134}$ were able to estimate the mean distance for Al-OH-Si acid protons in zeolites. Using the fact that the $^1\text{H}-^{27}\text{Al}$ dipolar coupling dominates the proton second moment, they were able to determine $^1\text{H}-^{27}\text{Al}$ distances of 2.38 Å and 2.48 Å from $^1\text{H}$ NMR spectra of static samples of ZSM-5 and zeolite Y respectively. $^1\text{H}-^{29}\text{Si}$ CP and REDOR experiments have been performed to investigate the Bronsted acid protons in the NH$^+$-exchanged forms of ZSM-5 and zeolite Y. $^{135}$ Although they report that they were able to fit the experimental data satisfactorily, specific $^1\text{H}-^{29}\text{Si}$ distances were not given.

Although one-dimensional MAS NMR spectra of microporous materials can be directly related to the crystallographically inequivalent T-sites in the asymmetric unit, assignment of the individual resonances to specific T-sites is not always straightforward for the reasons discussed above. The two-dimensional NMR techniques discussed in the next section can provide information about the connectivities between the various resonances, and thus between the T-sites in the lattice, which greatly assists the assignment.

**1.3.2.2 Determination of Framework Connectivities by Two-Dimensional NMR**

In solution-state NMR, the application of two-dimensional techniques has furnished considerable information about the connectivities between atoms within molecules. $^{28,34,36,136,137}$ The assignment of resonances in the MAS spectra to specific T-sites is an essential first step in the process of locating guest species within frameworks by NMR, since it is necessary to determine exactly which T-sites the nuclei in the guest species are closest to. These 2-D techniques include Heteronuclear Shift Correlation (HSC), which establishes heteronuclear
connections such as $^1$H-$^{13}$C, and Correlation Spectroscopy (COSY) that determines homonuclear correlations (e.g. $^1$H/$^1$H, $^{31}$P/$^{31}$P etc.). The INADEQUATE (Incredible Natural-Abundance Double QUantum Transfer Experiment) sequence was introduced to establish $^{13}$C/$^{13}$C connectivities in natural abundance samples. Benn and co-workers successfully demonstrated the application of COSY and INADEQUATE to solids, showing $^{29}$Si/$^{29}$Si connectivities in Q8M8 (the cubic octamer Si$_8$O$_{12}$[OSi(CH$_3$)$_3$)$_8$], and $^{13}$C/$^{13}$C connections in camphor. These experiments use the scalar or $J$-coupling between covalently bonded spin pairs, and can be utilized to determine the three-dimensional connectivities between nuclei in microporous materials such as zeolites.

Fyfe et al. were the first to apply these 2-D homonuclear correlation techniques to establish the three-dimensional Si-O-Si lattice connectivities in zeolites. Because of the low natural abundance of $^{29}$Si (4.7%), which means that spin pairs have only a 0.22% probability of occurring, the initial experiments were performed on $^{29}$Si isotopically-enriched (ca. 85%) samples. After optimization the experiments could be performed on samples with natural abundance $^{29}$Si.

To illustrate the important aspects of these two experiments, ZSM-12 will be used as an example. The structure of ZSM-12 is shown in Figure 1.12(a). The $^{29}$Si MAS NMR spectrum of highly siliceous ZSM-12 shows seven clearly separated resonances of equal intensity (Figure 1.12(b)). These reflect the seven inequivalent T-sites in the crystal lattice of ZSM-12 which have equal occupancy (Figure 1.12(a)).

An important aspect of the COSY 2-D spectrum is the doublet splitting observed in the cross peaks, which correspond to $^{29}$Si-O-$^{29}$Si $J$-couplings of 9 to 16 Hz. Knowledge of the magnitude of these $J$-couplings is important for the efficient application of the INADEQUATE experiment. The optimal value for the fixed delay $\tau$ in the INADEQUATE pulse sequence ($\pi/2 - \tau - \pi - \tau - \pi - t_1 - 3\pi/4$ - acquire) is $1/(4J)$. Because of the echo portion in the sequence, there is
Figure 1.12 (a) Framework structure of ZSM-12 showing the seven crystallographically inequivalent T-sites. (b) Contour plot of a $^{29}$Si INADEQUATE NMR experiment on purely siliceous ZSM-12 with the one dimensional MAS NMR spectrum above. Fifty-two experiments were carried out using a spectral width of 800 Hz, a fixed delay of 20 ms and 64 scans per experiment. Adapted from reference 115.
the added restriction that $T_2 < 1/J$ in order that acceptable S/N is obtained. Figure 1.12(b) shows the result of a 2-D INADEQUATE experiment on ZSM-12.

Compared to a COSY experiment, the INADEQUATE experiment has the significant advantage that there are no large signals on the diagonal. This makes it easier to observe connectivities between closely spaced resonances, which are often obscured by the single quantum resonances in a 2-D COSY spectrum. However, the successful implementation of an INADEQUATE experiment requires a reasonable estimate of the $J$-coupling. Overall, the INADEQUATE experiment has proven itself to be superior to COSY in investigations of molecular sieve frameworks. For example, in the case of ZSM-5 loaded with two molecules $p$-xylene per unit cell, 21 of the expected 22 connectivities were resolved from INADEQUATE experiments, but only 12 were determined using COSY. Using 2-D INADEQUATE experiments, Fyfe and co-workers have successfully assigned individual $^{29}$Si resonances to specific T-sites in several other highly siliceous zeolites including ZSM-22, and ZSM-11.

More recently several techniques that yield heteronuclear framework connectivities have been reported. These include 2-D cross polarization, TEDOR and INEPT experiments on several zeolites and AlPO$_4$s. Such experiments revealed connectivities between framework atoms ($^{27}$Al and $^{29}$Si in zeolites, and $^{27}$Al and $^{31}$P in AlPO$_4$s) that were in agreement with those anticipated from the known framework structures.

1.3.2.3 NMR Studies of Guest Species

Many of the guest species that may be located within the pore and cages of microporous materials contain NMR active nuclei. Consequently, there have been a large number of NMR investigations of the various occluded species and several reviews have been published. The vast majority of NMR studies of guest species have involved $^1$H and $^{13}$C, mainly because many of the guest species are organic.
The early $^1$H NMR studies of guest species were devoted to the adsorption of water and alcohols on zeolites, and later small hydrocarbon molecules such as acetylene and ethylene were investigated. However, the $^1$H-$^1$H homonuclear dipolar interactions are usually quite large which often means that the $^1$H spectra of static samples are very broad. The use of MAS and CRAMPS can provide $^1$H spectra with substantially improved resolution. The protons on sorbed organic molecules and templates are often utilized as a polarization source for improving the efficiency of NMR spectra of zeolite framework nuclei via CP. Recently, Fyfe and co-workers have used CP, TEDOR, and REDOR experiments between the $^1$H nuclei in selectively deuterated, sorbed $p$-xylene and $^{29}$Si in highly siliceous ZSM-5 to locate the guest molecules within the channels.

$^{13}$C NMR has also been widely used to investigate templating species, sorbed organic molecules, and to follow chemical reactions catalyzed by microporous materials. For example, the conversion of methanol to dimethyl ether and other hydrocarbons on ZSM-5 has been extensively studied in-situ by $^{13}$C NMR. $^{106,107}$ $^{13}$C MAS NMR spectra of tetrapropyl ammonium cations (TPA$^+$) in as-synthesized ZSM-5 are almost identical to that of the ion in aqueous solution, proving that the template remains intact. $^{10}$ Reischman et al. $^{144}$ observed splitting of the methyl group resonances in the $^{13}$C spectrum of ZSM-5 loaded with $p$-xylene, and interpreted this as evidence for the existence of two different sorption sites. This was later confirmed by a single-crystal X-ray structure. $^{19}$ Recently, Fyfe et al. have undertaken extensive NMR investigations of the ZSM-5 / $p$-xylene system, using CP, REDOR, and TEDOR to measure $^{13}$C-$^{29}$Si distances between the framework silicons and the $^{13}$C-labeled methyl groups of the sorbed $p$-xylene molecules, and $^{13}$C Spin-Diffusion experiments to study the molecular motions. $^{143}$

$^2$H NMR of static samples has yielded many insights into the nature, mechanisms, and timescales of the molecular motions of sorbed species. $^{32}$ A good example of this is provided by the study of the temperature dependence of the $^2$H spectra of selectively deuterated $p$-xylenes on
ZSM-5, which allowed the temperature ranges where various molecular rotations were present or absent to be determined.\textsuperscript{145}

The potential of $^{15}$N NMR to study nitrogen-containing guest species has not been fully exploited, mainly because of the low natural abundance of $^{15}$N (0.37 \%), which means that isotopic enrichment is necessary. $^{15}$N chemical shifts are very sensitive to the nature of the adsorption site, and $^{15}$N-labeled molecules such as ammonia, acetonitrile, and pyridine have been used to probe the strength and number of acid sites in zeolites.\textsuperscript{30,107} For example, the $^{15}$N NMR spectra of pyridine adsorbed on zeolite Y clearly show the conversion to pyridinium ions.\textsuperscript{107} Many of the molecules used as templates are quaternary ammonium salts (e.g. the TPA$^+$ cations used for ZSM-5), and could be more readily studied if materials were synthesized with $^{15}$N-labeled templates.

There have been several NMR studies of simple ions within the frameworks of zeolites and AlPO$_4$s. Most of the charge-compensating, exchangeable cations in zeolites can potentially be studied by NMR to, but only a few (such as $^7$Li, $^{21}$Na, $^{205}$Tl, and $^{133}$Cs) have been used to date.\textsuperscript{30} The NMR spectra of these cations can provide insights into their location and degree of hydration. $^{19}$F MAS NMR has been invoked to investigate the roles played by the fluoride ions that are often encapsulated within the framework structures of microporous materials synthesized from fluoride-containing media.\textsuperscript{146}

An interesting NMR technique used to investigate microporous materials involves the $^{129}$Xe NMR study of sorbed xenon gas. The $^{129}$Xe chemical has proved useful as a passive probe of the pore structures, occluded metal species and other adsorbed guest molecules.\textsuperscript{30,147}

1.3.3 Computer Modelling of Framework Structures and Guest Species

In recent years computer modelling techniques have become well established as powerful tools in the study of microporous solids, and comprehensive commercial software packages are now available.\textsuperscript{22} Several recent reviews have been published,\textsuperscript{148-151} and reference 152 contains
detailed accounts of the simulation techniques which have been used. Techniques which rest on the specification of interatomic potentials (Forcefield Methods) have been extensively used to model the structures of microporous materials, and to investigate the locations and diffusion of guest species. These Forcefield methods include Energy Minimization, Monte Carlo and Molecular Dynamics, and the reliability of the simulations depends critically on the quality of the interatomic potential models employed. The parameters for these techniques are derived from empirical methods or ab-initio calculations. When modelling the interactions between guest species and the framework, parameters are sometimes “borrowed” from those developed for organic systems. Using these parameters, simulations have been able to reproduce the qualitative aspects of adsorption isotherms, and yield diffusion coefficients that are in good agreement with those determined experimentally.

Freeman and co-workers have developed a “docking” procedure which uses a combination of Monte Carlo and Molecular Dynamics methods with energy minimization. This has been widely used for identifying low energy sites for sorbed molecules (e.g. butene in silicalite I, pyridine in zeolite L), and has successfully located the organic templating species in the frameworks at their X-ray determined positions.

By far the majority of the simulations of guest-host complexes in microporous materials have been performed using rigid frameworks, and often the organic species are also fixed at some predetermined configuration. Calculations which allow the (empty) framework to relax completely unrestrained to the local energy minimum have been able to reproduce the experimentally determined unit cell dimensions and fractional coordinates for zeolite A and silicalite. Titiloye et al. have simulated linear hydrocarbons adsorbed in MFI and faujasite frameworks including complete flexibility of the organic component.

The location of p-xylene in purely siliceous MFI frameworks has been studied by Pickett et al. and Reischman and co-workers. These calculations used rigid frameworks and similar potential functions, but different parameterizations. While the adsorption sites seem to be in
relatively good agreement with the X-ray determined locations,\textsuperscript{19} the presence of the sorbate molecules changes the local symmetry of the zeolite framework, and this was not revealed by, nor included in, the simulations.

In conclusion, although a considerable number of theoretical calculations have been carried out, the results are not always in agreement.\textsuperscript{158} The reliability of the computer simulations of framework-guest systems depends critically on the quality of the potential functions and the parameters used. These problems may be compounded by the subtle geometry changes induced by the guest species. There is a definite need for experimental techniques capable of locating guest species reliably within the channels and voids and providing detailed information about the frameworks. The aim of the research presented in this thesis is to develop solid-state NMR techniques to furnish exactly this information.

1.4 OUTLINE OF PROPOSED RESEARCH

As has been described above, diffraction techniques, solid-state NMR studies and computer modelling have been used to investigate the framework structures of crystalline microporous inorganic materials such as zeolites, and the host-guest complexes that are formed with occluded guest species. It is now possible to establish a direct relationship between the information provided by solid-state NMR, and the results of the X-ray diffraction studies using two-dimensional homonuclear solid-state NMR experiments such as COSY and INADEQUATE. Heteronuclear 2-D NMR techniques (e.g. INEPT, TEDOR and CP) can also provide detailed information about framework connectivities.

Overall, however, relatively little is known about the locations of the guest species within the channels and cages of microporous materials. Such information is vital if we are to improve understanding of the many unique properties of these materials. It is also important to obtain independent, reliable experimental data to assist refinement of structures from diffraction techniques and as a test of the correctness of solutions obtained from computer modelling.
methods. Solid-state NMR has considerable potential in solid-state structure investigations for directly determining internuclear distances from experiments based on the through-space $I-S$ dipolar interactions. With this in mind, the major thrust of the research was to develop the techniques of cross polarization, REDOR, and TEDOR to allow quantitative distance determinations between nuclei in the guest species and framework atoms.

It was decided to concentrate on highly crystalline, purely siliceous framework systems with fluorine-containing guest species for several reasons. Firstly, highly resolved $^{29}\text{Si}$ MAS NMR spectra can be obtained if the materials are of the very highest quality, allowing the individual NMR resonances to be assigned to specific T-sites using 2-D experiments such as INADEQUATE. This is a crucial first step in locating guest species. Secondly, $^{19}\text{F}$ is a spin 1/2 nucleus with a large gyromagnetic ratio, making $^{19}\text{F}/^{29}\text{Si}$ experiments attractive, since the dipolar couplings will be of the order of hundreds of hertz. Thirdly, although $^{19}\text{F}$ has 100% natural abundance, it is relatively rare, which dramatically reduces the likelihood of background interferences. Finally, many of the samples synthesized via the "Fluoride Method" of Flanigen and Patton contain fluoride ions in their as-synthesized form, and there is considerable interest in determining the roles which these ions play in the syntheses.

An important aspect of this work will be the development of appropriate protocols and analytical techniques capable of providing reliable measurements of the heteronuclear dipolar coupling in the situations typically encountered in these host-guest complexes. These techniques will be tested and refined using systems where the structure is known from single crystal X-ray diffraction studies. Once the reliability is established, they can be used to achieve the overall goal of the research: to locate guest species within framework structures where no detailed information concerning the locations is available.

Chapter 2 is concerned with the experimental details, spectrometer modifications, specialized equipment required, and preparation of samples. The CP, REDOR, and TEDOR techniques are introduced in detail in Chapter 3, before the results of $^{19}\text{F}/^{29}\text{Si}$ NMR experiments
on octadecasil are presented in Chapter 4. Octadecasil was chosen because it is a purely siliceous, fluoride-containing framework whose structure is known from single crystal study, and it contains two types of T-sites; one which interacts with only a single fluoride ion (i.e. an isolated Si-F spin pair), and the another that is dipolar coupled to several $^{19}$F nuclei. Thus octadecasil provides an ideal test case for the development of reliable fitting procedures. A critical comparison and assessment of these NMR distance determination techniques is presented in Chapter 5.

In Chapter 6 the results of the INADEQUATE, CP, REDOR, and TEDOR experiments used to locate 1,4-difluorobenzene molecules in ZSM-5 are discussed. Preliminary investigations of the powder X-ray diffraction of the low-loaded $p$-difluorobenzene / ZSM-5 complex are presented in Chapter 7. The successful single crystal refinement of the structure of the low-loaded complex of $p$-xylene in ZSM-5 is presented are detailed in Chapter 8. Chapter 9 summarizes the research results and conclusions, and outlines some proposals for future studies.

Several Appendices have been included. These contain schematics of the NMR spectrometer configurations, listings of the pulse and automation programs used, as well as detailed information concerning the fitting procedures, equations, and Mathematica scripts used to analyze the results of the CP, REDOR and TEDOR experiments.
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2.1 PREPARATION OF SAMPLES USED FOR NMR INVESTIGATIONS

2.1.1 Octadecasil

Highly crystalline samples of octadecasil prepared by hydrothermal crystallization (14 days at 80 °C) from a fluoride-containing medium with quinuclidine (1-azabicyclo[2,2,2] octane, [N(CH₂CH₂)₂CH]) as template in the presence of HF were kindly provided by Dr. P. Caullet and A. C. Faust of the Laboratoire de Matériaux Minéraux, Ecole Nationale Supérieure de Chimie, Université de Haute Alsace, France. Two different samples, designated as PC 752 and ACF 2134, were used. After synthesis, the product was washed with distilled water and dried at 90 °C. The samples were checked by powder X-ray diffraction and \(^{19}\text{F}\) and \(^{29}\text{Si}\) MAS NMR measurements. Carbon, nitrogen and silicon contents were determined by elemental analysis. Calculated (weight %) for 100% occupancy: C, 11.48%, N, 1.9%, Si 38.4%, Found: C, 10.5%, N, 1.78%, Si, 38.12%. Fluorine contents were not determined for the samples used, but typical fluorine contents in these materials are in the range 2.3% to 2.6%. All experiments were performed on as-synthesized samples; no calcination was done since this is known to result in a loss of the fluoride ions from the structure in addition to removal of the template.
2.1.2 Highly Siliceous ZSM-5

Siliceous, highly crystalline ZSM-5 was kindly provided by G.E. Barlow. The sample was crystallized from a boron-containing, aluminium-free hydrothermal synthesis. After washing with boiling water, the sample was calcined at 500 °C overnight to remove the organic template (tetrapropylammonium), refluxed overnight with 0.2 M ammonium bifluoride solution, re-calced at 500 °C, and then steamed at 800 °C for 6 days. Following this treatment the ZSM-5 sample had $^{29}$Si MAS NMR linewidths of ca. 0.1 ppm. Before use, samples were calcined at 500 °C for several hours to remove any adsorbed species.

2.1.3 Loading of ZSM-5 with $p$-difluorobenzene

Controlled amounts of $p$-difluorobenzene were added to freshly calcined ZSM-5 prepared as described above. For samples where $^1$H-$^{29}$Si CP was required, $p$-difluorobenzene (Aldrich 99+ %) was used. Because simultaneous decoupling of $^1$H and $^{19}$F was not possible on the available NMR probes, 1,4-difluorobenzene-$d_4$ (Aldrich 98 atom% D) which was fully deuterated at the 2-, 3-, 5-, and 6-ring positions was utilized to remove complications (e.g. line broadening) that could have arisen from $^1$H-$^{29}$Si dipolar interactions. The volume of liquid sorbate required to achieve a specific loading (molecules / unit cell) was calculated from the known density of the liquid, and added to a glass vial containing the zeolite using a 25 µL glass syringe with 0.5 µL divisions. For example, to achieve a loading of 4 molecules / u.c., 20 µL of $p$-difluorobenzene-$d_4$ was added to 280 mg of zeolite. The glass vial was then cooled briefly in liquid nitrogen and immediately flame-sealed. To ensure an equilibrium loading was attained throughout the sample, it was put into an oven at 60 °C or left at room temperature for at least 48 hours. To verify that the desired loading had been achieved, the samples were checked using thermal gravimetric analysis and $^{29}$Si MAS NMR.
2.2 SOLID-STATE NMR SPECTROSCOPY

2.2.1 NMR Spectrometer

All NMR experiments were carried out using a Bruker MSL-400 NMR spectrometer running \textit{ADAKOS 89} and \textit{DISMSL 91} software. Operating frequencies were 400.13, 376.434 and 79.495 MHz for $^1$H, $^{19}$F, and $^{29}$Si respectively. $^{29}$Si chemical shifts were referenced with respect to tetramethylsilane (TMS), using the highest field resonance of an Q$_8$M$_8$ (set to -109.7 ppm) as an intermediate standard. $^{19}$F NMR spectra were referenced to external CFCl$_3$. The $^{29}$Si offset was appropriately chosen, and $^1$H or $^{19}$F signals set on resonance. A third channel consisting of a Programmed Test Sources PTS 250 synthesizer (frequency range 0-250 MHz) and an American Microwave Technology broad-banded r.f. amplifier (300 W) had been added to the original MSL spectrometer. The phases and amplitudes of the r.f. pulses were calibrated using a Hewlett-Packard 8405A vector voltmeter.

Initial $^{19}$F / $^{29}$Si experiments were done using the F1 synthesizer set to 376.434 MHz to drive the high-power $^1$H 1 kW amplifier (retuned to 376.434 MHz) which provided about 300 W of r.f. power for the fluorine frequency. The silicon frequency was generated by mixing a 400.13 MHz signal (from the F2 synthesizer) with a frequency-doubled 160.3175 MHz signal provided by the F3 synthesizer. The frequency doubling and mixing was provided by a home-built unit. The $^{29}$Si signal was unmixed and observed at 400.13 MHz.

Later experiments made use of a commercial $^1$H decoupling amplifier retuned to 376.434 MHz. This tripled the 125.478 MHz input frequency (from the third channel synthesizer) and produced an output of approximately 20 W. This was sufficient to drive the (appropriately tuned) high-power amplifier, and allowed the F1 synthesizer to be used for $^{29}$Si. Although lower $^{19}$F r.f. powers were obtained with this set-up, it provided a significant increase in the S/N ratio when observing $^{29}$Si because it removed the need for frequency mixing and unmixing. Schematics detailing the components and connections needed for these experiments are given in Appendix A.
2.2.2 NMR Probes, Rotors, and Caps

Commercial Bruker H/X double-tuned probes with either Bruker or Doty Scientific MAS stators were used. These spun 7 mm diameter zirconia rotors holding 250-300 mg of sample. In some cases a layer of Teflon tape was packed on top to improve the spinning stability of the samples. Spinning speeds up to 5.2 kHz were available with a stability of better than 20 Hz over a period of several days. For room temperature experiments, Nylon or Kel-F caps were used, boron nitride stators and caps were required for low temperature work. The magic angle was set by observing the $^{79}$Br resonance of KBr, and the magnetic field was shimmed using a rotor filled with a dilute aqueous solution of copper sulfate (0.001 M) mixed with D$_2$O to prevent overloading the spectrometer receiver.

The performance of the Bruker double-tuned $^1$H/X NMR probes was carefully optimized. Modifications included soldering two or three 2 pF (5 kV) capacitors in series across the leads of the sample coil were often required to adjust the frequency of the $^1$H channel for correct matching and tuning at 376.4 MHz (for experiments involving $^{19}$F). These capacitors were "NP0" rated meaning they had very stable capacitance over the temperature range -55 to 125 °C. Suitable commercially-made and home-built filters were attached at the probe to improve noise rejection.

The air pressure for MAS sample spinning was controlled using a Bruker MAS pneumatic unit. Temperature regulation was achieved with a Bruker BVT 1000 temperature controller and a heater coil within the probe (insulated) bearing air supply line. A copper-constantan thermocouple positioned close to the sample allowed a temperature stability of better than ±1 °C to be maintained.

2.2.3 Measurement of Nuclear Relaxation Times, Pulse Lengths, and Spinning Speed

Measurement of the nuclear relaxation parameters was achieved using the pulse programs listed in Appendix B. Analysis of the spectra to determine $T_1$, $T_2$, and $T_{1p}$ was carried
out using the commercial Bruker software. Pulse lengths and r.f. field strengths were determined using the various pulse programs listed in Appendix B. The pulse lengths were always measured on the sample under investigation to ensure accurate values because this is crucial for the performance of the REDOR, TEDOR and INADEQUATE experiments. If cross polarization was used then the $^{29}\text{Si}$ channel pulse lengths were determined after polarization transfer. Typically, $\pi/2$-pulses were in the range 6-15 $\mu$s corresponding to r.f. field strengths of 16.6-41.6 kHz.

The spinning frequency, $v_s$, was determined using an optical spinning rate detector, or from the peak separations of the spinning sidebands in the $^{19}\text{F}$ MAS NMR spectra if no spinning rate detector was available. The spinning speed was checked before and after each experiment, and could be measured to an accuracy of better than 10 Hz. Knowledge of $v_s$ was required to calculate the rotor period and the various delays needed for precise positioning of the pulses in the TEDOR and REDOR experiments.

2.2.4 Low Temperature Operation

Many of the NMR experiments required stable spinning at low temperatures for extended periods. This was achieved using cold nitrogen gas as the bearing supply to the MAS rotor with further temperature regulation provided by a heating coil inside the probe. In order to ensure stable spinning speeds, the source gas pressure had to be maintained at a level which significantly exceeded that being used, and this was accomplished by utilizing the boil-off from a large (200 L) self-pressurizing liquid nitrogen Dewar operating at a pressure of 1100 kPa. The bearing gas was further cooled by it passing through loop immersed in 50 L Dewar filled with liquid nitrogen. A schematic of the equipment set-up for low temperature MAS experiments is shown in Figure 2.1. The drive gas was either nitrogen or dry air which was pressure regulated using the Bruker MAS unit. The probe electronics were flushed continuously with nitrogen gas.
Figure 2.1  Schematic of the equipment required for extended low temperature MAS NMR experiments. Temperatures as low as 200 K were readily attainable and stable spinning rate of 2 kHz could be maintained for up to 45 hours if nitrogen was used as the drive gas. The programmable timer allowed automated refills providing up to 10 hours of unsupervised operation. Dry air (routed through the MAS controller) could also be utilized as drive gas.
to prevent water condensation and ice formation within the probe which could result in deterioration of the probe performance during the experiment.

Approximately six hours were needed for the probe electronics to reach an equilibrium temperature (and for the tuning to become constant) after cooling from room temperature. Stable 2 kHz spinning for more than 45 hours at temperatures as low as 200 K was possible using this set-up. A digital timer controlled the automatic refilling of the small cooling Dewar from another liquid nitrogen Dewar, and permitted up to 10 hours of unsupervised operation. To maintain a temperature of 240 K, the timer was set to provide one minute of refilling every 2 1/2 hours. During the periods when the large Dewar was being refilled, a flow of nitrogen gas was flowed through the probe bearing supply, and after four days operating at low temperature the probe was taken out of the magnet and air dried overnight with the cover removed.

It was discovered that spinning the samples for long periods of time with nitrogen gas resulted in replacement of the air inside the spinner by nitrogen. This process was gradual but had a dramatic effect on the NMR experiments because it caused significant changes in the nuclear relaxation times. For example, over a 20 hour period, the $T_1$ values for $^{29}\text{Si}$ and $^1\text{H}$ increased from ca. 2 s and 46 ms to about 60 s and 4.5 s respectively. This problem was circumvented by using dry air as the drive gas which ensured the sample contained oxygen, providing a well-known relaxation mechanism via interactions with paramagnetic dioxygen.

2.2.5 Cross Polarization and Setting of the Hartmann-Hahn Matching Condition

The $^1\text{H}$-$^{29}\text{Si}$ Hartmann-Hahn cross polarization (HHCP) matching condition was established experimentally using Q$_6$M$_8$ with the $^1\text{H}$ radio-frequency power set on resonance and held constant and the $^{29}\text{Si}$ r.f. field strength adjusted to maximize the observed signal for a 2 ms contact time. For $^{19}\text{F}$-$^{29}\text{Si}$ cross polarization the appropriate Hartmann-Hahn matching condition was set on the sample being investigated (octadecasil or ZSM-5 loaded with p-difluorobenzene). The $^{19}\text{F}$ transmitter was set on resonance and the $^{19}\text{F}$ field strength set to a suitable level with
external attenuators. The $^{29}\text{Si}$ r.f. power was adjusted to optimize the $^{29}\text{Si}$ NMR signal using contact times ranging from 2 to 30 ms.

Quantitative cross polarization experiments require constant r.f. field strengths and spinning speeds, sometimes for periods of several days at low temperature in the work reported in this thesis. Under MAS conditions the HHCP-matching condition is split into several sideband conditions which depend directly on the spinning speed, making it necessary to maintain a steady spinning speed throughout the duration of the experiment. The maintenance of correctly matched r.f. field strengths was also crucial, and this is affected by the amplifier performance and probe tuning. For low temperature experiments, a period of 5-6 hours was required for the tuning to stabilize; this was the time needed for probe electronics to come to an equilibrium temperature. On occasion the forward and reflected r.f. power on both channels was monitored by placing a bi-directional coaxial coupler (Narda 3020A, frequency range 50-1000 MHz) in-line and observing the output on an oscilloscope. The Tektronix 2465 oscilloscope had a 300 MHz bandwidth and had been calibrated to compensate for roll-off at 376 and 400 MHz. Minimizing the reflected power was the most sensitive method for matching the probe to 50 Ω, and obtaining optimal probe tuning and performance.

2.2.6 REDOR and TEDOR Experiments

In all the REDOR experiments the observed nucleus was $^{29}\text{Si}$, and the trains of rotor-synchronous dephasing pulses were applied to $^{29}\text{Si}$ or $^{19}\text{F}$, depending on the pulse sequence used. The dephasing pulses were always timed to occur at half and full rotor periods, the $^{19}\text{F}$ offset was exactly on resonance, and the $^{29}\text{Si}$ frequency was set to be approximately in the middle of the spectrum. In the REDOR experiments which incorporated an initial cross polarization from $^{19}\text{F}$ to $^{29}\text{Si}$ to improve the efficiency, a 10 ms contact time was used. To eliminate artifacts from the effect of small but finite switching times within the spectrometer, dephasing pulses were applied in both the $S_0$ and $S_1$ experiments rather than removing the pulses for the $S_0$ as is normally done.
The desired effect of either reintroducing the dipolar interactions or not was then achieved by switching the frequency on and off resonance using a frequency offset list. A variety of null experiments confirmed that the 10 MHz offset employed was sufficiently large. Appendix B contains listings of the pulse programs, as well as automation programs used to calculate the required delays and increment the number of rotor periods.

For TEDOR experiments the $^{19}$F signal was set exactly on resonance and the observed nucleus was $^{29}$Si. For octadecasil the $^{29}$Si frequency was set so that one of the silicon signals was on resonance since no refocussing $\pi$-pulse was used in the period after coherence transfer. Null experiments performed without the transfer pulse showed that the observed signals arose from coherence transfer. Several different versions of the TEDOR experiment were used. These included applying the dephasing pulses on $^{29}$Si or $^{19}$F before the coherence transfer pulse, varying the spinning speed, the positions of the dephasing pulses, and incrementing the number of rotor cycles before or after the transfer pulse.

### 2.2.7 2-D INADEQUATE Experiments

The $^{29}$Si offset was appropriately chosen so that the individual resonances were clear of the transmitter and exact convergence of signals on either side of the central frequency was avoided if possible. The fixed delay was usually set to 15 or 16 ms based on values reported in the literature for previous 2-D INADEQUATE experiments on zeolites. Typically, spectral widths of 800-1000 Hz were used to reduce the noise in the final 2-D spectrum. Because no lock channel was available on the NMR spectrometer used, drift in the external magnetic field (< 5 Hz / day) was compensated for by acquiring several complete 2-D data sets (each containing up to 48 increments in the F1 dimension) of 12-14 hours duration which were subsequently co-added. The transmitter offsets were carefully adjusted so that 1-D $^{29}$Si MAS NMR spectra were exactly coincident. The number of scans in each experiment was determined by the $T_1$ relaxation times of the $^{29}$Si nuclei, or by that of the $^1$H nuclei if $^1$H-$^{29}$Si cross polarization was used. When high-
power decoupling of $^{19}$F or $^1$H was required, the maximum allowable acquisition time was restricted to ensure the duty cycle did not exceed 10%.

2.2.8 NMR Data Processing

2.2.8.1 Peak Integration and Deconvolution of 1-D NMR Spectra

For NMR spectra containing only a few well-defined and well-separated resonances, peak areas were obtained by integration of defined regions of the spectrum. This was used to measure relaxation times, and for processing of NMR data acquired for octadecasil. For the ZSM-5 samples loaded with sorbate where up to 12 or 24 overlapping resonances were present in the $^{29}$Si MAS NMR spectra, data were apodized if necessary (using a simple exponential function), Fourier transformed, and phased using the Bruker WIN NMR 1D software running on an IBM-compatible PC. If required, any baseline corrections were also done at this stage. The individual spectra were then exported using a J-Camp DX or ASCII file format suitable for import into the Grams-386 program.$^5$

Curve fitting of the experimental NMR spectra was done using the Grams-386 software utilizing the appropriate number of Lorentzian curves. The peak intensities were allowed to vary with the center frequencies and peak widths of the individual peaks constrained to values determined from fitting of quantitative spectra. A linear baseline was also included during the least squares fitting process (minimization of $\chi^2$) to match the calculated and observed spectra.

2.2.8.2 Processing of 2-D NMR Spectra

The individual 2-D data sets were zero-filled to at least twice the number of real data points, apodized using sine-bell functions in both F1 and F2 dimensions, and double Fourier transformed with a power presentation mode using Bruker DISMSL or WIN NMR 2D software. The number of real points in the time domain was often reduced to improve signal to noise in the final spectrum.
2.2.8.3 Distance Determinations from Analysis of NMR Data

For the CP, REDOR, and TEDOR experiments, the heteronuclear \(^{19}\text{F}-^{29}\text{Si}\) dipolar couplings were determined from nonlinear least squares fitting of the data in the Mathematica\(^6\) programming environment using the methods described in Chapter 3 and Appendix C. For experiments where analytical functions in terms of Bessel functions were not available, nonlinear regression was not practical, and appropriate integrals were determined and evaluated using point-by-point numerical integration over a sphere to produce a powder average as outlined in Appendix C.

Prior to commencing nonlinear regression analysis, trial fittings were used to determine approximate values for the parameters that were not fixed in the experiment. Weighted nonlinear fittings of the data were carried out using the Levenberg-Marquardt algorithm in Mathematica starting from these initial parameter values. If necessary some of the parameters were constrained to realistic (positive) limits. Further details are given in Section 4.2.3.

2.3 X-RAY DIFFRACTION EXPERIMENTS

2.3.1 Collection and Analysis of Powder X-ray Diffraction Data

ZSM-5 powder was calcined at 550 °C for 4 hours, cooled to room temperature and loaded into Lindemann glass X-ray capillaries (0.7 mm diameter). One sample was sealed directly, another had a measured amount of \(p\)-difluorobenzene (corresponding to slightly less than 4 molecules/u.c.) added before cooling in liquid nitrogen and flame-sealing. Powder XRD patterns were acquired on a Siemens D5000 system at the Institut für Mineralogie, Ruhr Universität, Bochum, Germany. To avoid preferred orientation of the crystallites, the capillary was mechanically rotated about the long axis throughout the experiment. Diffraction data were collected using a focused beam of monochromatic Cu \(K\alpha\) radiation (\(\lambda = 1.5406\) Å) and a position sensitive detector over the range 6.0 - 40.0° 2θ. A step size of 0.0077° was used and each scan took approximately six hours. Up to six of these scans were co-added to yield the final XRD
pattern. Diffraction data was acquired at 25°C and below 0°C, with cooling provided by a stream of air that had passed through a coiled length of copper tubing packed in dry ice and insulated within a vacuum flask. Refinement of the cell parameters from the baseline corrected XRD data was done using the program $AJUST^7$ as described in Chapter 7.

2.3.2 Loading of ZSM-5 Single Crystals with $p$-Xylene

Large single crystals of ZSM-5 were grown by Dr. W. Schwieger using hydrothermal synthesis (3-5 days at 175 °C) with tetraproplyammonium chloride, then calcined at 500 °C to remove the templating species. Several large (> 0.15 mm) crystals without obvious visible defects or twinning which were suitable for single crystal X-ray diffraction experiments were selected using an optical microscope. These were loaded into 0.3 mm diameter quartz X-ray capillaries (Charles Supper Company, wall thickness 0.01 mm) with graded quartz-Pyrex transition pieces attached at the open end, and joined to the purpose-built apparatus constructed of Pyrex glass shown in Figure 2.2. Freshly calcined highly siliceous ZSM-5 (ca. 300 mg) was loaded into the powder reservoir, and $p$-xylene (BDH, general purpose reagent 98.5%, ca. 25 µL) added to the liquid reservoir. After evacuating the single crystals and ZSM-5 powder for two hours, the $p$-xylene vapour was allowed to come into contact with the ZSM-5. Cooling of the powder reservoir by immersion in liquid nitrogen ensured complete transfer of the $p$-xylene into the part of apparatus containing the ZSM-5. The liquid reservoir was then sealed and removed. The entire apparatus was heated at 60 °C for 28 hours, then stored for two days at room temperature. Following this the individual capillaries were isolated by closing the stopcocks and the loading of the ZSM-5 powder verified by thermal gravimetric analysis and $^{29}$Si MAS NMR of the ZSM-5 powder. The capillaries containing the single crystals were then immersed in liquid nitrogen and flame-sealed as close as practical to the crystal. An equilibrium loading was ensured by keeping the sealed capillary at room temperature for several days before collecting the X-ray diffraction data.
Figure 2.2 Apparatus for loading up to three single zeolite crystals with precisely controlled amounts of volatile sorbates. The main body (approximate volume 10 mL) is constructed from borosilicate (Pyrex) glass and can be evacuated. The stopcocks (Kontes Air-less ware) have PTFE valves with Viton O-rings and polyacetal knobs and the entire system may be heated to 100°C during the equilibration procedure. Glass wool prevents loss of zeolite powder during evacuation.
2.3.3 Collection and Refinement of Single Crystal Diffraction Data

Dr. S. Rettig of the Chemistry Department at the University of British Columbia, collected X-ray diffraction data on a single ZSM-5 crystal loaded with ca. three molecules p-xylene/u.c. at a temperature of 180 K using graphite monochromated Mo Kα radiation. A Rigaku ACF7 diffractometer equipped with an Area Detector System Corporation charge-coupled device (CCD) detector was utilized and a total time of 21 hours was required for the data collection. The crystal was cooled by a flow of cold nitrogen gas. The indexed diffraction data was processed using the teXsan for Windows software, and refined using the program SHELX-97 running on an IBM-compatible PC with a Pentium 200 processor under the Windows NT operating system. Full details of the refinement are described in Chapter 8.

REFERENCES FOR CHAPTER 2

5 Grams-386, Galactic Industries Corporation, 395 Main Street, Salem, NH 03079 USA.
8 teXsan for Windows 1.01. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, U.S.A.
CHAPTER 3

HETERONUCLEAR DISTANCE DETERMINATIONS
FROM CROSS POLARIZATION, REDOR, AND TEDOR
NMR EXPERIMENTS

3.1 INTRODUCTION

Solid-state NMR spectroscopy has considerable potential in solid-state structure investigations via the direct determination of internuclear distances from experiments based on the through-space dipolar interactions between pairs of nuclei. The dipolar coupling, $D$, between two nuclei, $I$ and $S$, depends on the gyromagnetic ratios of the two nuclei, $\gamma_I$ and $\gamma_S$, and on the internuclear distance $r$ (Eq. 1.10). Furthermore, since $D \propto r^{-3}$, moderately accurate values of dipolar couplings can yield very accurate values for the corresponding internuclear distances, with the most unambiguous distance measurements coming from experimental systems where $I$ and $S$ interact as isolated spin-pairs.

In high-resolution solid-state NMR, magic angle spinning is used to narrow the otherwise extremely broad (up to several kHz) resonances. Under MAS conditions the heteronuclear dipolar interaction is not removed, but its average over each complete rotor cycle is zero.$^{1,2}$ Thus, in its simplest form, the use of MAS precludes a direct measurement of $D$.

In the cross polarization (CP) experiment, spin polarization, and thus net magnetization, is transferred via dipolar interactions from abundant $I$ spin system (usually $^1$H) to the dilute $S$ spins (e.g. $^{13}$C, $^{15}$N, or $^{29}$Si), which are then observed. Commonly, CP experiments are carried out
where the signal intensity is monitored as a function of the spin-locking time \( \tau \). The initial build-up of intensity is related to the strength of the \( I-S \) dipolar couplings, and thus analysis of CP experiments should permit discrimination between different \( I-S \) distances, and ideally, yield quantitative estimates for these distances.

Recently, Schaefer and co-workers have introduced the Rotational-Echo DOfuble Resonance (REDOR)\(^{2,3}\) and Transferred-Echo DOfuble Resonance (TEDOR)\(^{4,5}\) experiments which use radio frequency pulses applied at specific points in each rotor period to prevent the complete averaging out of the dipolar interactions, and thus permit dipolar dephasing to occur. Using appropriate analysis,\(^{6,8}\) the magnitude of the dipolar couplings can be experimentally determined and accurate interatomic distances can be determined. TEDOR and REDOR have been applied to amino acids,\(^{3,6}\) peptides,\(^{5,8,9}\) proteins,\(^{10,11}\) semiconductors,\(^{12}\) polymers,\(^{13}\) and molecular sieve frameworks.\(^{14-17}\) In cases where the distances are known independently from X-ray diffraction measurements, those obtained from REDOR and TEDOR experiments are in very good agreement.\(^{6,9}\)

In the present Chapter, the solid-state NMR techniques of cross polarization, REDOR, and TEDOR are introduced, and the background theory is outlined. The mathematical formalisms required to analyze the experimental data and obtain estimates for the \( I-S \) distances are then developed. Appendix C contains details of the implementation of these calculations on a computer utilizing the Mathematica\(^{18}\) programming environment.

The case of isolated \( IS \) spin pairs, where it is possible to obtain unambiguous heteronuclear distances, is treated first. The analysis is then extended to encompass cases where multiple \( I \) spins are coupled to a single observed \( S \) spin. The effects of molecular motions that occur on the timescale of these experiments are also described. Because these experiments rely on the heteronuclear dipolar coupling, and were carried out under MAS conditions, a brief discussion of the behavior of the dipolar interaction under MAS is presented first.
3.2 HETERONUCLEAR DIPOLAR INTERACTIONS UNDER MAS

As discussed in Section 1.2.3.2, spinning the sample sufficiently fast about an axis inclined at 54.74° to $B_0$ averages the effective dipolar coupling to zero over a complete rotor cycle. However, the dipole-dipole interaction does not vanish—indeed only those spin-pairs whose internuclear vectors are parallel to the spinning axis (*i.e.* $\beta = 0$, see Figure 1.6) will have a dipolar coupling of zero at all times during a rotor cycle. For all other orientations the dipolar coupling is still present and changes continuously during the rotor period. Eq. 3.1 gives the time dependence for the dipolar coupling under MAS.²

\[
D(\alpha, \beta, t) = \frac{1}{2} D \left[ \sin^2 \beta \cos 2(\alpha + \omega_r t) - \sqrt{2} \sin 2\beta \cos (\alpha + \omega_r t) \right] \tag{3.1}
\]

$\alpha$ and $\beta$ are the azimuthal and polar angles respectively, and define the position of the internuclear vector as shown previously in Figure 1.6. The behavior of the dipolar coupling for an isolated spin-pair as a function of the rotor period (calculated for two different orientations of the internuclear vector relative to the external magnetic field using Eq. 3.1) is plotted in Figure 3.1. Inspection of Figure 3.1 reveals that the value of the dipolar coupling has a periodic dependence on the rotor cycle. Since only the time average of the dipole-dipole interactions over each cycle is zero, the dipolar coupling can still be utilized to investigate connectivities and measure distances between nuclei.

3.3 CROSS POLARIZATION

As discussed in Chapter 1, Hartmann-Hahn cross polarization (HHCP) is the most widely used technique for heteronuclear double resonance experiments in solid-state NMR. Stejskal and Memory have written an excellent book on the fundamentals of CP under MAS conditions which presents a detailed overview of the topic.³ In the most common case we have abundant spins such as $^1$H coupled to dilute spins *e.g.* $^{13}$C. In the present discussion we consider the phenomenon
Figure 3.1  Behavior of the dipolar coupling as a function of the spinner orientation under MAS for the heteronuclear spin pair orientations indicated. Curves were calculated using Equation 3.1 with $D = 1000$ Hz and the time is given as a fraction of the rotor period.

In more detail, with specific emphasis on situations involving small numbers of spins (e.g. $I_S$, $I_2S$, etc.) where $I$-$S$ distances might be determined.

The pulse sequence used to accomplish the magnetization transfer from $I$ to $S$ spins via the Hartmann-Hahn spin-lock is shown in Figure 1.8. The CP experiment is selective in that only $S$ nuclei which are dipolar coupled to the $I$ spins will show signals in the CP spectrum, and any uncoupled $S$ spins will not be observed. Because the dipolar interaction is a through-space interaction, it is not necessary that the coupled $I$ and $S$ nuclei be covalently bonded; they only need to be close to one another.
3.3.1 Cross Polarization for Isolated IS Spin Pairs

3.3.1.1 Stationary Samples

For efficient magnetization transfer to occur during the contact time, the amplitudes of the r.f.-fields applied to the \( I (\omega_{1I} = -\gamma_I B_{1I}) \) and \( S (\omega_{1S} = -\gamma_S B_{1S}) \) spins must be adjusted so that the Hartmann-Hahn matching condition is met. For spin-1/2 nuclei in a static sample the Hartmann-Hahn match is described by Eq. 3.2.20

\[
\omega_{1I} = \omega_{1S}
\]

The separation of the Zeeman levels in the rotating frame is equal for both the \( I \) and \( S \) spins when this condition is satisfied, and mutual spin-flips allow the transfer of polarization between the two spin systems to occur.21 Since the r.f. field strength (in frequency units) is equal to the reciprocal of the \( 2\pi \)-pulse time, this condition corresponds experimentally to the \( \pi/2 \) pulse times on both channels being equal. For static samples the Hartmann-Hahn matching condition is usually broadened by the stronger \( I-I \) homonuclear interactions. The theoretical CP matching profile calculated for a static sample is shown in Figure 3.2. Matching profiles such as this represent the efficiency of the polarization transfer (signal intensity of the \( S \) spins) as a function of the mismatch of the r.f.-field strengths \( \omega_{1I} - \omega_{1S} \). The broad profile observed in this case indicates that there is still efficient polarization transfer even if the r.f. fields are not precisely matched.

As described by Hediger, for a static single crystal in the high-field approximation (\( | \omega_{1I} + \omega_{1S} | \gg | b_0 | \) ) with matched r.f. fields (\( \omega_{1I} = \omega_{1S} \)), the expectation value of the polarization on the \( S \) spin, \( \langle S_z \rangle (\tau) \) is,22

\[
\langle S_z \rangle (\tau) = \omega_{0I} \left[ 1 - \cos \left( b_0 \tau \right) \right] / 2
\]
Figure 3.2  Cross polarization matching curves calculated for a solid with relatively weak dipolar couplings. The MAS spinning rates ($\omega_r$) and sideband matching conditions ($f$) are indicated. Adapted from reference 22.

Here $\omega_0$ is the Larmor frequency of the $I$ spin and $b_0$ is the orientation dependent dipolar coupling defined by Eq. 3.4, where $D$ is defined in Eq. 1.10.

$$b_0 = D \frac{1}{4} [3 \cos^2 \theta - 1]$$  \hspace{1cm} (3.4)

Eq. 3.3 describes the shuttling of the polarization back and forth between the $I$ and $S$ spins with a frequency corresponding to $b_0$ and this will depend on the orientation of the $I$-$S$ internuclear vector relative to the static magnetic field $B_0$ (Figure 1.6). In a powder we must consider the orientations of the individual crystallites, and this is achieved by integrating over the angle $\theta$. For a powder the time dependence of the polarization on the $S$ spin is defined by:

$$<S_z>(\tau) = \omega_0 [1 - g_0(\tau)] / 2$$  \hspace{1cm} (3.5)

with

$$g_0(\tau) = \int_0^\pi \cos(b_0 \tau) \sin \theta \, d\theta$$  \hspace{1cm} (3.6)
This superposition of many different cosine functions in a powder gives rise to a damped oscillation as depicted in Figure 3.3(a). The Fourier transform, \( G_0(\omega) \), of the oscillatory part of Eq. 3.5 yields a Pake doublet which provides information about the dipolar coupling \( D \) directly (Figure 3.3(b)). Equation 3.6 can also be expressed in terms of Bessel functions of the first kind using the mathematical formalism reported by Mueller as described in Appendix C. This results in a more efficient calculation than numerical integration and simplifies non-linear least squares fitting to experimental data with Eq. 3.5.

The spin system under consideration reaches an internal quasi-equilibrium state, \( <S_z>_{qe} \), after a suitable time, and this is followed by further equilibration with the lattice on a longer time scale. With the Hartmann-Hahn polarization scheme for a truly isolated \( IS \) spin system (ignoring any relaxation), half of the polarization initially on the \( I \) spin is transferred to the \( S \) spin, i.e.

\[
<S_z>_{qe} = \frac{\omega_{0I}}{2}.
\]

In real systems it is necessary to consider the case where \( N \) (not necessarily equivalent) \( I \) spins are coupled to a single \( S \) spin. These additional couplings will influence the system in two ways. Firstly, there can be an additional damping due to spin diffusion among the \( I \) spins. Secondly there will be an increase in the maximum polarization which the \( S \) spin can attain in the quasi-equilibrium state. For a "real" isolated spin system it is likely that the \( S \) spin is strongly coupled to one \( I \) spin, and weakly coupled to many other remote \( I \) spins. If there is a coupling to the environment which can be considered as an infinitely large temperature bath (large, open spin system), the initial polarization on the \( NI \) spins will be distributed over the \((N+1)\) spins, and

\[
<S_z>_{qe} = \frac{\omega_{0I}}{N} \frac{N}{(N+1)}, \text{ which approaches } \frac{\omega_{0I}}{N} \text{ for large } N.
\]

Transient oscillations in CP signal intensities as a function of the contact time were first reported by Müller et al. in their \(^1\)H-\(^{13}\)C CP study of a stationary ferrocene crystal, and they derived an equation (Eq. 3.7) which describes the oscillatory behavior observed in the build-up of the \(^{13}\)C magnetization.
Figure 3.3 Evolution of the $S$ spin polarization for an isolated $I$/$S$ spin system in a powder sample and the Pake doublets obtained from the Fourier transform $G_f(\omega)$ of the oscillatory part. (a) Stationary sample at exact Hartmann-Hahn match. Samples under MAS at (b) $f = \pm 1$ and (c) $f = \pm 2$ sideband matching conditions. Adapted from reference 23.
\[ <S_z>(x) = \omega_0/ \left[ 1 - 0.5 \exp(-k_1 \tau) \cos(0.5 b_0 \tau) - 0.5 \exp(-k_2 \tau) \right] \] 3.7

The first order rate constants \( k_1 \) and \( k_2 \) describe the decay of the transient oscillation and the increase in the net magnetization respectively. Müller et al.\textsuperscript{24b} assumed that the spin system could be described by a Hamiltonian limited to the strongly coupled IS spin pair, with the effect of more remote \( I \) spins represented by an isotropic random-field spin-diffusion relaxation mechanism. Under this latter assumption they proposed that \( k_1 = 3R/2 \) and \( k_2 = R \) where \( R \) is the relaxation rate constant. Hediger has since determined that the rate constants \( k_1 \) and \( k_2 \) are better treated independently.\textsuperscript{25} If the spin-diffusion rate constant \( R \) is of the same order of magnitude or larger than all heteronuclear couplings, the model used to derive Eq. 3.7 is no longer valid.

Eq. 3.7 can easily be extended to the case of a powder by replacing the cosine function by its integral over \( \theta \), defined by \( g_0(\tau) \) in Eq. 3.6. Considering the quasi-equilibrium polarization \( <S_z>_{qe} \) obtained for long contact times we obtain:\textsuperscript{23}

\[ <S_z>(\tau) = \omega_0/ \left\{ 0.5 \left[ 1 - \exp(-k_1 \tau) g_0(\tau) \right] + \left[ \frac{<S_z>_{qe}}{\omega_0} - 0.5 \right] [1-\exp(-k_2 \tau)] \right\} \] 3.8

3.3.1.2 Samples Undergoing Magic Angle Spinning

Sample rotation such as MAS introduces a time dependence in the dipolar Hamiltonian which means that it cannot be solved analytically for most systems. Using Floquet Theory, Hediger was able to obtain approximate, time-independent Hamiltonians and to predict the explicit CP MAS behaviour for isolated IS spin pairs under spin-locking (Hartmann-Hahn) CP conditions.\textsuperscript{23,25} The relevant results from her work are summarized in this Section.

As discussed in Section 3.2, sample rotation causes the dipolar interactions to become time-modulated and averaged to zero of each complete rotor period. Stejskal et al.\textsuperscript{24} first described the effects of MAS on Hartmann-Hahn cross polarization. They showed that the
matching condition centered at $\omega_{fI} = \omega_{1S}$ splits into narrow sideband conditions $\omega_{fI} = \omega_{1S} + f \omega_r$ ($f = 0, \pm 1, \pm 2, \pm 3 \ldots$) separated by the rotation frequency $\omega_r$ (Figure 3.2). These sideband matching conditions will appear whenever the MAS frequency $\omega_r$ is comparable to, or exceeds, the width of the abundant $I$ spin resonance and the heteronuclear dipolar coupling frequencies. If the MAS frequency is slow compared to the homogeneous linewidth of the abundant $I$ spins, sample spinning does not significantly influence the polarization transfer obtained by HHCP.

However, if the sample rotation is sufficiently fast ($\omega_r / 2\pi \gg D$) then the CP efficiency can be dramatically affected. This can occur in solids such as hexamethylbenzene and adamantane where fast molecular motions significantly reduce the strong intramolecular homonuclear dipolar couplings, or if there are small, relatively isolated clusters of spins. This so-called fast MAS regime can now be reached in many samples with modern high-speed spinning systems (currently capable of achieving speeds in excess of 30 kHz), and must be taken into account in CP MAS experiments under these conditions.

For an isolated $IS$ spin system spinning sufficiently rapidly to reach the fast MAS regime, the HHCP matching condition is split into only four new sideband matching conditions (Figure 3.2(e)): $^{22,25}$

$$\omega_{fI} = \omega_{1S} + f \omega_r \quad f = \pm 1 \text{ or } \pm 2$$  \hspace{1cm} 3.9

The expectation value of the polarization on the $S$ spin at the matching condition $f$ is then defined by: $^{23}$

$$<S_z(x)> = \omega_{\theta f} \left[ 1 - g_f(\tau) \right]/2$$  \hspace{1cm} 3.10

with

$$g_f(\tau) = \int_\beta \cos(|h_f| \tau) \sin \beta \, d\beta$$  \hspace{1cm} 3.11

The orientation dependent dipolar couplings at the first ($f=\pm 1$) and second ($f=\pm 2$) sideband matching conditions are given by Eqs. 3.12 and 3.13. $^{23}$
\[
b_{z1} = \frac{-1}{2\sqrt{2}} D \sin(2\beta) \exp(\pm i\alpha) \quad 3.12
\]

\[
b_{z2} = \frac{1}{4} D \sin^2\beta \exp(\pm 2i\alpha) \quad 3.13
\]

The polar angles \(\alpha\) and \(\beta\) describe the orientation of the internuclear vector \(r\) with respect to a MAS rotor-fixed coordinate system with its \(z\)-axis along the spinning axis as shown previously in Figure 1.6. Eq. 3.11 can also be expressed in terms of Bessel functions for convenient fitting of experimental data as described in Appendix C.

The integration in Eq. 3.10 for an isolated spin system is taken over only a single angle (\(\beta\)) because it is not possible to detect the phase of the dipolar coupling. Note however, that if several \(I\) spins are coupled to the \(S\) spin, the integration would be over both angles.\(^2\) Figures 3.3(a-c) show the theoretical oscillatory behaviour predicted for an isolated \(IS\) spin pair by Eq. 3.10 at the MAS matching conditions and their corresponding Pake patterns. The evolution of the spin system is identical at matching conditions for \(f = 1\) and \(-1\), and for \(f = 2\) and \(-2\). No CP transfer is predicted to occur at the centerband position (\(\omega_{1S} = \omega_{1I}\)), although this is sometimes observed due to the contribution of flip-flop processes between remote \(I\) spins and from polarization transfer via heteronuclear \(J\)-coupling.\(^3\)

In the high-speed limit (\(\omega_r / 2\pi >> D\)), Eq. 3.8 can be extended to the case of a powder undergoing MAS by replacing the oscillatory part \(g_0(\tau)\) by the corresponding oscillation for rotating samples, \(g_r(\tau)\) depending on the matching condition used. Considering the quasi-equilibrium polarization \(\langle S_z \rangle_{qe}\) inside the spin system we obtain:\(^3\)

\[
\langle S_z \rangle(\tau) = \omega_{0r} \left\{ 0.5 \left[ 1 - \exp(-k_1 \tau) \right] g_r(\tau) + \left[ \frac{\langle S_z \rangle_{qe}}{\omega_{0r}} - 0.5 \right] \left[ 1 - \exp(-k_2 \tau) \right] \right\} \quad 3.14
\]
Sample spinning tends to reduce the $I-I$ homonuclear couplings somewhat, and thus under MAS $<S^2>_q$ can take on values between 0.5 (ideal isolated two-spin system, no $k_2$ as a consequence) and 1.0 (significant $I-I$ homonuclear coupling). Provided the spinning speeds are not vastly different, the oscillatory behavior should be independent of the MAS speed used.

Dipolar oscillations have been reported for several different systems under MAS conditions, and attempts have been made to determine the dipolar coupling in some cases. However, in all but two cases the data was fitted using slight modifications of the equation derived by Müller et al. (Eq. 3.7) i.e. for a stationary single crystal. Thus the effects of having a powder sample, MAS, and sideband matching conditions were not incorporated, and the couplings obtained must be viewed accordingly. Hawkes et al. included the effects of MAS, but not sideband matching to qualitatively reproduce the oscillatory behavior they observed, but made no estimate of $D$. To date the only reliable determination of the heteronuclear dipolar coupling from the oscillatory behavior in CP MAS experiments is for ferrocene in a powder sample of co-crystallized $C_{60}(\text{ferrocene})_2$ by Hediger using the mathematical treatment presented in this section.

### 3.3.2 Cross Polarization in Small Spin-Clusters

Systems with small clusters of spins which are relatively isolated from one another i.e. $I-S$ spin systems are also possible, especially in the presence of MAS and rapid molecular motions. However the equations in Section 3.3 for isolated $I-S$ spin pairs were derived using specific assumptions to define the Hamiltonian describing the interactions in such systems. The prediction of the Hartmann-Hahn CP behaviour for small spin clusters is much more complicated. The different $I-S$ couplings will behave homogeneously, and if all of the couplings (both $I-I$ and $I-S$) are of the same order of magnitude (e.g. in a CH$_2$ group) the Hamiltonian must be constructed taking into account both the number of spins and their explicit geometrical arrangement. A full quantum mechanical calculation could then be performed for each crystallite
orientation, which may be feasible for 3-spin system (i.e. \( I_2S \)) but would be very time consuming. It may also be possible to apply Floquet Theory to calculate the behavior of \( <S_z>(t) \) under the appropriate Hamiltonian.\^{26}

At present no simple way to calculate the CP behavior for small spin clusters has been presented in the literature, and although the calculations could theoretically be done, this was not attempted in the present work since it was considered outside the scope of this research. In the literature, oscillatory CP behavior is apparent in samples which very likely contain \( I_nS \) spin systems with \( N < 4 \). Such oscillatory behavior is anticipated provided that the number of \( I \) spins is small, and is also observed in the theoretical behavior calculated for some \( I_2S \) systems under REDOR and TEDOR conditions (see Chapter 5).

If the observed \( S \) spin is strongly dipolar coupled to many \( I \) spins, oscillations at several frequencies interfere and a smooth exponential rise to a maximum followed by a decay due to relaxation is typically observed.\^{33,34} The dynamics of magnetization transfer during Hartmann-Hahn CP for such a system is presented in the next section.

### 3.3.3 Cross Polarization in a Network of Strongly Coupled \( I \) Spins

For systems with a large number of \( I \) spins (e.g. \( ^1H \)) dipolar coupled to isotopically dilute \( S \) nuclei (e.g. \( ^{13}C \)), the spin-lattice relaxation in the rotating frame of the abundant \( I \) spins (\( T_{1p}(I) \)) is usually much faster than that of the \( S \) spins (\( T_{1p}(S) \)). In this case \( T_{1p}(I) \) dominates the decay and the relaxation due to \( T_{1p}(S) \) can be ignored.\^{35,36} An expression of the form of Eq. 3.15 describes the behaviour of the observed \( S \) spin net magnetization in such situations. Here \( M_0 \) is maximum magnetization obtainable in the absence of relaxation and \( M(\tau) \) are the net magnetization attained after matched Hartmann-Hahn CP for time \( \tau \).

\[
M(\tau) = M_0 \left[ \frac{1}{T_{1p}(I)} \right] \left( \exp\left[ \frac{-\tau}{T_{1p}(I)} \right] - \exp\left[ -\tau / T_{CP} \right] \right) \tag{3.15}
\]
In such a case the initial exponential build-up of signal intensity is characterized by the CP rate constant, $T_{CP}^{-1}$, as polarization is transferred from the $I$ spins to the $S$ spins during the Hartmann-Hahn match. An exponential decay due to loss of the spin-locked magnetization via spin-lattice relaxation in the rotating frame is superimposed on this growth (see Figure 3.4). In other cases, the equations describing the CP behaviour are more complicated, and these have been discussed by Mehring and Walter et al.

Pines et al. have reported that the time constant $T_{CP}$ is inversely proportional to the heteronuclear second moment, $<M_2(I-S)>$, and thus has a direct dependence on the sixth power of the $I-S$ internuclear distance (Eq. 3.16):

$$T_{CP}^{-1} = C_{IS} <M_2(I-S)> / <M_2(I-I)>^{1/2}$$

$<M_2(I-I)>$ is the $I-I$ homonuclear second moment and the $<>$ indicates an average taken over all possible orientations. The $S-S$ homonuclear interactions are assumed to be much smaller in magnitude and have been neglected. The term $C_{IS}$ is a geometrical factor defined as:

$$C_{IS} = 3\pi \sqrt{\sum_{i \neq j} a_i^2 b_j^2 \over N_i \sum_{i \neq j} a_i^2 [(2b_i + b_j)^2 + (b_i + 2b_j)^2]}$$

where

$$a_i = - [\gamma_I h^2 (3 \cos^2 \theta_i - 1)] / 8\pi^2 r_i^3$$

and

$$b_j = [\gamma_I \gamma_S h^2 (3 \cos^2 \theta_j - 1)] / 4\pi^2 r_j^3$$

The $r_i$ and $r_j$ are the $I-I$ and $I-S$ internuclear vectors which are at angles $\theta_i$ and $\theta_j$ to the static external magnetic field $B_0$, $h$ is Planck's constant, and $N_i$ is the number of $I$ spins.

Van Vleck derived expressions for the heteronuclear and homonuclear second moments which are related to the internuclear distances $r$ and $r_{II}$ respectively, and can be evaluated explicitly if these distances are known. For a polycrystalline sample in the absence of molecular motion, the expressions for the second moments (in s$^{-2}$) are.
Figure 3.4 Theoretical CP behavior for $S$ spins in a network strongly homonuclear coupled $I$ spins. The thick line was calculated using Equation 3.15 with $T_{CP} = 5$ ms and $T_{1p} = 100$ ms and shows the effect of the build up of the $S$ spin magnetization (thin line) in the presence of the $I$ spins $T_{1p}$ exponential decay (dashed line).

Figure 3.5 CP MAS curves for glycine showing the different behavior for the methylene (CH$_2$) and carbonyl (C=O) carbons as a function of the contact time. Adapted from reference 22.
\[ <M_2(I-S)> = (1/5) \left( \gamma_I \gamma_S \mu \hbar / 16\pi^3 \right)^2 / \Sigma r_{IS}^6 \] 3.20
\[ <M_2(I-I)> = (9/20) \left( \gamma_I^2 \mu \hbar / 16\pi^3 \right)^2 / \Sigma r_{II}^6 \] 3.21

Usually some suitable cut-off distance is chosen (typically 8-10 Å), after which the interactions are ignored. The effects of molecular motion on the second moment can be accounted for using the formalism presented by Michel et al. The derivation of the appropriate equations is given in Appendix D.

Thus, using Eq. 3.15 (or an appropriate function which describes the behaviour in a given system), it should be possible to fit the CP signal amplitude as a function of the contact time and to determine \( T_{CP} \). Discriminations between different \( I-S \) distances should follow from comparisons of the \( T_{CP} \) values; small \( T_{CP} \) values will correspond to short heteronuclear distances while larger \( T_{CP} \)'s indicate longer distances. The literature contains some examples where measurements of average internuclear distances from \( T_{CP} \) values have been made. This behavior is well illustrated by the \(^1\text{H}-^{13}\text{C} \) CP MAS curves measured for the carbonyl and alpha carbons in glycine (Figure 3.5).

3.4 ROTATIONAL ECHO DOUBLE RESONANCE

In the REDOR pulse sequence, a different approach is taken to make the effect of the dipolar coupling directly observable under MAS conditions. Trains of rotor-synchronized \( \pi \)-pulses which reverse the sign of the dipolar coupling are applied to reintroduce the effects of the heteronuclear dipolar coupling that are normally removed by sample rotation at the magic angle. Two dephasing pulses per rotor cycle are needed to prevent the spinning from averaging the heteronuclear dipolar interactions to zero, and to ensure the dephasing is accumulated. Figure 3.6 shows REDOR pulse sequences with and without initial cross polarization. They both consist of a simple spin echo sequence on the observed nucleus, and a train of rotor-synchronized \( \pi \)-pulses on the unobserved, dipolar-coupled spins.
Figure 3.6 REDOR Pulse sequences. Two experiments are performed; one with no dephasing pulses ($S_0$ experiment) and one with dephasing ($S_f$ experiment). A series of these two experiments is acquired using different numbers of rotor periods $n$. The dephasing $\pi$-pulses are shown at half and complete rotor periods which gives the maximum dephasing, but positions can be varied. (a) Spin-echo on observed ($S$) nuclei and dephasing $\pi$-pulses on the $I$ spins. (b) Sequence with initial cross polarization of the $S$ nuclei from an abundant nucleus (e.g. $^1$H).
Two experiments are performed, one with the dephasing π-pulses applied to the unobserved spins, and one without. The echo intensity of the experiment where no dephasing occurs is denoted by $S_0$, while that of the echo acquired under the influence of the reintroduced heteronuclear dipolar dephasing is labeled $S_f$. The normalized intensity difference, $\Delta S = S_0 - S_f$, is due to the effect of the heteronuclear dipolar coupling. The REDOR technique has been successfully applied to determine heteronuclear distances in a number of systems including amino acids, peptides, proteins, semiconductors, and polymers. Distances as large as 8 Å and 16 Å have been determined between isolated $^{19}$F-$^{13}$C and $^{19}$F-$^{31}$P nuclei respectively.

3.4.1 REDOR Behavior for Isolated IS Spin Pairs

For an isolated IS spin pair, $\Delta S/S_0$ shows a non-periodic oscillation (whose "period" is related to the heteronuclear dipolar coupling, $D$) when plotted against the number of rotor cycles, $n$, the evolution time, $n\tau_r$, or the dimensionless parameter $\lambda = nD\tau_r$. Here $\tau_r = 1/\nu_r = 2\pi / \omega_r$ is the time for one complete rotor revolution. The phase accumulation from dipolar dephasing for an isolated heteronuclear spin-pair may be calculated by integrating over the time of the evolution to yield the normalized REDOR difference signal as defined by Eq. 3.22 with the integration limits $\alpha \in [0, 2\pi]$ and $\beta \in [0, \pi]$.

$$\Delta S/S_0 = 1 - (4\pi)^{-1} \int_0^{2\pi} \int_0^\pi \cos[\Delta \Phi_R(\alpha, \beta, \lambda)] \sin \beta \, d\beta \, d\alpha$$

3.22

Here $\alpha$ is the azimuthal angle and $\beta$ is the polar angle defined by the internuclear vector in a coordinate system defined with the $z$ axis parallel to the rotor axis as illustrated previously in Figure 1.6. The factor of $(4\pi)^{-1}$ is required to normalize this integral, and the $\sin \beta$ is a geometrical weighting factor required to account for the statistical (spherical) distribution of the pairs of nuclei in a powder about the spinning axis. For two dephasing π-pulses per rotor cycle
positioned at one-half and complete rotations of the spinner, the REDOR phase accumulation
ΔΦ_R is given by Eq. 3.23.\(^7\)

\[ ΔΦ_R(α, β, λ) = (32)^{\frac{1}{2}} λ \sin β \cos β \sin α \] 3.23

Mueller has derived an elegant analytical mathematical formalism which allows the
REDOR behavior to be expressed in terms of Bessel functions of the first kind.\(^7\) Using this, Eq.
3.22 can be evaluated with a significant reduction in computation time. It also makes possible
non-linear least squares fitting of experimental data. Details of this approach are presented in
Appendix C.

In a REDOR experiment AS/S_0 may be monitored as a function of either the number of
rotor periods or the position during the rotor cycle at which the dephasing pulses are applied,
with the number of rotor periods constant.\(^7\) Commonly, a series of dephasing π-pulses is applied
to the unobserved heteronuclear spins, with a simple spin-echo sequence on the observed spins as
shown in Figure 3.6(a), but other variations have been reported.\(^45,46\) The importance of phase
cycling the dephasing pulse, finite pulse lengths and accurate positioning of the pulses have been
investigated.\(^45-49\) Because the REDOR experiment involves the formation of an echo for the
observed nucleus, it is the nuclear relaxation characteristics of this nucleus which determines
how quickly the sequence can be repeated (T_1), and the maximum dephasing time at which viable
signal intensity can be recorded (T_2).

Figure 3.7 illustrates the theoretical REDOR behaviour predicted for an isolated IS spin
pair with different dipolar couplings. These REDOR curves agree exactly with those previously
published, and were calculated assuming that the spins were at fixed positions within a rigid
lattice. If the system can be described as an isolated IS spin pair, then the magnitude of the
dipolar couplings can be determined by fitting of the experimental data with an appropriate
expression (e.g. Eq. 3.22), and this permits accurate measurements of interatomic distances for
Figure 3.7  Theoretical REDOR behavior calculated for an isolated $I^S$ spin pair. (a) Effect of different dipolar couplings at spinning rate of 4.0 kHz: $D=1000$ Hz (solid line), $D=500$ Hz (dashed line), and $D=100$ Hz (dotted line). (b) "Universal" REDOR curve with $\Delta S/S_0$ plotted as a function of the dimensionless parameter $\lambda = nD\tau_r$. 

\[ \frac{\Delta S}{S_0} \]

Rotor Periods

$\lambda = nD\tau_r$
systems of isolated heteronuclear spins. Experimentally, the requirement of isolated spin-pairs has usually been met by isotopically labelling the molecules of interest (e.g. $^{13}$C-$^{15}$N in natural compounds) and diluting these in a large excess of the unlabelled compound.

Schaefer et al. have noted that the initial behavior of the universal REDOR curve (i.e. that plotted versus the dimensionless parameter $\lambda = nD\tau$, (see Figure 3.7(b)) is parabolic, being described by $\Delta S/S_0 = 1.066 \lambda^2$. In principle, this allows the dipolar coupling to be quickly determined from the initial dephasing, but this approach is valid only when the spin system under investigation can be described as a truly isolated IS spin pair (see Chapter 5).

Positioning the dephasing pulses at half and full rotor periods produces the maximum dephasing, but other pulse positions can be used. If the pulses are not at $\tau/2$ and $\tau$, then appropriate functions $\Delta \Phi_{\alpha}(\alpha, \beta, \lambda)$ must be determined (see Appendix C). These may then be evaluated using point-by-point numerical integration over a sphere to produce a powder average, or alternatively derived in terms of Bessel functions using the formalism presented by Mueller.

Fourier transformation of the REDOR dephasing signal $S/S_0$ (Figure 3.8(a)) yields a resonance with a width proportional to the dipolar coupling (Figure 3.8(b)). In practice however, it is usually difficult to determine $D$ precisely due to problems associated with determining the exact width of the peak. Recently Mueller et al. derived a new analytical transform method, analogous to the Fourier transform, that produces resonances at the dipolar coupling frequencies present in the REDOR signal. They named this the REDOR transform, and theoretically this permits direct determination of I-S distances provided that the dephasing $S/S_0$ is due to isolated IS spin pairs. Figure 3.8(c) shows the dipolar spectrum resulting from a REDOR transform of the REDOR data in Figure 3.8(a). The REDOR transform has been successfully applied to determine $^6$Li-$^{13}$C distances, and for simultaneous multiple distance measurements in peptides. Further details of this approach are presented in Appendix C.
Figure 3.8 (a) REDOR dephasing $S/S_0$ calculated for $D = 300$ Hz and MAS spinning speed of 4 kHz. (b) Fourier transform of this signal (20 Hz Lorentzian line-broadening applied). (c) REDOR transform of the $S/S_0$ data (3-point Blackman-Harris apodization applied) yields a single peak at 300 Hz. After reference 57.
3.4.2 REDOR Behavior for a Single $S$ Spin Dephased by Several $I$ Spins

When the observed magnetization of a single $S$ spin is dephased by simultaneous dipolar interactions with more than one $I$ spin, the dephasing will normally be most affected by the nearest $I$ spin (since $D \propto 1/r^3$). However, when the distances are comparable, dephasing from multiple spins will be cumulative. REDOR distance determinations are thus much more complicated if several $I$ nuclei contribute to the dephasing. Such a situation can arise in isotopically enriched samples when there is a significant presence of natural abundance "background" spins. Even in non-enriched samples, there can be cases where a single $S$ spin is dipolar coupled to several $I$ spins as will be seen later in this thesis. These multiple $I$ spins can substantially influence the observed dephasing, especially if the nuclei under investigation have large gyromagnetic ratios. Corrections for this background dephasing may be made by subtracting the dephasing measured for a natural abundance sample but this is not always feasible. Another option is to generate or propose a model structure assuming an appropriate statistical and geometric distribution of the dephasing spins, and then to calculate the multi-spin dephasing as described below.

Several approaches which permit the calculation of the REDOR behavior for systems where multiple spins are dipolar coupled to the observed spin have been reported. Calculations for three-spin systems indicate virtually no difference between the dephasing calculated either including or neglecting the effects of homonuclear couplings, provided these interactions are significantly smaller than the magic angle spinning speed. In the equations presented here, the effects of homonuclear coupling are assumed to be averaged out by the sample spinning, and are thus not included.

Naito et al. detailed the derivation of an expression for a three spin system based on the assumption that it could be represented as the summation of two pairwise interactions with permutations of the possible spin states. They demonstrated that the geometrical arrangement of the spin-pairs had a measurable effect on the calculated curves. Schaefer and co-workers derived
a more general equation for the REDOR behavior of an $S$ spin dipolar coupled to any number of $I$ spins provided that the geometric arrangement of these spins is known.\textsuperscript{54,55} This is also based on the addition of pairwise interactions. Further, Schaefer et al. were able to formulate their final equations for multi-spin REDOR in terms of a product of cosine terms, rather than as the sum of cosine sums. The product representation gives a substantial improvement in the efficiency of the computations, and this efficiency becomes more important as the number of spin pairs involved increases.

The calculation of multinuclear dephasing is based on the additivity of exponential products,\textsuperscript{56} and requires a knowledge of the relative geometry as well as the internuclear distances.\textsuperscript{57} Where the structure is known this can be incorporated, otherwise a model of the spin cluster must be proposed. The dephasing of a single observed $S$ spin dipolar coupled to more than one $I$ spin can be calculated directly as the powder average of a sum of independent dephasings assuming that the $I$ nuclei are not coupled to each other, and that the $I$ spin dephasings of the $S$ spins are independent of one another.\textsuperscript{54,55} The first condition can be satisfied when the sample is undergoing magic angle spinning at speeds that greatly exceeded the largest homonuclear $I-I$ dipolar coupling. The second condition has not been demonstrated to date but is assumed to hold because satisfactory fits to REDOR data under this approximation have been obtained in a few systems.\textsuperscript{53,54,57}

For a collection of two or more $I$ spins dipolar coupled to an observed $S$ spin, three angles are required to produce all possible relative orientations of the internuclear vectors in a spinning powder sample. While it is possible to parameterize a multiple spin system by specifying the spherical polar angles ($\alpha$, $\beta$) of the axis of rotation and a third angle $\gamma$ to define the angle of the rotation about this axis (Figure 3.9), it is more convenient to use the Euler angles ($\phi$, $\theta$, $\psi$) as this simplifies the calculations required to perform the vector rotations. To describe the REDOR behavior for the case when two or more spin-1/2 nuclei dipolar coupled to the observed spin-1/2 nucleus, it is thus necessary to express $\Delta \Phi_R$ in terms of the three Euler angles.
We define \( v = \{v_1, v_2, v_3\} \) to be a vector of unit magnitude which lies along the heteronuclear vector, and \( x, y, \) and \( z \) to be unit vectors along the principal axes of the coordinate system (\( z \) is coincident with the spinner axis). A rotation of \( v \) through \((\phi, \theta, \psi)\) gives \( v' = R(\phi, \theta, \psi) \) \( v \) where \( R(\phi, \theta, \psi) \) is a \( 3 \times 3 \) rotation matrix defining a rotation about the \( z \)-axis by \( \phi \), followed by a rotation about the \( y \)-axis by \( \theta \), and then a rotation about the \( z \)-axis by \( \psi \).\(^{58}\)

The following functions of the spherical polar angles \( \alpha \) and \( \beta \) can be defined in terms of the dot products of these vectors:\(^{55}\)

\[
\begin{align*}
\sin\beta \cos\alpha &= v' \cdot x \\
\sin\beta \sin\alpha &= v' \cdot y \\
\cos\beta &= v' \cdot z
\end{align*}
\]

Using these identities gives:

\[
\sin\beta \cos\beta \sin\alpha = (v' \cdot y)(v' \cdot z)
\]

\( \Delta \Phi_R \) can thus be expressed (neglecting any homonuclear interactions) as:

\[
\Delta \Phi_R(\phi, \theta, \psi, \lambda) = 32^{1/2} \lambda (v' \cdot y)(v' \cdot z)
\]

where

\[
(v' \cdot z) = v_1 (\cos\phi \sin\theta) + v_2 (\sin\theta \sin\phi) + v_3 \cos\theta
\]

and

\[
(v' \cdot y) = v_1 (-\cos\psi \sin\phi - \cos\theta \cos\phi \sin\psi) + v_2 (\cos\phi \cos\psi - \cos\theta \sin\phi \sin\psi) + v_3 (\sin\theta \sin\psi)
\]

For a system of \( N \) independent \( I \) nuclei interacting with a single observed \( S \) nucleus, there will be \( N \) dipolar couplings, \( D_i \) (\( i = 1 \) to \( N \)), needed to account for the different heteronuclear distances. We must determine the \( \Delta \Phi_R \)'s for all possible combinations of \( \Sigma \pm \lvert D_i \rvert \), recognizing that the individual \( \pm 1/2 \) spin states occur with equal probability so there are \( 2^N \) combinations of \( \Sigma D_i \) (or \( \Sigma \lambda_i \)). Because the sample is a powder, we must average these sums over space (indicated by the angular brackets) to account for the possible crystallite orientations.
Figure 3.9 Definitions of angles used to calculate dipolar dephasing for a powder undergoing MAS. When two or more $I$ nuclei interact with a single $S$ nucleus three angles $\alpha \in [0, 2\pi]$, $\beta \in [0, \pi]$, and $\gamma \in [0, 2\pi]$ are required to describe the possible $I-S$ orientations. For actual calculations of the it is convenient to use the Euler angles $\phi$, $\theta$, and $\psi$ since the matrices defining the rotation are simpler.

(assumed to be isotropic), add them together, and divide by the number of combinations, $c$ (Eq. 3.31). This function is thus a sum of the appropriate powder averaged sums.

$$\Delta S / S_0 = 1 - c^1 \Sigma_j < \cos [\Sigma \Delta \Phi_R (\phi, \theta, \psi, \lambda_j)] >_\text{space} \quad (j = 1 \text{ to } c) \quad \text{3.31}$$

For two $I$ spins interacting with a single observed $S$ spin, we have two dipolar couplings ($D_1$ and $D_2$), $N = 2$, and $c = 2$. REDOR experiments yield only the magnitude and not the sign of $D$, and since $|D_1 + D_2| = | -D_1 - D_2|$, the number of terms in the sums can be reduced by a factor of two. The averaging over space is accomplished by numerical integration over the three Euler angles, with $\phi$ and $\psi$ varied from 0 to $2\pi$, and $\theta$ from 0 to $\pi$. Additional factors are needed to normalize the integral ($1/8\pi^3$), and to account for the statistical (spherical) distribution of the spins in a powder about the spinning axis vector ($\sin \theta$). A step size of one degree (or less) is
desirable, but larger step sizes may be used to reduce the computation time and still provide acceptable accuracy (see Appendix C). For such a 3-spin system Eq. 3.31 becomes:

\[
\Delta S/S_0 = 1 - (4\pi^2)^{-1} \left[ \int_0^{\pi} \int_0^{\phi} \{ \cos[\Delta \Phi_R (\phi, \theta, \psi, +\lambda_i) + \Delta \Phi (\phi, \theta, \psi, +\lambda_i)] \} \, d\phi \, \sin \theta \, d\theta \, d\psi \right.

+ \left. \int_0^{\pi} \int_0^{\phi} \{ \cos[\Delta \Phi_R (\phi, \theta, \psi, +\lambda_i) + \Delta \Phi (\phi, \theta, \psi, -\lambda_i)] \} \, d\phi \, \sin \theta \, d\theta \, d\psi \right] 3.32
\]

Schaefer et al. have shown that the dephasing can also be calculated as a product over the \( N \) dipolar interactions, with spatial (powder) averaging.\(^{54,55}\) In this form (Eq. 3.33) it is no longer necessary to consider the two possible signs of the dipolar couplings as this is implicitly included.\(^{55,56}\) This considerably reduces the number of calculations required, and thus the computation time. This efficiency gain in the computations gets progressively larger as the number of spin pairs increases.

\[
\Delta S / S_0 = 1 - (8\pi^2)^{-1} \left[ \int_0^{\pi} \int_0^{\phi} (\Pi_i \cos[\Delta \Phi_R (\phi_i, \theta, \psi, \lambda_i)]) \, d\phi \, \sin \theta \, d\theta \, d\psi \right] (i = 1 \text{ to } N) 3.33
\]

The analysis will be less straightforward for pulse placements other than \( \tau_r/2 \) and \( \tau_r \) described above because, in general, the functions describing the dephasing are more complex (see Appendix C).

The validity of programs written to perform the calculations based on Eqs. 3.31 and 3.33 in the present work was checked by comparing the results for a variety of 3-spin geometries against the data presented in reference 8. Details of the implementation of these calculations using the Mathematica programming environment are given in Appendix C. The theoretical REDOR behavior for a variety of 3-spin \( I_S \) systems clusters is examined in Chapter 5.

### 3.4.3 REDOR Behaviour of Isolated \( S \) Spins in a Network of Many \( I \) Spins

Blumenfeld et al.\(^{16}\) have proposed a formalism for calculating the REDOR dephasing of isolated \( S \) spins in the presence of a large number of \( I \) spins where the explicit geometrical arrangement is unknown. Their approach is analogous to that used to relate \( T_{CP} \) to the
heteronuclear second moment (Eq. 3.16). They assume that the heteronuclear lineshape is inhomogeneous, and can thus be considered as a superposition of a large number of doublet resonances with splitting $2D_0$. Under the further assumption that this lineshape is Gaussian, they sum the REDOR curves calculated (vs. $n\tau$) for the individual $D_0$'s with a weighting $w(D_0)$ of each to the final curve determined by a Gaussian distribution (Eq. 3.34):

$$w(D_0) = \frac{1}{\sqrt{2\pi M_2(I-S)}} \exp \left( -\frac{D_0^2}{2M_2(I-S)} \right)$$

3.34

The resulting REDOR curve obtained in this manner will show a smooth rise to a maximum and may be considered as the response of a spin system with a given heteronuclear second moment $M_2(I-S)$. Analytical functions were derived to calculate the REDOR behavior assuming a Gaussian distribution. Full details are presented in Appendix C together with the Mathematica scripts used to perform the calculations.

REDOR experiments may be complicated by the presence of background signals arising from uncoupled spins (e.g. natural abundance $^{13}$C in natural compounds) and in some cases it is desirable to remove these interactions. The signal intensity that has been “lost” due to dephasing in a REDOR experiment has not vanished; it has just been transferred to another type of coherence which is not directly observable. However, the application of appropriate pulses makes it possible to recover this magnetization, and to transfer it to observable $S$ spin magnetization. The TEDOR experiment which is specifically designed to do this is described in the next section.

### 3.5 TRANSFERRED ECHO DOUBLE RESONANCE

TEDOR experiments were originally developed by Schaefer and co-workers as an alternative to the REDOR experiment to measure weak dipolar coupling of heteronuclear $IS$ spin pairs while eliminating unwanted background signals from uncoupled spins. This is particularly
important for $^{13}$C in organic and biological systems, where there will always be natural abundance $^{13}$C. The TEDOR experiment uses a coherence transfer analogous to the solution-state INEPT experiment.

As seen from Figure 3.10(a), a TEDOR experiment is essentially comprised of two REDOR-type sequences: an initial one on the $I$ spins, and a subsequent one on the $S$ spins following the application of simultaneous $\pi/2$-pulses to both spins. These simultaneous pulses allow for a coherence transfer of polarization from the $I$ to the $S$ spins. Thus, there are two time periods of dipolar dephasing; one before the transfer of coherence, and another after. The pulse sequence in Figure 3.10(b) includes an initial cross polarization transfer from a third, abundant nucleus.

During the $n$ rotor periods before the coherence transfer, a series of dephasing $\pi$-pulses (two per rotor cycle) are applied to prevent the refocussing of the $I$-$S$ dipolar interaction by MAS. As in the REDOR experiment, the dephasing pulses are placed at specific points within each rotor period. TEDOR experiments are usually performed with the dephasing pulses at $\tau_r/4$ and $3\tau_r/4$, but they may be placed at different fractions of the rotor period. Some other possibilities are examined in Section 3.5.2.

Once an effective heteronuclear dipolar dephasing has accumulated, a coherence transfer is performed that selects only those $S$ spins that are dipolar coupled to $I$ spins. Because of this selective transfer, the TEDOR effectively eliminates contributions from uncoupled $S$ spins. In the $m$ rotor periods that follow, the antiphase magnetization that was transferred from the $I$ spins to the $S$ spin is modulated by the dephasing pulses, and evolves into observable $S$ spin magnetization.$^4$

The ability to vary $n$ with $m$ fixed, or to vary $m$ with $n$ fixed, gives more flexibility to the TEDOR experiments compared to REDOR, since it allows the selection of the experimental parameters best suited to the $T_1$ and $T_2$ relaxation values of a particular system, although this has not been described in the literature to date. This flexibility may be especially useful if $T_2$ values...
Figure 3.10 Pulse sequences for TEDOR with: (a) dephasing pulses on the observed (S) spins before coherence transfer (achieved by simultaneous \( \pi/2 \)-pulses), and on the unobserved (I) nuclei after; (b) initial cross polarization from an abundant nucleus (e.g. \(^1\text{H}\)) to the unobserved spins. A series of experiments are acquired with \( n \) held constant and \( m \) varied or vice versa. The simultaneous \( \pi \)-pulses ensure that the chemical shifts are refocussed.
are short, as can often be the case for inorganic solids. $^{13}$C-$^{15}$N distances which are in agreement with those determined from diffraction studies have been successfully determined using TEDOR experiments. In addition, Klug and Schaefer have demonstrated a double TEDOR experiment for the direct detection of $I-S-I$ triads.

3.5.1 TEDOR Behavior for Isolated $I'S$ Spin Pairs

For an isolated heteronuclear $I'S$ spin pair, the TEDOR signal, $S_T$, arising from placement of the dephasing $\pi$-pulses at one-quarter and three-quarters of a rotor cycle is described by Eqs. 3.35-3.37. The integration limits are $\alpha \in [0, 2\pi]$ and $\beta \in [0, \pi]$, $\lambda_n = nD\tau$, and $\lambda_m = mD\tau$.

$$S_T = (4\pi)^{-1} \int \int_{\alpha, \beta} \sin[\Delta \Phi_{Tn}(\alpha, \beta, \lambda_n)] \sin[\Delta \Phi_m(\alpha, \beta, \lambda_m)] \sin \beta \, d\beta \, d\alpha$$  \hspace{0.5cm} (3.35)

where

$$\Delta \Phi_{Tn}(\alpha, \beta, \lambda_n) = 32^{1/2} \lambda_n \sin \beta \cos \beta \cos \alpha$$  \hspace{0.5cm} (3.36)

and

$$\Delta \Phi_m(\alpha, \beta, \lambda_m) = 32^{1/2} \lambda_m \sin \beta \cos \beta \cos \alpha$$  \hspace{0.5cm} (3.37)

3.5.2 TEDOR Curve Families and Experimental Considerations

TEDOR dephasing behavior is best presented by plotting curves of $S_T$ versus the number of rotor periods $n$ or the dephasing time $m\tau$, if the number of rotor periods after coherence transfer was fixed. If $n$ was fixed then $S_T$ vs. $m$ or $m\tau$ is appropriate. The analysis of TEDOR experiments requires that both the spinning rate and the exact value of the dipolar coupling during the period before coherence transfer are known in order to calculate the curve for the period after the transfer, and vice versa. In real situations the coupling is usually not known a priori, but can often be estimated by using known values for similar systems. As for REDOR, it is advantageous to use the analytical expressions in terms of Bessel functions derived by Mueller as these avoid the more complex (and time-consuming) numerical integration and permit nonlinear least squares fitting as described in Appendix C.
Figure 3.11 illustrates several families of theoretical TEDOR curves including variation of \(n\) with \(m\) fixed for different values of \(m\), \(n\) fixed with \(m\) varied, different rotor speeds, dipolar couplings, and several values of the parameter used to "dampen" the curves to account for the homogeneous \((T_2)\) decay that occurs after the coherence transfer. For a TEDOR experiment, the theoretical maximum transfer of coherence (neglecting \(T_2\) decay) is predicted to occur when \(n D\tau = 0.84\).

Inspection of Figure 3.11(a) and (b) shows how the position of the initial maximum in the curves shifts to higher number of rotor periods as the magnitude of the dipolar interaction decreases, or as the spinning rate increases. Calculation of a series of curves with appropriate parameters corresponding to the experimental conditions prior to beginning TEDOR experiments is invaluable for selecting the best experimental variables. For a given spin system certain values of \(n\) or \(m\) may be preferable depending on nuclear relaxation parameters and available spinning speeds.

Because the TEDOR signal intensity \(S_T\) is not normalized as it is for REDOR, the experimental intensities need to be scaled to match the theoretical curves. In addition to experimental constraints (such as available pulse lengths and spinning speeds), it is important to take into consideration the nuclear relaxation parameters of the nuclei as these limit the range of \(n\) or \(m\) values that will give viable signal intensities. If the TEDOR pulse sequence contains additional simultaneous \(\pi\)-pulses to generate a spin-echo, it is \(T_2\) rather than \(T_2^*\) that is important. This will be the case where a refocussed TEDOR pulse sequence is used (Figure 3.10). During the period before coherence transfer, the spin-spin relaxation rate, \(T_2\), of the \(I\) nuclei is important, and after the transfer it is the \(T_2\) of the observed \((S)\) nuclei which limits the number of rotor periods after coherence transfer that signal can be detected.

Other alternatives for optimizing TEDOR experiments for specific samples include using different spinning speeds, or changing the positions of the dephasing \(\pi\)-pulses. For example they can be at \(\tau/3, 2\tau/3\) before coherence transfer and \(\tau/4, 3\tau/4\) after, or at \(\tau/4, 3\tau/4\) before transfer
Figure 3.11 Theoretical TEDOR curves illustrating the effects of different dipolar couplings (a) and different spinning speeds (b). The curves were calculated for an isolated $I\bar{S}$ spin pair assuming $n = 2$ with $m$ varied.
Figure 3.11 (continued) Theoretical TEDOR curves illustrating the effects of different numbers of fixed rotor periods (c) and dampening to account for $T_2$ decay (d). The curves were calculated for an isolated $1S$ spin pair assuming $v_r=4.0$ kHz, $D=1000$ Hz, $n$ held constant, and $m$ varied.
and \( \tau_r/5, 4\tau_r/5 \) after. If the pulses are shifted from \( \tau_r/4 \) and \( 3\tau_r/4 \), appropriate theoretical functions must be determined, and numerical integration is now required to calculate the theoretical TEDOR curves. The appropriate functions for a selection of pulse placements have been derived and are presented in Appendix C.

3.5.3 TEDOR Behavior for a Single Spin Dephased by Several \( I \) Spins

The theoretical treatment presented above for the case of REDOR multi-spin dephasing can be extended to the TEDOR experiment. For dephasing pulses positioned at \( \tau_r/4 \) and \( 3\tau_r/4 \), using Eqs. 3.24 and 3.25 gives:

\[
\sin \beta \cos \beta \cos \alpha = (v' \cdot x)(v' \cdot z)
\]

3.38

\( \Delta \Phi_{Tn} \) can thus be expressed (neglecting any homonuclear interactions) as:

\[
(\nu_1 \cdot \nu_2 \cdot \nu_3) = 32^{1/2} \lambda_n (v' \cdot x) (v' \cdot z)
\]

3.39

where

\[
(v' \cdot z) = \nu_1 (\cos \phi \sin \theta) + \nu_2 (\sin \phi \sin \psi) + \nu_3 \cos \theta
\]

3.40

and

\[
(v' \cdot x) = \nu_1 (\cos \theta \cos \phi \cos \psi - \sin \phi \sin \psi) + \nu_2 (\cos \theta \cos \psi \sin \phi + \cos \psi \sin \phi) - \nu_3 (\cos \theta \sin \phi)
\]

3.41

An identical expression is obtained for \( \Delta \Phi_{Tm} \) with \( \lambda_m \) replacing \( \lambda_n \). If the dephasing pulses are not at the one- and three-quarters points of each rotor period, these equations will become very complex (see Table C.4, Appendix C).

Since there are now contributions from several dipolar couplings, the theoretical TEDOR curves must be plotted versus the dephasing time \( nt_r \) if the number of rotor periods before the transfer was varied (or versus \( mt_r \) if \( m \) was varied). Using the expressions derived above, it was possible to calculate the TEDOR dephasing for \( I_n S \) systems as a sum of sums in an analogous manner to that described for REDOR in Section 3.4.2. Attempts to express the multi-spin
TEDOR dephasing in terms of a product of sums produced dephasing behavior which was not physically meaningful ($S_T$ very small). This stems from the nature of the functions that are evaluated. The theoretical TEDOR behavior for a variety of 3-spin $I_S$ clusters is examined in Chapter 5.

3.6 EFFECTS OF MOLECULAR MOTIONS

Any relative motions of the nuclei within a heteronuclear spin system can affect the dipolar interactions since the internuclear distance will vary. Clearly CP, REDOR and TEDOR experiments will all be affected by any changes in the magnitude of the $I-S$ dipolar couplings which occur during the course of the experiment. Such motions will need to be considered if they occur on time scales which are shorter than the reciprocal of the heteronuclear dipole-dipole interaction \( i.e. \) of the order of milliseconds. In systems with weak dipolar couplings where the evolution of the dephasing needs to be observed for 30 ms or more, the inclusion of the effects of motion may be very important in correctly determining $D$. However, the effects of motions should only be included where they are known to exist from other independent evidence.

The net effect of relative motions of the $I$ and $S$ spins will be to average the dipolar coupling, and the exact form of the averaging will depend directly on the explicit nature of the geometrical displacement, and the timescale on which it occurs. Any motion will reduce the magnitude of the overall dipolar coupling. In this section a qualitative description of the effects of molecular motions, and techniques for calculating the effects if details of the motion are known is presented.

For an isolated $IS$ spin pair during a cross polarization experiment, motion will result in a situation where at a given instant some $S$ spins will experience weak dipolar coupling, while others will be influenced by stronger couplings. Each different coupling will give rise to an oscillatory behavior whose period is determined by the dipolar coupling. The observed signal will be the superposition of a large number of these oscillations and will thus be a relatively
smooth curve without oscillations. Depending on the timescale of the motions, the couplings within each spin pair may also change during the experiment, which would also result in a smooth, non-periodic behaviour.

In spin systems with a large excess of \( I \) spins which experience strong \( I-I \) homonuclear couplings, the averaged, reduced dipolar couplings will mean that the \( T_{CP} \) value will increase. However, provided the motion can be modelled then the effect on the heteronuclear second moment \( (M_2) \) can be calculated using the formalism presented by Michel et al.\(^ {41} \) (see Appendix D).

Goetz and Schaefer have described how to calculate the REDOR dephasing in the presence of such motions.\(^ {55} \) Basically a three-dimensional powder average is performed in the same manner as in the multiple-spin case, except that the argument of the cosine term Eq. 3.33 is replaced by a sum of terms which depend on the trajectory of the moving spin(s). The presence of such motions will result in an apparent reduction in dephasing compared to that predicted for a rigid spin system. A similar approach may also be valid for TEDOR.

### 3.7 SUMMARY

REDOR and TEDOR experiments are proven, reliable techniques for measuring \( I-S \) distances from the magnitude of the heteronuclear dipolar couplings in rigid lattices. Although it is anticipated that heteronuclear distances can also be determined from CP experiments where oscillatory behavior is observed, this has only been reliably demonstrated in very few cases.

Quantitative CP experiments require that the Hartmann-Hahn matching condition is sustained for the entire duration of the spin-locking pulse, which places stringent requirements on the amplifiers to provide constant r.f. fields for several tens of milliseconds. Under MAS the requirements become even more demanding since the spinning speed must remain constant to ensure that the chosen sideband matching condition can be maintained; slight mismatching will result in dramatic loses in the CP signal. Thus CP MAS is very demanding on both the mechanical and electrical instrumentation.
REDOR and TEDOR require much shorter pulses than CP (typically 10-20μs) which do 
however, need to be quite precisely positioned to prevent the complete averaging out of the 
dipolar interaction. Thus in addition to maintaining a constant spinning rate, the speed must be 
accurately determined so that the delays between the pulses can be correctly calculated.

REDOR experiments yield normalized intensities which can provide information about 
the statistical occupancy of the \( I \) spin sites. Although TEDOR experiments eliminate unwanted 
background signals arising from observed nuclei which are not dipolar coupled to the 
heteronuclear spins, the analysis requires an estimate of the dipolar coupling in order to calculate 
the dephasing that occurs during the period where the number of rotor periods is held constant.

TEDOR offers advantages because of the larger number of experimental variables 
available, and the corresponding increased flexibility to accommodate large \( T_1 \) or small \( T_2 \) values 
of either nucleus. Another advantage of TEDOR over REDOR is that it is possible to perform 2-
D TEDOR correlation experiments\(^{14,15,17,61}\). This is potentially very useful in cases where there 
are several resonances for both nuclei.

Incorrect internuclear distances could be obtained from fitting REDOR and TEDOR 
experimental data if more than one spin is dipolar coupled to the observed spin and the fitting 
assumes only a single, static, isolated spin pair. The use of only a few data points acquired at 
small numbers of rotor periods may give incorrect answers and should thus be avoided. 
Independent information which verifies that the experimental data relates to an isolated spin pair 
should be obtained if possible. For spin systems which cannot be considered as isolated spin 
pairs, it may be possible to determine the dipolar couplings (and thus distances) accurately from 
REDOR and TEDOR experiments. However, because there is a strong dependence on the 
number of spins involved, as well as the specific geometrical arrangement and motions of these, 
direct determination of the dipolar couplings cannot be achieved as it can for isolated spin pairs, 
and the experimental data must be fit to a model structure.
Simulations with various clusters of spins have shown that the dephasing is typically dominated by the closest heteronuclear contacts when homonuclear interactions are ignored. If an accurate model which specifies the positions (and motions) of all the spins within a cluster can be proposed, then distances from observed spins to multiple heteronuclear dephasing spins may be inferred. Such a model must explicitly include the number of spins, any motional averaging, the statistical probability that each site is occupied by an NMR-active isotope, the relative spatial arrangement, and the heteronuclear distances. The quality of the model will be determined by the ability of the theoretical curve to account for the experimentally observed behavior as a function of dephasing time. Because the dephasing predicted for different geometries can be very similar at short dephasing times, it is generally important that data be acquired at sufficiently long dephasing times to discriminate between different models.

However, other problems associated with the use of long dephasing times such as poor signal-to-noise, relative motions of the spins, and significant dephasing from more distant spins may complicate these analyses. Reliable distance determinations for multiple spin systems may only be obtained with knowledge of the spin cluster geometry. If unambiguous distance determinations are needed, the system under investigation should be prepared in manner that will produce only isolated spin pairs (e.g. by isotopic dilution) if at all possible. It is also desirable to ensure complete occupancy of each labeled site since this avoids further complications arising from the need to consider the statistics of different distributions of the spins.

Recently, Blumenfeld et al. have reported that in cases where there are a large number of spins dephasing a single (observed) spin, it may be appropriate to assume a Gaussian distribution of isolated IS spin pairs, and calculate the REDOR behavior as a sum of these. The resulting curves are thus related to a single measurable variable, the heteronuclear second moment. This approach may prove useful in many cases, especially where the structure is not known, and oscillations are not seen.
REFERENCES FOR CHAPTER 3

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26 Hediger, S. Eidgenössische Technische Hochschule Zürich, Personal Communication, August 1997.


CHAPTER 4

$^{19}$F – $^{29}$Si DISTANCE DETERMINATIONS IN FLUORIDE-CONTAINING OCTADECASIL FROM SOLID-STATE NMR MEASUREMENTS

4.1 INTRODUCTION

The framework structures of microporous materials contain regular systems of cavities and channels of molecular dimensions (3-13 Å) which are critical in the application of these materials as sorbents, catalysts and molecular sieves. One of their most important characteristics is the size and shape selectivity which they display towards sorbed organic molecules and thus there is considerable interest in investigating the detailed three-dimensional structures of zeolite frameworks containing intercalated species in order to understand in detail the nature of these sorbate-framework interactions.

Unfortunately, there is relatively little direct experimental information regarding the exact location of sorbed molecules within these frameworks; theoretical calculations are not always in agreement with one another, and it is difficult to determine these structures by single crystal X-ray diffraction as discussed in Chapter 1. For these reasons other techniques must be developed to obtain this structural information. In this chapter results from NMR experiments and calculations which locate the fluoride ions within the framework of octadecasil are presented. The feasibility of extending these experiments to other framework-host / fluorine-containing-guest systems is clearly demonstrated.
4.1.1 Synthesis of Molecular Sieves in Fluoride-Containing Media

The fluoride-synthesis route to molecular sieves, which was originally developed by Flanigen and Patton and extended by Guth and co-workers and others, produces very highly crystalline samples having high degrees of both long range and local ordering. This is indicated by the sharp reflections extending to high 2θ values which are observed in their X-ray powder diffraction patterns, and by the narrow resonances in their \(^{29}\)Si MAS NMR spectra. During the synthesis, fluoride anions can play several roles, acting as mineralizers, templates or structure-directing agents. Chemical analysis and \(^{19}\)F MAS NMR spectroscopy reveal that most of the as-synthesized materials have incorporated fluoride anions.

However, it is often difficult to locate the fluoride ions by X-ray diffraction as the single crystals may be too small, or twinned, and recourse must be made to other techniques. There are additional complications in that fluoride ions and the OH groups (which can occur as defects within these framework structures) have very similar numbers of electrons making them difficult to distinguish. In several cases, however, fluoride anions have been clearly located in the double 4-ring (D4R) units of the framework. These include octadecasil, the tetragonal variant of AIPO\(_4\)-16, three GaPO\(_4\)s (cloverite, GaPO\(_4\)-LTA, and ULM-5), and also an LTA-type AIPO\(_4\) containing some cobalt and silicon.

The D4R moiety is not the only possible location for the fluoride ions; in the triclinic CHA-like AIPO\(_4\)-34 and GaPO\(_4\)-34, fluorine is part of the framework and it apparently bridges two Al (or Ga) atoms. In AIPO\(_4\)-5, the fluoride anion has been located in the 4-ring columns of the framework, far from the organic counter-ion. In some cases it is not localized, and for purely siliceous MFI-type zeolites a discrepancy exists: Price et al. reported that the F\(^-\) was located close to the nitrogen of the tetrapropylammonium ion (TPA\(^+\)), while Mentzen et al. located it in the framework close to a 4-ring, but also found an unassigned site close to the TPA\(^+\). In a few cases, such as the recently reported precursor of FER-type zeolite, F\(^-\) is not...
incorporated, suggesting that its role in this case is restricted to that of a mobilizing agent. Thus, there is also interest in being able to locate the fluoride ions in these types of samples to improve understanding of the various roles they play in the syntheses.

4.1.2 $^{19}$F–$^{29}$Si Distance Determinations from Solid-State NMR Experiments

Solid-state NMR in conjunction with Rietveld refinement of powder XRD data has been successfully demonstrated to be a powerful technique for the investigation of zeolite structures. The $^{29}$Si MAS NMR spectra of highly siliceous zeolites can be directly related to the framework structure, the number and relative intensities of the resonances reflecting the numbers and occupancies of the crystallographically inequivalent T-sites in the asymmetric unit. This makes it possible, in principle, to determine the locations of species within the frameworks by determining the distances between their component atoms and specific T-sites in the framework. This can be done using experiments based on the through-space dipolar interactions between pairs of nuclei $I$ and $S$ as described in Chapter 3.

The magnitude of the dipolar coupling between two nuclei depends on the gyromagnetic ratios of the two nuclei, $\gamma_I$ and $\gamma_S$, and on the $I$-$S$ internuclear distance (Eq. 1.10), making $^{19}$F attractive for these studies. Furthermore, while the $^{19}$F isotope is 100% abundant, fluorine is relatively uncommon in chemical systems, and thus the likelihood of potential background interferences is minimal.

In high-resolution solid-state NMR, magic angle spinning (MAS), is used to narrow the otherwise extremely broad (up to several kHz) resonances. However, in addition to averaging the chemical shift to its isotropic value, the heteronuclear dipolar interactions for an isolated spin-pair are averaged to zero during each complete rotor cycle. Thus, in its simplest form, the use of MAS precludes a direct measurement of $D$, although this interaction is responsible for the coherence transfer in the cross polarization (CP) process. In those cases where the spin system behaves essentially as an isolated heteronuclear spin-pair, an oscillatory behavior in the
amplitude of the CP signal at short contact times is observed for both non-rotating solid samples and those undergoing magic angle spinning. Such dipolar have been reported for several different systems under MAS conditions. Fitting of these oscillations with appropriate functions allows the heteronuclear dipolar coupling and thus the internuclear $I-S$ distances to be determined as discussed in Chapter 3. If the observed spins experience dipolar coupling to several heteronuclear spins, oscillations at several frequencies interfere and a smooth exponential rise to a maximum followed by a decay due to relaxation is typically observed.

Recently, Schaefer and co-workers have introduced the REDOR and TEDOR experiments. The magnitude of the dipolar couplings can be experimentally determined from these experiments using appropriate analyses. As discussed in Chapter 3, REDOR and TEDOR distance determinations are more complicated if several nuclei contribute to the dephasing.

In this chapter the results of Si-F distance measurements on as-synthesized octadecasil are presented. Octadecasil, chosen to be representative of molecular sieve framework structures, is the purely siliceous analogue of AlPO$_4$-16, and was recently synthesized by Caullet et al. from fluoride-containing media. The crystal structure was solved using single crystal X-ray methods, the fluoride anions located, and accurate Si-F distances determined. The low natural abundance of $^{29}$Si (4.7%) in the framework, combined with the weak homonuclear couplings means that the $^{19}$F-$^{29}$Si dipolar interactions should approximate clusters of isolated heteronuclear spin-pairs for which theoretical CP, REDOR, and TEDOR behavior can be calculated. Octadecasil, which contains two distinct T-sites and two quite different Si-F interatomic distances, was chosen as a model case for determining the best experiments to use, as well as the optimization of these experiments and the subsequent analysis of the experimental data.
4.2 MATERIALS AND METHODS

The pure, highly crystalline octadecasil sample (crystal size 80 μm), was kindly provided by Dr. P. Caullet. The structure was checked by powder X-ray diffraction and $^{19}$F and $^{29}$Si MAS NMR measurements, all of which agreed with previously reported results. Fluorine contents in these materials are usually in the range 2.3% to 2.6%, which corresponds to occupancies of 80% to 100% of the D4R units by fluoride ions. The idealized elemental composition of octadecasil is $\text{Si}_{20}\text{O}_{40} \cdot 2(\text{Q}^+\text{F}^-)$ where Q$^+$ is the quinuclidinium cation.

The NMR experiments were carried out using a Bruker MSL-400 spectrometer, operating at frequencies of 376.434 MHz and 79.495 MHz for $^{19}$F and $^{29}$Si respectively as described in Chapter 2. A Bruker double-tuned $^1$H/X MAS probe with the $^1$H channel tuned to the $^{19}$F frequency was used, and spinning speeds of 2.0-5.2 kHz were attainable. The peak separations of the spinning sidebands in the $^{19}$F MAS NMR spectra were used to determine the spinning frequency, $v_s$, to an accuracy of better than 10 Hz. Further details are given in Chapter 2.

4.2.1 Cross Polarization Experiments

For the CP experiments the Hartmann-Hahn sideband matching condition was established experimentally by fixing the $^{19}$F radio-frequency power and adjusting the $^{29}$Si radio-frequency power to maximize the observed signal. Field strengths up to 33 kHz were available for the $^{19}$F channel. For variable contact time CP experiments, spectra were acquired using contact times from 10 μs to 60 ms. The Hartmann-Hahn matches were optimized using a 2 ms contact time for non-spinning (static) samples, and 10 ms for samples undergoing MAS.

4.2.2 REDOR and TEDOR Experiments

In all the REDOR experiments the observed nucleus was $^{29}$Si, and the trains of rotor-synchronous dephasing pulses were applied to $^{29}$Si or $^{19}$F, depending on the pulse sequence used.
The dephasing pulses were always timed to occur at half and full rotor periods, the $^{19}$F offset was exactly on resonance, and the $^{29}$Si frequency was set to be approximately midway between the two silicon resonances. In the REDOR experiments which incorporated an initial cross polarization from $^{19}$F to $^{29}$Si to improve the efficiency, a 10 ms contact time was used. Further details of the experimental set-up are described in Chapter 2.

For TEDOR experiments the fluorine signal was set exactly on resonance and the observed nucleus was $^{29}$Si. Several variations of the TEDOR experiment were used. These included applying the dephasing pulses on $^{29}$Si or $^{19}$F before the coherence transfer pulse, varying the spinning speed, the positions of the dephasing pulses, and incrementing the number of rotor cycles before or after the transfer pulse.

4.2.3 Calculations and Data Analysis

Fitting to determine the relaxation times was carried out using the commercial Bruker software. Values of the expected $^{19}$F-$^{29}$Si dipolar coupling constants for a range of Si-F distances were calculated using Eq. 1.10 and are summarized in Table 4.1. The boldface entries in the table correspond to the experimental Si-F interatomic distances determined from the crystal structure data for octadecasil reported by Caullet et al.,$^{16}$ and the corresponding dipolar couplings.

For the CP, REDOR, and TEDOR experiments, the heteronuclear $^{19}$F-$^{29}$Si dipolar couplings for the T-1 silicons were determined from nonlinear least squares fitting of the data in *Mathematica* $^{37}$ using the methods described in Chapter 3. For all the calculations the spins were assumed to be at fixed positions within a rigid lattice and homonuclear dipolar interactions were ignored because the $^{19}$F-$^{19}$F couplings and the much weaker $^{29}$Si-$^{29}$Si couplings were much less than the sample spinning speeds employed (2-5 kHz).
Table 4.1 \[^{19}\text{F}-\text{Si}\] spin-pair dipolar couplings (D) calculated for various Si-F interatomic distances (r). Boldface entries are for the distances and corresponding dipolar couplings calculated from the single crystal X-ray structure of octadecasil by Caullet et al.\(^{16}\)

<table>
<thead>
<tr>
<th>r (Å)</th>
<th>D (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.775</td>
<td>1050</td>
</tr>
<tr>
<td>2.692</td>
<td>1100</td>
</tr>
<tr>
<td>2.655</td>
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</tr>
<tr>
<td>2.632</td>
<td>1200</td>
</tr>
<tr>
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<td>1230</td>
</tr>
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<td>1350</td>
</tr>
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<td>2.521</td>
<td>1400</td>
</tr>
<tr>
<td>2.492</td>
<td>1450</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>r (Å)</th>
<th>D (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.077</td>
<td>5.801</td>
</tr>
<tr>
<td>5.887</td>
<td>5.719</td>
</tr>
<tr>
<td>5.688</td>
<td>5.6420</td>
</tr>
<tr>
<td>5.568</td>
<td>5.433</td>
</tr>
<tr>
<td>5.433</td>
<td>4.824</td>
</tr>
</tbody>
</table>

Table 4.2 \[^{26}\text{Si}\] and \[^{19}\text{F}\] MAS NMR relaxation time measurements (performed at frequencies of 79.495 MHz and 376.434 MHz respectively).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>F</th>
<th>T-1 Si</th>
<th>T-2 Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ(CFCl(_3)) = -37.8 ppm</td>
<td>8.06 ppm</td>
<td>8.11 ppm</td>
<td></td>
</tr>
<tr>
<td>δ(TMS) = -108 ppm</td>
<td>8.11 ppm</td>
<td>8.06 ppm</td>
<td></td>
</tr>
<tr>
<td>T(_1)</td>
<td>2.6 s</td>
<td>2.6 s</td>
<td></td>
</tr>
<tr>
<td>T(_2)</td>
<td>3.5 ms</td>
<td>3.5 ms</td>
<td></td>
</tr>
</tbody>
</table>

Values determined by fitting using the commercial Bruker software.

Data acquired with rotor-synchronization.
Prior to commencing nonlinear fitting, trial fittings were used to determine approximate values for the parameters that were not fixed in the experiment, the dipolar coupling and a scaling factor to match the experimental and theoretical intensities if required. During fitting of the CP data, some constraints were necessary to prevent physically unrealistic values for some of the parameters. For TEDOR experiments there is no normalization as there is for REDOR, so the scaling factor was arbitrary, and an exponential damping factor was incorporated to take into account $T_2$ decay during the evolution period. Weighted nonlinear fittings of the data were carried out starting from these initial parameter values, and these were constrained to realistic (positive) limits. The Levenberg-Marquardt algorithm was utilized to minimize the value of the parameter $\chi^2 = \sum |F_i - f_i|^2$ where $F_i$ is the value of the $i^{th}$ data point and $f_i$ is the value obtained from the fit. The best values for the parameters were taken as those which gave the smallest $\chi^2$ values. Because the spectra acquired for small numbers of rotor cycles had better signal-to-noise ratios, they yielded more accurate intensities, and consequently these data were given more emphasis during the fitting procedure. Several data-weighting schemes were evaluated, and weighting by the inverse of the number of rotor periods proved to be the most reliable, giving very reproducible results if the initial parameter values were varied.

For experiments where the positions of the pulses were not those used for the derivations of the analytical functions reported by Mueller and also when multiple spin analysis was required (T-2 Si), the appropriate integrals for the TEDOR and REDOR functions were determined and then evaluated using point-by-point numerical integration over a sphere to produce a powder average as described in Chapter 3 and Appendix C.

4.3 RESULTS AND DISCUSSION

4.3.1 Octadecasil Crystal Structure

The structure of octadecasil, the purely siliceous analogue of AlPO$_4$-16 (IZA Structure Commission Framework Code AST), has been solved by single crystal X-ray methods. The
framework consists of octadecaheiral $[4^6]^12$ cages and hexahedral $[4^6]$ cages, and can be built by linking the octadecaheiral through all their common 6-membered ring faces (Figure 4.1(a)). Since these octadecaheiral cages do not completely fill 3-dimensional space another type of void, the very small $[4^4]$-cage or double 4-membered ring (D4R) unit is created.

When prepared from a fluoride-containing medium, the as-synthesized product contains the quaternary ammonium templating cation (quinuclidinium in this case) in the large cages, and the negatively charged fluoride anion (needed to balance the positive charge of the organic cation) in the D4R units, and crystallizes in a tetragonal phase (space group $I4/m$, No. 87). The octadecasil structure contains two types of T-sites (Figure 4.1), T-1 sites at the vertices of the D4R units and T-2 sites located at the vertices of 6-rings in the ratio 4 T-1: 1 T-2. There are 20 $[SiO_4]$ tetrahedra, and thus 16 T-1 and 4 T-2 sites per unit cell. Each T-2 links 4 T-1's from four different D4R units (Figure 4.1(b)). From the X-ray crystal structure data, the T-1 silicons are 2.63 Å from the fluoride ion inside their D4R unit and more than 7 Å from the fluoride ions in the adjacent D4R units. The T-2 silicons are 5.69 Å from each of four equivalent fluoride anions, and the closest F-F distance is 9.33 Å.

4.3.2 1-D $^{19}$F and $^{29}$Si NMR Experiments

Qualitative $^{19}$F and $^{29}$Si MAS NMR spectra were in general agreement, both with previously reported data and the crystal structure as discussed above. In order to best implement the different experiments, a knowledge of the different nuclear relaxation parameters is essential. $T_1$ and $T_2$ were measured for both nuclei, and are summarized in Table 4.2. For CP experiments the value of $T_{1p}$ was measured using an $^{19}$F spin locking field of 17 or 33 kHz.

The room-temperature 1-D $^{19}$F MAS NMR spectrum (Figure 4.2(a)) shows a single resonance at -38.2 ppm with respect to CFCl$_3$. The chemical shift is indicative of a single, unique environment, and is similar to those reported for other $^{19}$F / $^{29}$Si systems where the fluoride ion is located within a D4R unit. The static $^{19}$F NMR spectrum consists of a single peak with a full-
Figure 4.1 (a) Schematic representation of the framework structure of octadecasil showing the packing arrangement of the two types of cages, the large [4\(^6\)6\(^1\)]-cages, and the small [4\(^6\)]-cages (or D4R units). Silicon atoms lie at each vertex, and oxygen atoms are located approximately midway along the lines. Thick lines indicate connections closer to the viewer. The [4\(^6\)6\(^1\)]-cages pack in a tetrahedral arrangement by sharing all their 6-membered ring faces and [4\(^6\)]-cages fill the voids thus created. Fluoride anions lie at the center of ca. 90\% the double four-ring units. (b) Portion of the octadecasil framework showing the four D4R units surrounding each T-2 silicon. Each T-1 silicon is connected to three other T-1 sites in the same D4R unit and to one T-2 silicon. Fluoride anions are 2.63 Å from each T-1 silicon in the [4\(^6\)]-cage and 5.69 Å from the nearest T-2 silicon. The distance between fluoride anions in adjacent D4R units is 9.33 Å.
Figure 4.2 (a) $^{19}$F MAS NMR spectrum of octadecasil, obtained with 132 scans, spinning speed 4.296 kHz, pulse width 9 µs, relaxation delay 10 s (spinning sidebands marked *).
(b) Quantitative $^{29}$Si MAS NMR spectrum of octadecasil showing the two resonances assigned to the T-1 and T-2 silicons respectively. The relative peak intensities (4:1) are as expected from the crystal structure. The spectrum was acquired with 48 scans, spinning speed 2.2 kHz, pulse width 8 µs, relaxation delay 110 s, and no $^1$H decoupling.
width at half-height (FWHH) of 6200 Hz. The room temperature 1-D $^{29}$Si MAS NMR spectrum of octadecasil shows two resonances at -107.7 ppm and -111.6 ppm with respect to tetramethylsilane (TMS) (Figure 4.2(b)). These peaks have an intensity ratio of 4:1, and can thus be assigned to the silicons in the T-1 and T-2 sites respectively. The static $^{29}$Si NMR spectrum shows a single resonance with a FWHH of 1700 Hz.

Clearly, the known framework structure of octadecasil containing fluoride anions in the D4R units with its two different Si-F interatomic distances and two distinct silicon environments provides an ideal test case for evaluating the reliability and robustness of $^{19}$F / $^{29}$Si CP, REDOR and TEDOR NMR experiments involving molecular sieve frameworks, as well as for determining the optimum experimental conditions for them. For clarity the different experiments will be discussed separately.

4.3.3 $^{19}$F-$^{29}$Si Cross Polarization Experiments

4.3.3.1 Hartmann-Hahn Matching Profiles

Hartmann-Hahn matches for the $^{19}$F-$^{29}$Si cross polarization were determined by fixing the $^{19}$F field strength and varying the $^{29}$Si r.f. power. For a non-spinning sample, a single match condition was found (Figure 4.3(a)) which corresponded to the exact Hartmann-Hahn condition ($\omega_{1F} - \omega_{1Si} = 0$) as expected. Under MAS up to four matching conditions which exhibited a clear dependence on the spinning speed were found (Figure 4.3). Moreover, under MAS almost no polarization transfer was observed at the exact Hartmann-Hahn match, but four other matching conditions separated by integral multiples of the spinning speed were found. In some cases the available $^{29}$Si r.f. power range was not sufficient to observe all four conditions.

For an isolated IS spin pair the heteronuclear dipolar interactions are modulated by one and two times the spinning frequency under MAS conditions, and this leads to strong first and second order sidebands in the CP matching profile if the spinning speed exceeds the width of the abundant I spin resonance line and the heteronuclear dipolar coupling frequency. Although the
Figure 4.3 Hartmann-Hahn $^{19}$F-$^{29}$Si CP matching profiles for the two T-sites in octadecasil: (a) non-spinning sample, (b) 3.37 kHz MAS, and (c) 4.15 kHz MAS. The $^{19}$F field strength was 17 kHz, and contact times of 2 ms and 10 ms were used for the static and MAS experiments respectively. The MAS sideband matching conditions, $f$, are also indicated.
spinning speeds employed were only approximately three times greater than the $^{19}$F-$^{29}$Si dipolar coupling calculated from the crystal structure of octadecasil for the T-1 Si (1230 Hz), the Hartmann-Hahn matching profile indicates that the T-1 Si / F$^-$ ion pair is essentially behaving as an isolated spin pair with sideband matching conditions corresponding to $f = \pm 1$ and $\pm 2$ observed as predicted by Eq. 3.9. The small amount of polarization transfer observed at the centreband ($f = 0$) matching condition may be due to flip-flop processes between remote $^{19}$F spins or polarization transfer mediated through heteronuclear J-coupling.$^{52}$

The matching profiles for the T-2 Si are also shown in Figure 4.3 and seem to mimic the behaviour seen for the T-1 Si. The signal to noise ratio for the T-2 Si was quite poor at the 10 ms contact time employed as indicated by the relative intensities of the signals.

### 4.3.3.2 Variable Contact Time Experiments

In variable-contact time CP experiments, the $^{29}$Si signal intensity is monitored as a function of the spin-locking time $t$. The initial exponential build-up of intensity is usually characterized by the CP rate constant, $T_{CP}^{-1}$, as polarization is transferred from $^{19}$F to $^{29}$Si during the Hartmann-Hahn match.$^{54}$ An exponential decay with first order rate constant $T_{1p}^{-1}$ due to loss of the spin-locked magnetization via spin-lattice relaxation in the rotating frame is superimposed on this growth. For a system of isolated spin pairs, the magnetization transfer process via matched Hartmann-Hahn spin-locked cross polarization under MAS conditions should exhibit oscillatory behavior as the polarization shuttles between the connected spin-pairs, as reported previously for a few cases.$^{36-41,52}$ Variable contact time CP experiments from $^{19}$F to $^{29}$Si on octadecasil were carried out at several spinning speeds and different behaviors were observed for the two types of T-sites.

For the T-1 silicons the variable contact time CP experiments showed a rise to a maximum, with a clear oscillatory behavior in the signal amplitude at short contact times, followed by an exponential decay (Figure 4.4). On some occasions these oscillations were absent
and this was attributed to mismatching arising from variations in the r.f. power or the spinning speed during the course of the experiment (the CP matching sidebands become narrow at high spinning speeds, and efficient CP under MAS requires highly stable r.f. amplitudes and constant spinning rates over extended periods of time). The "period" of the oscillatory behavior was dependent on the matching condition employed, but independent of the spinning speed.

Moreover, the oscillatory behavior was virtually identical under equivalent matching conditions, i.e. at \( f = +1 \) and \(-1\) (or \( f = +2 \) and \(-2\)). For samples undergoing MAS, the dampening of the oscillations showed a noticeable dependence on the spinning speed; becoming more clearly resolved with increasing spinning rates. The rate of decay at longer contact times was found to be directly dependent on the magnitude of the \(^{19}\text{F}\) spin locking field, becoming less with increasing \(^{19}\text{F}\) r.f. power, indicating that \( T_{1p} \) was increasing (as would be expected).

Because the silicons in the T-1 sites are very close (< 3 Å) to the fluoride ion which occupies their D4R, and the next-nearest \(^{19}\text{F}\) nuclei in adjacent D4R units are much further away (> 7 Å), these silicons and their corresponding F\(^-\) may be considered as isolated \(^{19}\text{F}\)-\(^{29}\text{Si}\) spin-pairs. An oscillatory behavior is thus predicted for the T-1 silicons, and is clearly seen in Figure 4.4.

For the T-2 silicons a fairly smooth rise to a maximum, followed by a decay was observed (Figure 4.4). Since the T-2 silicons are surrounded by up to 4 equidistant (5.69 Å) fluoride anions, they are not expected to show the pronounced oscillatory behavior predicted for isolated spin pairs. Unfortunately no explicit analytical functions are available at present to describe the cross polarization behavior of small spin clusters, however calculations for the REDOR dephasing of an \( I_4S \) system with tetrahedral geometry show oscillations (see Section 4.3.4.2). Based on the similarities in the oscillatory REDOR and CP signal amplitudes seen for isolated spin pairs, some oscillatory behavior might be expected for the T-2 Si. This would be far less obvious than that seen for the T-1 Si, and could be easily obscured (e.g. by \(^{19}\text{F}\) spin diffusion processes). A crude estimate of the period of the oscillation expected for the T-2 Si can
Figure 4.4 ¹⁹F-²⁹Si CP behaviour for the two T-sites in octadecasil under MAS conditions as a function of the contact time at the $f = -1$ sideband matching condition. The oscillatory behaviour for the T-1 Si and the decay due to $T_{1\rho}$ are clearly seen. The theoretical fit calculated using Eq. 3.14 for the T-1 Si with $D = 1360$ Hz is also shown.

Figure 4.5 ¹⁹F-²⁹Si CP behaviour for the T-1 Si in a non-spinning octadecasil sample as a function of the contact time. The line shows the fit calculated using Eq. 3.8 with $D = 1440$ Hz, $S_{eq} = 0.9$, $k_1^{-1} = 2.2$ ms, $k_2^{-1} = 26.7$ ms, and $T_{1\rho} = 2$ s. The $¹⁹F$ field strength was 17 kHz.
be made by assuming these behave as isolated $^{19}\text{F-}^{29}\text{Si}$ spin pairs with a dipolar coupling of 120 Hz. From Figure 3.3 the oscillation period is found to be about 35 ms; much longer than the time it takes for the oscillatory behaviour to be dampened for the T-1 Si (ca. 15 ms).

As described in Chapter 3, Hediger\textsuperscript{52} has reported analytical functions for fitting the oscillatory CP behavior in isolated $^{13}S$ spin pairs at specific Hartmann-Hahn matching conditions and these were used to determine the dipolar coupling for the T-1 Si as discussed in the following sections.

### 4.3.3.3 Fitting of the Oscillatory Cross Polarization Behavior for the T-1 Silicon

**Non-spinning Samples at the Centerband Matching Condition**

Figure 4.5 shows the area of the $^{29}\text{Si}$ resonance for a static sample as a function of the contact time. At short contact times a clear oscillatory behavior is seen, which is progressively damped. An upward trend at longer contact times is also apparent. Although this resonance includes signals from both the T-1 and T-2 silicons, the contribution to the total area from the T-2 Si will be small. Under MAS where the two T-sites are well resolved, an estimate of the relative areas of the contribution arising from each T-site can be made (e.g. from Figure 4.4) and is found to be less than 10\% for contact times up to 10 ms. This is about same as the uncertainty in determining the area of the static resonance by integration. On this basis the analysis and fitting of the data in terms of only T-1 Si was considered valid.

Fitting of the data was carried out using Eq. 3.8 in order to determine the $^{19}\text{F-}^{29}\text{Si}$ dipolar coupling. The increasing signal amplitude at longer contact times indicates that the spin system cannot be considered as a truly isolated spin pair, as this would level out as seen in Figure 3.3 (a)). Thus in addition to $k_1$ (the rate constant describing the dampening of the transient oscillations), a rate constant ($k_2$) which describes the build-up of the net magnetization is needed to allow a good fit to the experimental data, and this means $\langle S_z \rangle_{qe}$ must be greater than 0.5. However, $\langle S_z \rangle_{qe}$ and $k_2$ are strongly correlated (Eq. 3.8), and in order to ensure reliable fitting
between different data sets the value of $<S_z>_q$ was fixed at 0.9. This value was arrived at based on an evaluation of the number of fluoride ions surrounding the T-1 Si determined from the X-ray determined structure of octadecasil. Within a 12 Å-radius sphere surrounding a T-1 Si (corresponding to $^{19}$F-$^{29}$Si dipolar couplings > 15 Hz), there are eight F" ions which yields $<S_z>_q = N/N + 1 \approx 0.9$ when the statistical occupancy of the D4R’s is taken into consideration.

Additional parameters are required to match the intensities of the experimental data and theoretical curves, and to include the effects of decay due to $T_{1p}$.

The best fit to the envelope of experimental data was obtained with $k_1^{-1} = 2.2$ ms, $k_2^{-1} = 26.7$ ms, and $T_{1p} = 2$ s. The actual values of these parameters do not affect the dipolar coupling since this is defined by the period of the oscillations. Once suitable values for these five parameters were found, nonlinear least squares regression to fit the data with Eq. 3.8 (expressed in terms of Bessel functions) was undertaken and the best fit found with $D = 1440$ Hz. The resulting theoretical curve calculated using these values is overlaid on the experimental data in Figure 4.5 and shows quite good agreement. The largest discrepancies occur at contact times up to 1 ms, and this is attributed to the slight variation (decrease) in the output of the $^{19}$F amplifier power with increasing contact time; the Hartmann-Hahn match had been optimized for a 2 ms contact time. $D = 1440$ Hz corresponds to a Si-F distance of 2.49 Å, which is slightly shorter than the 2.63 Å determined from XRD. The slightly larger dipolar coupling found from fitting of the experimental data may reflect the contribution from fluoride ions in other D4R’s, and to a lesser extent the T-2 Si intensity.

**Spinning Samples at the $f = \pm 1$ Sideband Matching Conditions**

Under MAS conditions, the transient oscillations became significantly more pronounced than those observed for static samples. This phenomenon is readily seen by comparison of the experimental data presented in Figures 4.5, 4.6 and 4.7. According to the theoretical treatment presented by Hediger, the oscillatory behaviour at the $f = +1$ sideband matching condition
Figure 4.6 $^{19}$F-$^{29}$Si CP behaviour for the T-1 Si in octadecasil at the $|f|=1$ sideband matching conditions under various MAS speeds. Curves calculated using Eq. 3.14 with $D = 1340 \text{ Hz} (v_r = 3.37 \text{ kHz}, f = -1)$, $D = 1380 \text{ Hz} (v_r = 3.37 \text{ kHz}, f = +1)$, and $D = 1360 \text{ Hz} (v_r = 4.66 \text{ kHz}, f = -1)$ are overlaid. The intensities have been arbitrarily scaled to separate the curves.

Figure 4.7 $^{19}$F-$^{29}$Si CP MAS behaviour for the T-1 Si in octadecasil at the $f = +2$ sideband matching condition. The line shows the fit calculated using Eq. 3.14 with $D = 1400 \text{ Hz}$, $S_{eq} = 0.9$, $k_1^{-1} = 6 \text{ ms}$, $k_2^{-1} = 14 \text{ ms}$, and $T_{1p} = 125 \text{ ms}$. The spinning speed was 4.15 kHz, and the $^{19}$F field strength was 17 kHz.
should be identical to that observed when the $f = -1$ match is used, and should be independent of the spinning speed. As seen from Figure 4.6, the periodicity of the transient oscillations observed for the T-1 silicons is very similar at equivalent sideband matching conditions and different spinning speeds, in good agreement with the theoretical predictions.

Fitting of the experimental data to Eq. 3.14 (expressed in terms of Bessel functions) was done as described for the non-spinning data. Because the oscillations were quite clearly defined at contact times of up to 8-10 ms, more periods of the oscillations were thus available to check the goodness of fit for given dipolar couplings, which reduced the uncertainty in the final $D$ values. The reduction in the rate of damping of the oscillatory behavior with increasing spinning speeds (and the corresponding increase in the values of $k_1$ used in the fitting) is exactly as anticipated; at higher spinning speeds the effects of the relatively weak $^{19}$F-$^{19}$F interactions are progressively “spun out”.

Values of the parameters determined from the fittings were: $k_1^{-1} = 3.5 - 6$ ms, $k_2^{-1} = 20 - 80$ ms ($<S_z>_q$ fixed at 0.9), $T_{1p} = 70 - 400$ ms. In Figures 4.4 and 4.6 the data from three experiments are presented with the theoretical curves determined from the regression analyses. Small discrepancies are apparent at very short contact times, and are again attributed to the performance of the amplifiers; the Hartmann-Hahn matches were optimized using 10 ms contact time as a compromise to ensure the matching was maintained up to the longer contact times (50 - 60 ms) needed to observe the effects of $T_{1p}$ decay (see Figure 4.4). The dipolar couplings determined from fits to seven experimental data sets acquired at the $f = +1$ and $-1$ matching conditions ranged from $D = 1330$ to 1400 Hz with a mean of 1360 Hz and estimated standard deviation of 50 Hz. This corresponds to Si-F distances of 2.54 (0.03) Å, which is slightly shorter than the X-ray determined distance.

*Spinning Samples at the $f = \pm 2$ Sideband Matching Conditions*

The oscillatory behaviour at the $f = +2$ and $-2$ sideband matching conditions should be identical, but have a longer period compared to that observed at the $f = \pm 1$ matches. This
behavior was observed in the experimental data acquired for the T-1 Si under MAS conditions when the field strengths were appropriately adjusted. Fitting of the data to Eq. 3.14 was carried out as described in the preceding sections and similar values of the various parameters were found. Experimental data obtained for the T-1 Si at the $f = +2$ matching condition for a spinning speed of 4.15 kHz is shown in Figure 4.7 together with the curve calculated using the parameters listed in the caption. At the $f = \pm 2$ matching condition only two periods of the oscillation were observed up to a contact time of 10 ms compared with the three to four seen when $f = \pm 1$. Thus the uncertainty of the dipolar couplings is reduced somewhat compared to those obtained from data acquired at the first sideband matches, and is similar to that determined from the static sample data.

The average of the dipolar couplings determined from fitting of all the CP data at the five possible matching conditions (static and MAS) for the T-1 Si is given in Table 4.3. Comparison with Si-F distances determined from REDOR, TEDOR, and X-ray diffraction experiments reveals that, for isolated spin pairs at least, analysis of variable contact time data from $^{19}$F-$^{29}$Si CP experiments can yield reliable and quite accurate interatomic distances providing oscillatory behaviour is observed.

### 4.3.4 $^{19}$F-$^{29}$Si REDOR Experiments

In a REDOR experiment the signal intensity is monitored as a function of either the number of rotor periods or the position during the rotor cycle at which the dephasing pulses are applied, with the number of rotor periods constant. Commonly, a series of dephasing $\pi$-pulses is applied to the unobserved heteronuclear spins, with a simple spin-echo sequence on the observed spins. However when the resonance offsets are large, pulse errors can accumulate, and while phase-cycled pulse trains help to compensate for pulse imperfections, they too become ineffective at large offsets. In such cases it is desirable to minimize the number of pulses on those nuclei having large offset effects. Garbow and Gullion have reported a modified REDOR
Table 4.3 Comparison of the dipolar couplings ($D$) and $^{19}$F-$^{29}$Si interatomic distances ($r$) for octadecasil determined by various methods. Standard deviations are given in parenthesis.

<table>
<thead>
<tr>
<th>T-Site</th>
<th>Parameter</th>
<th>Cross Polarization$^{(a)}$</th>
<th>REDOR$^{(b)}$</th>
<th>TEDOR$^{(b)}$</th>
<th>X-ray$^{(b)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-1 (Si in D4R)</td>
<td>$D$ (Hz)</td>
<td>1380 (80)</td>
<td>1150 (50)</td>
<td>1130 (50)</td>
<td>1230 (5)</td>
</tr>
<tr>
<td></td>
<td>$r$ (Å)</td>
<td>2.53 (0.04)</td>
<td>2.69 (0.04)</td>
<td>2.70 (0.04)</td>
<td>2.632 (0.003)</td>
</tr>
<tr>
<td>T-2 (Si not in D4R)</td>
<td>$D$ (Hz)</td>
<td>n.d.$^{(e)}$</td>
<td>120 (20)$^{(d)}$</td>
<td>120 (20)$^{(d)}$</td>
<td>122 (5)</td>
</tr>
<tr>
<td></td>
<td>$r$ (Å)</td>
<td>n.d.$^{(e)}$</td>
<td>5.7 (0.4)$^{(d)}$</td>
<td>5.7 (0.4)$^{(d)}$</td>
<td>5.688 (0.003)</td>
</tr>
</tbody>
</table>

$^{(a)}$ Dipolar couplings determined from nonlinear least-squares fitting of experimental data and internuclear distances calculated from these.
$^{(b)}$ Distances determined from the single crystal X-ray data of Caullet et al.$^{16}$ and dipolar couplings calculated from these.
$^{(c)}$ Dipolar couplings determined from visual fitting of experimental data and internuclear distances calculated from these.
$^{(d)}$ Standard deviation estimated from visual fittings.
$^{(e)}$ Not determined.
pulse sequence that requires only a single dipolar dephasing pulse on the unobserved heteronuclear spins to minimize these problems.$^{54}$

Several pulse sequence schemes were used to implement the REDOR experiments, two of which are presented in Figure 3.6. REDOR experiments were performed with either a train of dephasing pulses applied to the unobserved ($I$) nuclei ($^{19}F$), or by applying just a single dephasing pulse on the unobserved nuclei. Because the REDOR experiment involves the formation of an echo for the observed nucleus, it is the spin-lattice relaxation behavior of this nucleus which determines how quickly the sequence can be repeated. As $^{29}Si$ was the observed nucleus in these experiments, and the $T_1$ values for the silicons in octadecasil are relatively long (ca. 20 s), an initial presaturation sequence was incorporated to achieve a more efficient recycling time, while still ensuring quantitative reliability. In experiments which utilized an initial cross-polarization from $^{19}F$ to $^{29}Si$ prior to beginning the REDOR portion of the sequence, the repeat time was governed by the much shorter $^{19}F T_1$ (see Table 4.2), and presaturation was not necessary.

4.3.4.1 REDOR Experiments on the D4R Silicons (T-1 Si)

Experimental REDOR results for the Si in the T-1 site using three different pulse sequences are shown in Figure 4.8. In the absence of an initial polarization transfer from $^{19}F$, the experimental values of $\Delta S/S_0$ did not reach the theoretical maximum of about 1.05 during the first 4.5 ms of dipolar evolution, but seemed to oscillate around 0.85 - 0.92. The explanation for this is that only about 90% of the D4R units contain a fluoride ion, as determined by elemental analysis. This would allow signals from $^{29}Si$ nuclei in D4R units without fluoride anions to contribute to the intensity of the peaks in the off-resonance ($S_0$) experiments, which limits the value of $\Delta S/S_0$ attainable. In the case of octadecasil then, these maximum normalized $\Delta S/S_0$ intensities provide a direct method for estimating the percentage occupancy of the D4R units by fluoride ions.
Figure 4.8 $^{19}$F-$^{29}$Si REDOR data and fits for the T-1 Si in octadecasil at the spinning speeds indicated. The theoretical curves were calculated assuming $D = 1150$ Hz and either complete (dashed line) or incomplete (solid line) occupancy of the D4R by fluoride ions. (a) Dephasing pulses on $^{19}$F, solid curve calculated for 85% occupancy. Data at $v_r = 3.950$ kHz acquired with initial cross polarization from $^{19}$F. (b) Dephasing pulses on $^{29}$Si, solid curve calculated for 92% occupancy.
The oscillations observed for the T-1 silicons at short contact times in the CP experiments justify the analysis of the REDOR behavior for these silicons in terms of an isolated $^{29}\text{Si}-^{19}\text{F}$ spin pair. To permit fitting of the data, the theoretical values of $\Delta S/S_0$ were multiplied by a scaling factor to account for the incomplete occupancy. This scaling factor does not affect the "period" of the oscillation from which the distance is determined. Nonlinear least squares fitting of the REDOR data for the T-1 Si included this scaling factor as a variable, and gave an average value for the dipolar coupling of 1150 Hz (standard deviation 50 Hz). This corresponds to a Si-F distance of $2.69 \pm 0.04 \, \text{Å}$, in excellent agreement with the value of $2.63 \, \text{Å}$ determined from the X-ray structure. The plots in Figure 4.8 illustrate how well the scaled theoretical curves (solid lines) calculated using the dipolar couplings and scaling factors determined from the fitting match the observed experimental data. REDOR experiments with cross polarization from $^{19}\text{F}$ to $^{29}\text{Si}$ prior to the REDOR sequence were also successful (Figure 3.6(b)). The use of an initial polarization transfer from $^{19}\text{F}$ means that the observed REDOR signals will originate only from $^{29}\text{Si}$ nuclei which have F- ions in their associated D4R, and hence the incomplete occupancy will not be apparent. Consequently the $\Delta S/S_0$ value should oscillate about 1.0 as was observed (see Figure 4.8(a)).

A drift towards a $\Delta S/S_0$ value of unity at longer dephasing times ($> 4.5$ ms, $n > 12$) was noted (Figure 4.8(a), open circles), and this probably arises from additional dipolar couplings between the T-1 silicons and the next closest ($> 7 \, \text{Å}$) fluoride ions, whose contributions take a much longer time to build up. It is also apparent that data acquired using the pulse sequence with a single dephasing pulse on the unobserved nuclei attain a somewhat higher maximum $\Delta S/S_0$ ratio ($ca. 0.92$) compared with the value of $ca. 0.85$ if the train of dephasing pulses was applied to the unobserved nuclei. This small difference in efficiency between the two pulse sequences may be due to resonance offset effects. However the curve fitting for both experiments yielded exactly the same value for the $^{29}\text{Si}-^{19}\text{F}$ dipolar coupling within experimental error. It should be noted that this may not be the case for other $^{19}\text{F}$-containing systems, (e.g. fluoro-organic
sorbates), where there may exist large chemical shift anisotropies, $^{19}\text{F}$ homonuclear and $^{1}\text{H}$$^{19}\text{F}$ heteronuclear line broadening interactions. In such cases the choice of pulse sequence may be critical in obtaining the most reliable measurement of $D$.

Figure 4.9 shows the result of applying the REDOR transform reported by Mueller\textsuperscript{55} to the data acquired at a spinning speed of 3.950 kHz. The peak maximum occurs at 1188 Hz which corresponds to a Si-F distance of 2.663 Å. The full width at half maximum (ca. 590 Hz) is primarily a result of the limited number of data points acquired (10), and the apodization function (three-point Blackman-Harris) used. Although several REDOR data sets were acquired having more than ten $\Delta S/S_0$ values, the spinning speeds in these experiments were not sufficiently high for the REDOR transform to be applied. To see a coupling of about 1200 Hz, the REDOR data must be acquired with $\nu_r \geq 3$ kHz since the REDOR transform will only show a range of frequencies from 0 to $\nu_r / 2$. The fluctuation in the spectrum below 500 Hz is an artifact arising from the initial decay in the $S/S_0$ values at small numbers of rotor periods.

4.3.4.2 REDOR Experiments on Silicons not in the D4R (T-2 Si)

For the T-2 silicons, the $^{19}\text{F}$$^{29}\text{Si}$ dipolar coupling was estimated to be 122 Hz from the Si-F distance of 5.69 Å calculated from the crystal structure. However, depending on the exact occupancy of the D4R units, there can be up to four fluoride anions in a tetrahedral arrangement about each T-2 silicon, and therefore equidistant from it (Figure 4.1(b)). This represents a more complicated situation than for the Si in the D4R (T-1 site) as the experiment no longer involves a single, isolated spin pair. Coupling to several fluorines can produce extra dephasing which translates into a stronger apparent dipolar coupling, and thus to an underestimate of the true heteronuclear distance. The theoretical curve calculated for a single, isolated $^{29}\text{Si}$$^{19}\text{F}$ spin pair with a dipolar coupling of 120 Hz (not shown) does not fit the experimental data at all, but a reasonable fit at short dephasing times ($< 4$ ms) assuming an $I\!S$ spin pair could be obtained with $D = 220$ Hz, corresponding to a Si-F distance of 4.67 Å. This is much shorter than that known
Figure 4.9 REDOR transform of REDOR data acquired for the T-1 Si in octadecasil at a spinning speed of 3.950 kHz. Ten experimental $S/S_0$ data points were acquired up to $n = 20$, apodized with a three-point Blackmann Harris function of the form $0.424 + 0.497 \cos(\tau n/10) + 0.079 \cos(2\tau n/10)$, and zero-filled to 128 points. The peak maximum occurs at 1188 Hz and has a FWHH of approximately 590 Hz.

Figure 4.10 $^{19}\text{F}-^{29}\text{Si}$ REDOR data and fits for the T-2 Si in octadecasil at a spinning speed of 2.350 kHz. The curves were calculated for: a tetrahedral arrangement of four fluoride ions about the T-2 Si with $D = 120$ Hz (dashed line); a binomial distribution assuming a (partial) tetrahedral arrangement of (up to) four fluoride ions having $D = 120$ Hz and an 85% probability that each D4R is occupied (solid line); (c) the superposition of a large number of REDOR curves calculated for isolated $^{19}\text{F}-^{29}\text{Si}$ spin pairs and weighted using a Gaussian distribution with variance defined by $M_2(\text{Si}-\text{F}) = 151450$ Hz$^2$ (dotted line).
from the X-ray structure, and it illustrates a potential problem when multiple spins could be involved and no clear oscillation is observed.

When an observed spin magnetization is dephased by dipolar interactions with more than one other spin, the dephasing will normally be dominated by the nearest one (since \( D \propto 1/r^3 \)). However, when the distances are comparable, dephasing from multiple spins will be cumulative.\textsuperscript{45-48} Naito et al.\textsuperscript{48} demonstrated that the geometrical arrangement of the spin pairs had a measurable effect on the calculated REDOR curves, and Schaefer and co-workers\textsuperscript{45,54} derived a general equation for the REDOR behavior of an \( S \) spin dipolar coupled to any number of \( I \) spins provided that the geometric arrangement of these spins is known as described in Chapter 3. Blumenfeld et al.\textsuperscript{57} have also proposed the use of the superposition of many REDOR curves for isolated spin pairs weighted by a Gaussian distribution with variance related to the \( I-S \) heteronuclear second moment, \( M_2(I-S) \). Calculations based on these two methods are presented in the following sections.

\textit{Exact Multi-Spin Calculations with Statistical Occupancy}

Calculation of theoretical dephasing of a single \( ^{29}\text{Si} \) by multiple \( ^{19}\text{F} \)'s was undertaken for the T-2 silicons assuming an exact tetrahedral arrangement, and additional corrections for the partial occupancy of each D4R unit were also incorporated. The dephasing of a single observed \( ^{29}\text{Si} \) spin dipolar coupled to more than one \( ^{19}\text{F} \) spin can be calculated directly\textsuperscript{57} as the powder average of a sum of independent dephasings assuming that the fluorines are not coupled to each other, and that the fluorine dephasings of the silicons are independent of one another. For octadecasil the first condition is satisfied because the sample is undergoing magic angle spinning at speeds (2-5 kHz) that greatly exceeded the largest homonuclear \( ^{19}\text{F}-^{19}\text{F} \) dipolar coupling (130 Hz for 9.3 Å separation). The second condition is assumed to hold because of the good fits obtained in other systems\textsuperscript{47,48,56} and for the T-1 silicons in the present work.
The theoretical curves calculated for an exact tetrahedral arrangement of four $^{19}$F nuclei about a central $^{29}$Si using Eq. 3.33 with $D = 120$ Hz fit the experimental data for the T-2 Si quite well (Figure 4.10, dashed line). This corresponds to complete occupancy of the D4R units. In a further refinement, the effect of incomplete occupation of the D4R units by fluoride anions was included. This was achieved by assuming contributions from four, three, two, and one equivalent, non-interacting fluorine nuclei, coupled ($D = 120$ Hz) to a single T-2 $^{29}$Si nucleus. Curves were calculated for these four sets of $^{29}$Si-$^{19}$F spin-pairs assuming that each T-2 silicon was surrounded by a (partial) tetrahedral arrangement of (up to) four equidistant $^{19}$F nuclei. The normalized $\Delta S/S_0$ values thus determined were then multiplied by an appropriate weighting factor and added together produce the final theoretical REDOR curves. The weightings were determined assuming a binomial distribution of fluoride anions in the D4R units with a probability $p$ that a fluoride anion occupies any given D4R. The probability, $P_q$ that $q$ of the four D4R units surrounding a given T-2 Si are occupied is:

$$P_q = C_q (p)^q (1-p)^{4-q} \tag{4.1}$$

where $C_q$ is the number of ways of obtaining $q$ occupied D4R units:

$$C_q = \frac{4!}{q! (4-q)!} \tag{4.2}$$

For $p=0.9$ Eq. 4.1 yields $P_4 = 0.6561$, $P_3 = 0.2916$, $P_2 = 0.0486$, $P_1 = 0.0036$ and $P_0 = 0.0001$.

Including the effect of incomplete (85%) occupation of the D4R units gives a significant improvement in the goodness of fit (Figure 4.10, solid line), however the experimental data is not of good enough quality to permit the occupancy to be determined to an accuracy of better than 5-10%.

It was apparent that the calculated multiple-spin REDOR curves had a much stronger dependence on the magnitude of the dipolar coupling than on the occupancy, and due to the complexity of these calculations, nonlinear least squares fitting was not attempted. The
uncertainty in $D$ was estimated to be less than 20 Hz from inspection of curves calculated assuming 100% occupancy of the D4R units and a range of dipolar couplings (not shown). Thus, the REDOR fits for the T-2 Si yield a Si-F distance of $5.7 \pm 0.4$ Å, in very good agreement with the value of 5.69 Å determined from the X-ray crystal structure. This analysis is also in good agreement with the maximum dephasing observed in the REDOR experiments for the T-1 silicons, and indicates that the actual occupancy of the D4R units is probably slightly higher than 85%.

Although in the case presented here (T-2 Si in octadecasil), all of the $I-S$ distances were equal, the method outlined above accommodates different distances within the group of nuclei. It should be emphasized that the possibility of obtaining distances directly. However these results demonstrate that these exact analyses are reliable and should work for any geometrical arrangement, provided this is known.

**Gaussian Distribution of Isolated $^{19}F-^{29}Si$ Spin Pairs**

Nonlinear least squares regression analysis of the T-2 Si REDOR data in terms of a Gaussian distribution of isolated $^{19}F-^{29}Si$ spin pairs was also undertaken. Using Gaussian-Hermitian quadrature integration with 180 roots of the Hermite polynomials (see Appendix C), the best fit (lowest $\chi^2$) was obtained with $M_2$(Si-F) = 151450 Hz$^2$ and the simulated curve is shown in Figure 4.10 (dotted line). The heteronuclear second moment calculated from the XRD determined structure (assuming complete occupancy of the D4R units and a 8 Å cut-off) is 305660 Hz$^2$. The overall fit of the curve to the data is not good; the shape of the curve deviates quite significantly from the trend in the experimental data. This probably indicates that the Gaussian distribution model is not very appropriate in this case.
4.3.5 $^{19}\text{F}$-$^{29}\text{Si}$ TEDOR Experiments

TEDOR experiments were originally developed as an alternative to REDOR to measure the heteronuclear dipolar coupling between nuclei while eliminating unwanted background contributions from uncoupled spins. The TEDOR experiment involves two time periods of dipolar dephasing, one before the transfer of coherence (achieved by simultaneous $\pi/2$ pulses), and another after the coherence transfer (Figure 3.10). This allows more permutations of the experiment, which give the added flexibility of being able to select the experiment best suited to the $T_1$ and $T_2$ relaxation parameters of a particular system. This flexibility may be particularly useful, especially if one $T_2$ value is unacceptably short, as is often the case for inorganic solids. The theoretical TEDOR behavior can be calculated as described in Chapter 3.

Variations of the TEDOR experiment included the application of $\pi$-pulses on $^{29}\text{Si}$, or $^{19}\text{F}$ before the coherence transfer pulse, varying the spinning speed, the position of the pulses, and the number of rotor cycles before and after the transfer pulse. The pulse sequences used for experiments (Figure 3.10) were such that the minimum increment allowed for the number of rotor cycles before coherence transfer was two because of the use of the simultaneous $\pi$-pulses to form an echo to ensure that the chemical shifts are refocussed at the transfer point. Larger increments are possible but only in even numbers of rotor cycles, 4, 6, 8, etc. For the number of rotor cycles after coherence transfer, increments of 1, 2, 3, or more were permitted since no simultaneous refocussing $\pi$-pulses were applied in this part of the sequence. All TEDOR experiments were performed with one of the silicon signals set exactly on resonance and several "periods" of the oscillations were acquired to verify the accuracy of the $D$ values.

It is important to take into consideration the nuclear relaxation parameters of the nuclei as these limit the range of $n$ or $m$ values that will give viable signal intensities. During the period before coherence transfer, the spin-spin relaxation rate, $T_2$, of the source nuclei (e.g. $^{19}\text{F}$) is important, and after the transfer it is the $T_2$ of the observed nuclei (e.g. $^{29}\text{Si}$) that limits the maximum time (and thus the number of rotor periods) after coherence transfer that signal can be
detected. Because the TEDOR pulse sequences used in the present work all contain an additional π-pulse which generates a spin-echo, it is $T_2$ rather than $T_2^*$ for the source nuclei that is important.

4.3.5.1 TEDOR Experiments on the Silicons in the D4R (T-1 Si)

Figure 4.11 shows typical TEDOR spectra obtained for octadecasil. TEDOR data obtained for the T-1 silicons with all dephasing pulses at $\frac{\tau}{4}$ and $3\frac{\tau}{4}$ with the number of rotor cycles after the coherence transfer varied, and the number of rotor cycles before the coherence transfer held constant are presented in Figure 4.12 for several $n$ values. The overlaid theoretical curves were calculated from nonlinear leastsquares fitting assuming a single $^{19}\text{F}$-$^{29}\text{Si}$ spin pair. Because the TEDOR signal intensity $S_T$ is not normalized as it is for REDOR experiments, the experimental intensities were scaled to match the maxima of the theoretical curves. In order to obtain a good match to the experimental intensities at higher numbers of rotor periods, the theoretical curves were also damped by multiplying them by an exponential factor of 70 Hz to account for homogeneous spin-spin decay during the period after transfer which is consistent with the observed $^{29}\text{Si}$ linewidths (FWHH ≈ 60 Hz). During the analysis of data from different TEDOR experiments, this damping factor was found to vary slightly but typically it was in the range 60 ± 20 Hz.

Figure 4.12(d) shows T-1 Si TEDOR data for $n = 2$ and $m$ varied together with theoretical curves calculated assuming dipolar couplings of 1000 Hz (dashed line), 1100 Hz (solid line) and 1200 Hz (dotted line). Clearly the quality of the fits is excellent, with less than 100 Hz uncertainty in $D$. Figure 4.13 shows the data obtained for the T-1 Si when $n$ was varied and $m$ was fixed. The experimental data again agree closely with the theoretical curves determined from nonlinear fitting. Furthermore, because in these experiments there are more
Figure 4.11 $^{19}$F-$^{29}$Si TEDOR spectra of octadecasil acquired using a spinning speed of 4.540 kHz and the T-1 Si on resonance. The number of rotor periods before the coherence transfer was fixed ($n = 2$), and the number of rotor periods after the transfer, $m$, was incremented as indicated.
Figure 4.12 TEDOR data and fits determined from nonlinear least-squares fitting of the T-1 silicon by varying $m$ with $n$ held constant and all dephasing pulses at $\tau_r/4$ and $3\tau_r/4$.

(a) $n = 2$, $\nu_{rot} = 4.770$ kHz, $D = 1131$ Hz, (b) $n = 4$, $\nu_{rot} = 4.770$ kHz, $D = 1100$ Hz, and (c) $n = 6$, $\nu_{rot} = 5.244$ kHz, $D = 1077$ Hz. (d) Indication of the sensitivity of the fit for $n = 2$, $\nu_{rot} = 4.296$ kHz: curves calculated with dipolar couplings of 1200 Hz (dashed line), 1100 Hz (solid line) and 1000 Hz (dotted line). An exponential damping of 70 Hz was applied to all curves to account for $T_2$ decay. The $S_T$ scales are in arbitrary units.
Figure 4.13 TEDOR data and fits determined from nonlinear least squares fitting of the T-1 silicon as a function of $n$ for different $m$ values at a spinning rate of 4.540 kHz with all dephasing pulses at $\pi/4$ and $3\pi/4$. (a) $m = 1$, $D = 1176$ Hz, (b) $m = 2$, $D = 1207$ Hz, and (c) $m = 3$, $D = 1213$ Hz. (d) Indication of the sensitivity of the fit for $m = 2$, spinning speed 5.244 kHz. The curves were calculated assuming dipolar couplings of 1200 Hz (dashed line), 1100 Hz (solid line) and 1000 Hz (dotted line). An exponential damping of 70 Hz was applied to all curves to account for $T_2$ decay. The $S_T$ scales are in arbitrary units.
“periods” of the oscillation to fit, these represent a quite stringent test of the fit of the experimental data to the theoretically predicted behavior. This is the first time TEDOR experiments have been reported where $n$ was varied and $m$ fixed. There was no discernible difference between TEDOR experiments performed with the dephasing pulses before the coherence transfer on either $^{29}\text{Si}$ or $^{19}\text{F}$.

Weighted, nonlinear fittings of the TEDOR experiments with all dephasing $\pi$-pulses at $\tau_r/4$ and $3\tau_r/4$ yielded an average value of $D = 1130$ Hz with a standard deviation of 50 Hz for the silicons in the D4R units. From these values the Si-F interatomic distance was calculated to be $2.70 \pm 0.04$ Å, which is slightly longer than the value of 2.63 Å calculated from the diffraction measurements, but still in very good agreement. As seen from Table 4.3, the Si-F distance for the T-1 silicons determined from TEDOR experiments is in very close accord to that found from REDOR experiments, but slightly longer than found from fitting of the CP data, although all techniques have comparable accuracy.

The TEDOR data obtained by changing the positions of the dephasing pulses from $\tau_r/4$, $3\tau_r/4$ required integration of the appropriate functions describing the dipolar interactions, and subsequent numerical point-by-point integration of those functions. Results from these experiments were plotted versus the dimensionless parameter $\lambda_n = nD\tau_r$ (or $\lambda_m = mD\tau_r$) so that “universal” curves (for isolated IS spin pairs) were obtained that could be used for fitting data acquired at different spinning speeds. The resulting curves (calculated using $D = 1100$ Hz and 70 Hz dampening) showed very good agreement with the experimental data. Figure 4.14 shows data for the T-1 Si and the theoretical curves for TEDOR experiments performed with the dephasing pulses moved to (a) $\tau_r/5, 4\tau_r/5$ and (b) $\tau_r/6, 5\tau_r/6$ after the coherence transfer. The dephasing pulses were at $\tau_r/4$ and $3\tau_r/4$ before the transfer. The dipolar coupling determined from experiments performed with the pulses moved from $\tau_r/4$ and $3\tau_r/4$ was generally less (by about 50 Hz) than that determined for other TEDOR experiments and probably indicates that moving the pulses yields a less efficient TEDOR experiment.
Figure 4.14 TEDOR data and fits for the T-1 silicon with all dephasing pulses before the coherence transfer at $\tau /4$ and $3\tau /4$ and those after the transfer positioned at: (a) $\tau /5$ and $4\tau /5$, and (b) $\tau /6$ and $5\tau /6$. The number of rotor periods before the transfer was fixed at 2, $m$ was varied, and the spinning speed was 4.285 kHz. The theoretical curves were calculated for $D = 1100$ Hz with an exponential damping of 70 Hz to account for $T_2$ decay. The $S_T$ scale is in arbitrary units.

Figure 4.15 TEDOR data for the T-2 silicon ($n$ varied, $m = 3$, $v_r = 4.53$ kHz, dephasing pulses at $\tau /4$ and $3\tau /4$), and the theoretical curves calculated assuming an exact tetrahedral arrangement of four fluoride ions about the T-2 Si and $^{19}$F-$^{29}$Si dipolar couplings of: (a) 100 Hz, (b) 120 Hz, and (c) 140 Hz. An exponential damping of 70 Hz was applied to account for $T_2$ decay. The $S_T$ scale is in arbitrary units.
4.3.5.2 TEDOR Experiments on the Silicons not in the D4R (T-2 Si)

As seen in Figure 4.15, TEDOR data for the T-2 Si were also well fit by theoretical curves calculated for a tetrahedral arrangement of four fluorides about a central T-2 silicon \( (D = 120 \text{ Hz}) \) using multiple spin analysis as outlined in Chapter 3. Statistical occupancy was not incorporated because of the arbitrary scaling between experimental data and theoretical intensities. This dipolar coupling corresponds to \( r = 5.71 \text{ Å} \) in good agreement with that determined from the crystal structure and the REDOR fits. If an isolated \(^{29}\text{Si}-^{19}\text{F} \) spin pair was assumed, nonlinear least squares fitting to the TEDOR data for the T-2 Si yielded a value of \( D = 205 \text{ Hz} \), which corresponds to a Si-F distance of 4.78 Å. This result again illustrates the danger of obtaining incorrect internuclear distances from fitting TEDOR experimental data if more than two spins are present and the fitting assumes only a single, isolated spin pair.

4.4 CONCLUSIONS

These results clearly establish the viability of these experiments for determining the precise location of \(^{19}\text{F}-^{29}\text{Si} \) dipolar coupling derived from CP, REDOR, and TEDOR. Such experiments could be extended to determine \(^{19}\text{F}-^{31}\text{P} \) interatomic distances in aluminophosphate molecular sieves (AlPO₄₅) with fluorine-containing guests and to other framework/sorbate host-guest complexes. REDOR experiments yield normalized intensities which are useful for testing the goodness of the fit of experimental data to the theory, and even in the present case for estimating the percentage occupancy of the D4R units by fluoride ions. TEDOR experiments eliminate unwanted background signals arising from observed nuclei which are not dipolar coupled to the heteronuclear spins, and can provide additional advantages because of the larger number of experimental variables available, and the corresponding increased flexibility to accommodate large \( T_1 \) or small \( T_2 \) values of either nucleus. An advantage of TEDOR experiments over REDOR is that it is possible to extend them to 2-D correlation experiments. This could be very useful.
in cases where there are several resonances for both nuclei as it should permit a differentiation between the connectivities. This will important for three-dimensional host guest-structure determinations in frameworks of the type studied here.

It is possible to obtain incorrect internuclear distances from fitting REDOR and TEDOR experimental data if more than one spin is dipolar coupled to the observed spin and the fitting assumes only a single, static, isolated spin pair. Independent information which verifies that the experimental data relates to an isolated spin pair should be obtained. For spin systems which cannot be considered as isolated spin pairs (e.g. the T-2 Si in octadecasil), it may be possible to determine the dipolar couplings (and thus distances) accurately from REDOR and TEDOR experiments (provided the geometry of the spin system is known) as demonstrated in the present work. In order to more fully explore the uniqueness of the REDOR and TEDOR behavior for multi-spin systems a series of 3-spin calculations were undertaken. The results of these simulations are presented in Chapter 5.
REFERENCES FOR CHAPTER 4


CHAPTER 5

INVESTIGATIONS INTO THE UNIQUENESS OF NMR DISTANCE DETERMINATIONS IN MULTIPLE SPIN SYSTEMS

5.1 INTRODUCTION

As discussed in the Chapter 3, the REDOR and TEDOR behavior in $I_S$ spin systems is generally different than the dephasing for an isolated $I_S$ spin pair. Theoretical REDOR and TEDOR curves can be calculated for multiple $I$ spins about a single (observed) $S$ spin as described in Sections 3.4.2 and 3.5.3, provided the precise geometrical arrangement (number and relative orientations) of the spins is specified. Naito et al. were the first to describe the mathematical framework necessary for calculating the REDOR dephasing in a 3-spin $I_2S$ system, and demonstrated the application of this in a simple peptide system. This methodology was later extended by Schaefer and co-workers who introduced a convenient method for performing the calculations in terms of vector dot products between the $I$-$S$ vectors. The expansion of these techniques to describe the dephasing in TEDOR experiments was derived and presented in Chapter 3. Using these approaches, experimental REDOR and TEDOR data for the T-2 silicon in octadecasil could be well fitted (Chapter 4). This study represents the only multi-spin TEDOR analysis reported to date. Furthermore, only very few studies reported in the literature have included multi-spin REDOR analysis, and in most of these cases the geometry of the spin system was known, or could be predicted with a fair degree of certainty, from other methods (e.g. X-ray diffraction studies) prior to the analysis of the experimental data.
Any relative motions of the nuclei within a heteronuclear spin system can also affect the REDOR and TEDOR dephasing because the internuclear distances (and thus the dipolar coupling) will vary. The presence of such motions will result in an apparent reduction in dephasing compared to that predicted for a rigid spin system. Goetz and Schaefer\(^7\) have presented a mathematical formalism for calculating the dephasing where the trajectory of the motion is known, and Naito \textit{et al.}\(^{11}\) have proposed a method to include the effect of thermal motions.

At the time the experiments reported in this thesis were undertaken no systematic evaluation of the theoretical REDOR and TEDOR behavior in \(I_N S\) spin systems was available. It was unclear if the REDOR and TEDOR dephasing in multiple spin systems could be identified and quantified directly, or whether the dephasing behavior was unique for different spin systems. In many of the systems that REDOR and TEDOR might be utilized to characterize, the structural information available will be somewhat limited. The investigations of sorbate / zeolite structures, which is the topic of this thesis, will fall into this category. For this reason it is crucial to determine the situations where analysis of REDOR and TEDOR data may be unable to furnish unambiguous, dependable distance information. A series of theoretical REDOR and TEDOR calculations on a selection of \(I_N S\) spin systems assess the practicality of extracting useful structural information from analysis of REDOR and TEDOR experiments in such cases, and the results are summarized in this Chapter.

### 5.2 SELECTION OF PARAMETERS FOR SIMULATIONS

A selection of 3-spin, \(I_S S\) systems were chosen to simplify the calculations, and the effects of varying two parameters were investigated: (a) the \(I-S\) dipolar couplings, and (b) the \(I-S-I\) angle, \(\zeta\). A pictorial representation of these systems is given in Figure 5.1. The full range of \(\zeta\) (\(0^\circ \leq \zeta \leq 180^\circ\)) was considered, and values for the two dipolar couplings, \(D_I\) and \(D_{I^2}\) (\textit{i.e.} between \(I_A-S\) and \(I_B-S\) respectively) were chosen to represent couplings in typical \(^{13}\)C-\(^{15}\)N
systems. This is because many REDOR and TEDOR experiments have focused on C-N distance determinations in biological systems such as peptides and amino acids.

Figure 5.1 Pictorial representation of the $I_S$ spin systems for which the theoretical REDOR and TEDOR dephasing was investigated. The dipolar coupling for $I_A-S$ ($D_1$) was fixed at 100 Hz, while $D_2$ (the dipolar coupling between $I_B$ and $S$) and the $I_A-S-I_B$ angle, $\zeta$, were varied.

Three distinct $I_A-S-I_B$ systems with $D_1 = 100$ Hz and $D_2 = 100$ Hz, 75 Hz, or 50 Hz were considered in detail. Preliminary calculations on a 5-spin $I_S$ system indicated that the step size utilized ($\pi/20$) for the 3-spin calculations provided sufficient accuracy for the integration to produce the powder average (Table C.2, Appendix C. For clarity, the results of the REDOR and TEDOR 3-spin simulations are discussed separately.

It should be emphasized that the features of the REDOR behavior calculated for these cases can be related directly to other $I_S$ systems. Because the dephasing time (i.e. the product of the number of rotor cycles ($n$ or $m$) and the rotor period, $\tau_r$) was used in calculations, the curves are independent of the spinning speed. Furthermore, so long as the ratio of relative magnitudes of the two dipolar couplings are in a ratio similar to those used here (1.0:1.0, 1.0:0.75 and 1.0:0.5)
the curves are related by a simple scaling: the larger the dipolar couplings, the shorter the time needed for a given degree of dephasing to occur.

When considering the TEDOR behavior, there is the small additional complication that the dephasing time in the part of the experiment which has a constant number of rotor cycles must be known in order to calculate the dephasing. The theoretical curves presented in this chapter were calculated assuming a spinning speed was 2.5 kHz, with the number of rotor periods before the coherence transfer \( n \) varied, and the number of rotor periods after the transfer \( m \) fixed. For an isolated \( IS \) spin pair, the maximum theoretical dephasing occurs when \( mD\tau_r = 0.84 \). On the assumption that the net dipolar coupling would be approximately 100 Hz in the spin systems investigated, a value of \( m = 20 \) was selected.

5.3  REDOR SIMULATIONS

5.3.1  Theoretical REDOR Behavior for 3-Spin \( I-S-I \) Systems

Curves calculated for \( D_1 = D_2 = 100 \text{ Hz} \) and selected values of the angle \( \zeta \) (some of which are commonly encountered in chemical systems) are shown in Figure 5.2(a). The data used to generate Figure 5.2(a) are listed in Table C.3 (Appendix C). The curve for an isolated \( IS \) spin pair with \( D = 100 \text{ Hz} \) is also given. It should be emphasized that these curves are not the same as those calculated by simply adding curves calculated for the individual spin systems, \( I_A-S \) and \( I_B-S \), even though the calculation involved a sum of independent \( S \) spin dephasings by the \( I \) nuclei (see Section 3.4.3).

The dephasing curves are identical for \( \zeta \) and \( 180^\circ - \zeta \) due to the symmetry of the cosine function in the dephasing equations (Eqs. 3.31 and 3.33). The most distinctive behavior is observed when \( \zeta \) is small (or close to \( 180^\circ \)), otherwise there are quite minor differences in the dephasing when \( \zeta \) is in the range from approximately \( 20^\circ \) to \( 160^\circ \). In general the initial dephasing occurs faster in the 3-spin systems than for the \( IS \) spin pair. Also the nearer \( \zeta \) is to \( 90^\circ \), the faster the value of \( \Delta S/S_0 \) approaches the equilibrium value of 1.0. Obviously, in systems with larger
dipolar couplings these differences would evolve more quickly, but the relative behaviors of the curves will be similar.

Two special cases occur if $D_1 = D_2$: (i) when $\zeta = 90^\circ$, and (ii) when $\zeta = 180^\circ$. In the first case (data not shown) the dephasing is identical to that calculated for an isolated spin pair with a dipolar coupling of $\sqrt{2} D_1$. In the second situation, the equilibrium $\Delta S/S_0$ value is 0.5 rather than 1.0. This arises because two of the four possible combinations of the dipolar couplings cancel ($+D_1 - D_2 = -D_1 + D_2 = 0$), and thus only the two remaining combinations contribute to the dephasing. This behavior is identical to that predicted for an isolated $IS$ spin pair having a dipolar coupling of $2 D_1$ with the $I$ spins present only 50% of the time.

Figure 5.2(b) shows the dephasing curves calculated for three different values of $D_2$ with $\zeta = 180^\circ$, and two general trends are evident. Firstly, the dephasing during the early stages is faster for larger $D_2$. Secondly, except in the special case where $D_1 = D_2$, the smaller $D_2$, the shorter the dephasing time needed to approach the equilibrium $\Delta S/S_0$ value of 1.0. As $D_2$ becomes a smaller fraction of $D_1$, the $I_n$-$S$ interaction has a correspondingly smaller effect on the total dephasing. In fact when the magnitude of $D_2$ is $\leq 10\%$ of $D_1$, the effect of the third spin ($I_n$) becomes almost negligible, and the dephasing is very similar to that predicted for an isolated $IS$ spin pair.

Figures 5.3, 5.4 and 5.5 illustrate the dependence on $\zeta$ where $D_1 = 100$ Hz and $D_2 = 100$ Hz, 75 Hz, or 50 Hz, respectively. Inspection of these plots reveals that the variation between the three cases is quite small once $\zeta$ is larger than about $30^\circ$. It is also apparent that a variation in $\zeta$ of the order of $10^\circ$ is required to effect a noticeable change, and spins systems with quite distinct geometries may exhibit very similar dephasing behavior. For example, the curve calculated for $D_1 = D_2 = 100$ Hz with $\zeta=20^\circ$ (Figure 5.2(a)) closely mimics that obtained with $D_1 = 100$ Hz, $D_2 = 50$ Hz and $\zeta=180^\circ$ (Figure 5.2(b)). The relatively small changes that are observed in the calculated data will be even more difficult to detect in experimental data due to uncertainties.
Figure 5.2 REDOR curves calculated for some 3-spin $I_S$ systems. (a) $D_1 = 100$ Hz, $D_2 = 100$ Hz, and the $I-S-I$ angle, $\zeta$, indicated. (b) $\zeta = 180^\circ$ with $D_1 = 100$ Hz, and $D_2 = 100, 75, \text{ or } 50$ Hz. The curve for an isolated $IS$ spin pair with $D = 100$ Hz is included for comparison.
Figure 5.3 REDOR curves calculated for a 3-spin $I_S$ system ($D_1 = 100$ Hz, $D_2 = 100$ Hz) as a function of the $I$-$S$-$I$ angle $\zeta$. Only curves for $0^\circ < \zeta < 90^\circ$ are shown since the dephasing is identical for $\zeta$ and $180^\circ - \zeta$. 
Figure 5.4 REDOR curves calculated for a 3-spin Is system ($D_I = 100$ Hz, $D_R = 75$ Hz) as a function of the I-S-I angle $\zeta$. Only curves for $0^\circ < \zeta < 90^\circ$ are shown since the dephasing is identical for $\zeta$ and $180^\circ - \zeta$. 
Figure 5.5 REDOR curves calculated for a 3-spin $I_S$ system ($D_1 = 100$ Hz, $D_2 = 50$ Hz) as a function of the $I$-$S$-$I$ angle $\zeta$. Only curves for $0^\circ < \zeta < 90^\circ$ are shown since the dephasing is identical for $\zeta$ and $180^\circ - \zeta$. 

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure5.5.png}
\caption{REDOR curves calculated for a 3-spin $I_S$ system ($D_1 = 100$ Hz, $D_2 = 50$ Hz) as a function of the $I$-$S$-$I$ angle $\zeta$. Only curves for $0^\circ < \zeta < 90^\circ$ are shown since the dephasing is identical for $\zeta$ and $180^\circ - \zeta$.}
\end{figure}
arising from a finite signal-to-noise (S/N) ratio. Thus even in a “best-case” scenario where both interatomic distances are known (i.e. $D_1$ and $D_2$ can be fixed) and only $\zeta$ needs to be varied, it is anticipated that $\zeta$ could only be determined to an accuracy about $\pm 15^\circ$.

5.3.2 The REDOR Transform Applied To Multi-Spin Data

The REDOR transform is an analytic transform method, analogous to a Fourier transform, which provides a means of analyzing REDOR data in such cases. When applied to $S_f/S_0$ REDOR data, the REDOR transform produces a frequency-domain spectrum containing resonances at the dipolar coupling frequencies present in the time-domain REDOR signal. Provided that the experimental data is of adequate quality (i.e. good signal-to-noise ratio and collected up to a sufficiently large number of rotor periods), and the spinning speed used exceeds $ca.$ three times the largest dipolar coupling present, the REDOR transform can successfully extract the correct dipolar frequencies from real experimental REDOR data where the spin system contains discrete sets of heteronuclear spin pairs.

It was not apparent from the literature what information, if any, the REDOR transform would yield when applied to REDOR data acquired for samples containing multiple spin systems. In particular, it was hoped to determine whether the REDOR transform was capable of providing correct dipolar couplings from multiple spin data. There was also interest in the actual appearance of the REDOR transform spectrum for multiple spin systems (e.g. $I_N S$ systems), to determine if the transform spectrum contained features which might be diagnostic of the presence of multiple spins, or act as indicators that the spectrum should be interpreted with caution. Information such as this is vital to determine the validity of applying the REDOR transform in cases where little or no information about the nature of the spin system is available prior to beginning REDOR $I$-$S$ internuclear distance determinations.

For the REDOR transform to be well behaved, the $S_f/S_0$ data must decay completely to a value of 0.0. Because of a finite signal-to-noise ratio and the incomplete dephasing inherent in
real experimental data, an apodization function must be applied to ensure this requirement is met. Reports to date favor the use of a 3-point Blackman-Harris function\textsuperscript{14,15} and this was used in the present work.

To investigate the strengths and weaknesses of the REDOR transform method, it was applied to S\textsubscript{f}/S\textsubscript{0} REDOR data calculated for several I\textsubscript{2}S systems. The data were calculated in two rotor cycles increments up to 64 rotor periods for a spinning speed of 2.5 kHz using the product formalism described in Section 3.4.2. Following apodization the data were zero-filled up to 256 rotor periods to improve the appearance of the transform spectrum.

One effect of apodization is to smooth the data, however any oscillatory fine-structure present in the data is also modified. While this is potentially troublesome for data from isolated IS pairs, it becomes a major problem in the case of I\textsubscript{2}S spin systems because the relatively minor differences which distinguish the I\textsubscript{2}S spin system geometries will be further reduced. Furthermore, apodization preferentially weights the contribution of the data at short dephasing times (where the behavior is very similar for different geometries), and thus discriminates against the information present in the behavior seen at longer times. Application of the REDOR transform to non-apodized data generally produces a periodic dipolar spectrum (due to truncation effects) which is very difficult to interpret.

The appearance of the REDOR transform was found to depend on the I-S-I angle $\zeta$ and on the dipolar couplings used for the calculation of the S\textsubscript{f}/S\textsubscript{0} data. In some instances the transform spectrum indicated that only a single dipolar coupling was present, while for other values of $\zeta$, several resonances were clearly evident. The dipolar couplings determined directly from the transform spectra varied significantly; in some cases the values exceeded those assumed for the calculation of the S\textsubscript{f}/S\textsubscript{0} data, while in others smaller couplings were seen. No features were observed which might indicate that the REDOR data was not from isolated spin pairs.

In summary, the REDOR transforms calculated for theoretical $I_2S$ data did not exactly reproduce the known dipolar couplings, and the initial apodization overshadowed any unique
features apparent in the raw $S_1/S_0$ data in many cases. The situation will be even worse for experimental data where the finite signal-to-noise ratio introduces additional uncertainties in the precise $\Delta S/S_0$ values. These results were not unexpected because the REDOR transform was developed assuming only contributions from isolated spin pairs.

5.3.3 Gaussian Distribution of Dephasing Spins

Blumenfeld et al.\textsuperscript{15} have proposed an approach where the REDOR behavior is calculated in terms of the $I-S$ second moment, $M_2(I-S)$, for cases where a large number of $I$ spins dephase a single $S$ spin. The applicability of this approach was demonstrated by these authors using the experimental $^{27}$Al-observed, $^1$H-dephased REDOR data for two minerals. The fitting yielded values for $M_2(I-S)$ which were in good agreement with those calculated from crystal structure.\textsuperscript{15} This is discussed in Section 3.4.3 and details of the calculations are presented in Appendix C.

By using, for example, a Gaussian distribution of dephasing spins, no information regarding the specific geometrical arrangement needs to be provided. However, since any dependence on the effect of the $I$-$S$-$I$ angles is neglected, the potential to determine specific $I$-$S$ distances is relinquished. The caveat is that the number of dephasing spins is sufficient to approximate the assumed distribution.

In Figure 5.6, Gaussian REDOR curves calculated assuming $M_2(I-S) = 5000 \text{ Hz}^2$, $10000 \text{ Hz}^2$, and $50000 \text{ Hz}^2$ are shown together with that for REDOR dephasing in an isolated $IS$ spin pair ($D = 100 \text{ Hz}$). The rate of dephasing increases with increasing magnitude of the heteronuclear second moment, and shows a smooth rise without oscillations; precisely the behavior expected when a large number of oscillatory curves having different periods are added.

5.4 THEORETICAL TEDOR BEHAVIOR FOR 3-SPIN $I$-$S$-$I$ SYSTEMS

As for the REDOR calculations, three spin systems with dipolar couplings of $D_1 = 100 \text{ Hz}$ and $D_2 = 100 \text{ Hz}$, $75 \text{ Hz}$, or $50 \text{ Hz}$ were considered for various $I_1$-$S$-$I_2$ angles. Curves
Figure 5.6 REDOR curves calculated for a single (observed) $S$ spin dipolar coupled to a large number of $I$ spins and different $I-S$ heteronuclear second moments, $M_2(I-S)$. A Gaussian distribution was used to weight the contributions of the individual $I-S$ dipolar couplings to the total dephasing. The curve for an isolated $I$S spin pair with $D = 100$ Hz is included for comparison.
calculated for $D_1 = D_2 = 100$ Hz and selected values of the angle $\zeta$ are shown in Figure 5.7(a), together with that calculated for an isolated $I_S$ spin pair having $D = 100$ Hz. The data used to generate Figure 5.7(a) are listed in Table C.5 (Appendix C). As was also the case for the multi-spin REDOR behavior, these curves are not the same as those calculated by simply adding curves calculated for the individual spin systems, $I_A-S$ and $I_B-S$. The $I_S$ TEDOR curves calculated for $\zeta$ and $180^\circ - \zeta$ are identical because of the nature of the expression (a product of the sine functions) describing the dephasing (see Appendix C). When $\zeta$ is in the approximate range $30^\circ < \zeta < 150^\circ$, the dephasing is slightly faster for the 3-spin system than for an isolated $I_S$ spin pair (Figure 5.7(a)).

Figure 5.7(b) shows the dephasing curves calculated for three different values of $D_2$ with $\zeta = 180^\circ$, and two trends are evident. Firstly, the initial maximum for $S_T$ occurs at essentially the same dephasing time (ca. 8 ms) in all cases, and is also the same as that for an isolated $I_S$ spin pair. This could potentially be very problematic when attempting to fit experimental data, since the theoretical $S_T$ values must be multiplied by a scale factor to match the experimental TEDOR data. This need arises because, unlike $\Delta S/S_0$ values determined for a REDOR experiment, $S_T$ is not normalized. Secondly, the time between successive maxima in $S_T$ becomes longer as $D_2$ gets smaller. It is essentially these variations which distinguish the behavior in the different systems. However, at longer dephasing times in the TEDOR experiment, $T_2$ induced-damping can quickly "wash-out" these oscillations.

Figures 5.8, 5.9, and 5.10 illustrate the dependence on $\zeta$ where $D_1 = 100$ Hz and $D_2 = 100$ Hz, 75 Hz, or 50 Hz, respectively. Inspection of these plots reveals that the variation between the three cases is quite small once $\zeta$ is larger than about $30^\circ$. It is also apparent that, as for the REDOR data, a variation in $\zeta$ of the order of $10^\circ$ is required to effect a noticeable change. Again, the relatively small changes observed in the calculated data will be even more difficult to detect in real experimental data due.
Figure 5.7 TEDOR curves calculated for some 3-spin $I_S S$ systems. (a) $D_1 = 100$ Hz, $D_2 = 100$ Hz, $\nu_r = 2.5$ kHz, $n$ varied, $m = 20$, and the $I-S-I$ angle, $\zeta$, indicated. (b) $\zeta = 180^\circ$ with $D_1 = 100$ Hz, and $D_2 = 100, 75$, or 50 Hz. The curve for an isolated $I_S$ spin pair with $D = 100$ Hz is included for comparison.
Figure 5.8 TEDOR curves calculated for a 3-spin $I_S$ system ($D_1 = 100$ Hz, $D_2 = 100$ Hz, spinning speed 2.5 kHz, $n$ varied, $m = 20$) as a function of the $I$-$S$-$I$ angle $\zeta$. Only curves for $0^\circ < \zeta < 90^\circ$ are shown since the dephasing is identical for $\zeta$ and $180^\circ - \zeta$. 

$S_T$

$n_\tau$, Dephasing Time (ms)
Figures.

TEDOR curves calculated for a 3-spin $I_2S$ system ($D_1 = 100$ Hz, $D_2 = 75$ Hz, spinning speed 2.5 kHz, $n$ varied, $m = 20$) as a function of the $I$-$S$-$I$ angle $\zeta$. Only curves for $0^\circ < \zeta < 90^\circ$ are shown since the dephasing is identical for $\zeta$ and $180^\circ - \zeta$.
Figure 5.10 TEDOR curves calculated for a 3-spin I₂S₂ system ($D_1 = 100$ Hz, $D_2 = 50$ Hz, spinning speed 2.5 kHz, $n$ varied, $m = 20$) as a function of the I-S-I angle $\zeta$. Only curves for $0^\circ < \zeta < 90^\circ$ are shown since the dephasing is identical for $\zeta$ and $180^\circ - \zeta$. 
A major limitation with TEDOR data is that the S_T intensities are not normalized which means that a scaling factor is required to match the experimental and theoretical S_T values. Inspection of Figures 5.7-5.10 reveals that the shape of the curves (which is effectively what must be matched) is not completely unambiguous in many cases. In addition, any differences visible in the theoretical curves will probably vanish when working with real experimental data due to finite S/N and damping of the oscillations due to spin-spin relaxation. These difficulties are compounded because the S/N decreases with increasing dephasing time.

Any relative motions of the nuclei within a heteronuclear spin system can also affect the TEDOR dephasing because the internuclear distances (and thus the dipolar coupling) will vary. Overall, the presence of such motions will be more problematic in TEDOR experiments than in REDOR because there are two dephasing periods.

In summary, the likelihood of determining reliable distances in a I_2S systems from TEDOR behavior is potentially even less than for REDOR. Even in the "best-case" scenarios where both interatomic distances, or one distance and the angle, are known, it would be difficult to determine the complete geometry unless T_2 is sufficiently long that data of adequate S/N can be obtained at large numbers of rotor cycles.

5.5 CONCLUSIONS

In conclusion, these calculations indicate that it is highly unlikely that direct and unambiguous distance determinations can be obtained from REDOR and TEDOR experiments on multiple spin systems when the number of spins and geometrical arrangement of these is unknown. This is true even for the simple 3-spin geometries investigated here, and the problem will be compounded when more spins and/or relative motions are present. Furthermore, there is no discrimination between I_2S systems with \( \zeta \) and 180°-\( \zeta \), and it is possible to obtain the wrong answer if an isolated spin pair is assumed and multiple spins are present. REDOR transforms of
data from multiple spin systems yields transform spectra devoid of features which might indicate that the spin system was not composed of isolated spin pairs, and could thus be mis-interpreted.

The algorithm used to calculate the powder averaging in the present work is very computationally intensive (Appendix C), which significantly hinders fitting experimental multi-spin data within a reasonable time period. Increasing the efficiency of the integration over the two angles to produce the powder average is thus highly desirable. This is especially true for TEDOR data where a summation must be used to performed the calculations. Methods which could be implemented include the approaches proposed by Aldermann et al., Wang and Hanson, and the recently reported REPULSE algorithm.

Even with improved calculation efficiency, the best approach will be to try and ensure that the spin system approximates an isolated spin pair as closely as possible, (e.g. by isotopic substitution and dilution in the unlabeled compound), or several isolated spin pairs. If this is not feasible, one possibility is to acquire several REDOR and TEDOR data sets (with different parameters). Alternatively, CP data from groups of spins could be obtained and analyzed to obtain $T_{CP}$. In both cases a model of the spin system which fully describes the relative geometric arrangement (i.e. with all angles and distances implicitly defined) must be proposed, and the theoretical dephasing or heteronuclear second moments are calculated and compared to the experimental data. The model is modified and the calculations re-run until optimal agreement between the calculated and experimental dephasing is obtained for all of the experimental data sets. With these approaches there will be no direct determinations of distances, but structural information can still be (indirectly) obtained. This method will be most efficient if constraints can be placed upon the model which limit the possible number of spins and internuclear distances. This may be the case for sorbate molecules in zeolites since the guests must lie within the channels or voids. This approach was applied to locate $p$-difluorobenzene in the zeolite ZSM-5 as described in the next Chapter.
REFERENCES FOR CHAPTER 5


CHAPTER 6

PRELIMINARY SOLID-STATE NMR INVESTIGATIONS
OF THE STRUCTURE OF THE LOW-LOADED
PARA-DIFLUOROBENZENE / ZSM-5 COMPLEX

6.1 INTRODUCTION

As discussed in Chapter 5, the direct determinations of distances between nuclei on organic guests and the framework nuclei of microporous hosts will usually not be possible. The porous nature of the hosts means that the framework nuclei will interact with several nuclei on the guest molecules, even if they are isolated on the guests themselves. Thus a model must be postulated and tested for agreement with experimental data. The simplest such experiment is CP from a “group” of nuclei on the organic guest with no assumption of isolated spin pairs. Such experiments are described in the present chapter with the $^{19}$F and $^1$H nuclei of $p$-difluorobenzene as independent magnetization sources. The microporous framework system chosen was purely siliceous ZSM-5.

ZSM-5 was selected because it is one of the few microporous materials for which single crystals suitable for single crystal X-ray diffraction experiments can be synthesized and XRD studies provide an independent a check of the appropriateness of the experimental protocol outlined in this chapter. In addition ZSM-5 has considerable significance as a catalyst in many industrial processes, including the conversion of methanol to gasoline, the interconversion of aromatic compounds, and paraffin cracking. Information on the preferred locations of sorbed
molecules inside the channels of zeolites would greatly aid understanding of the catalytic, diffusive, and shape-selective properties of these materials. The changes which can occur in the ZSM-5 framework lattice due to temperature and the presence of guest species (e.g. sorbed organic molecules). Factors including the dependence on temperature, the number of guests present (loading), as well as the nature of sorbate-sorbate and sorbate-framework interactions have been studied by a variety of physical and theoretical methods as discussed in Chapter 1.

Only six sorbate / ZSM-5 single crystal structures (some closely related) have been reported to date, and at the present time, these represent the only cases where the locations of the sorbed organic molecules been reliably determined. Although sorption sites have been proposed from theoretical calculations, these are not always in agreement with one another, or the X-ray determined structures.

There is a definite need to expand the database of dependable structures to improve the reliability, and verify the results, of the calculation methods before they can be relied upon to yield accurate locations of sorbates in zeolite structures. However, it is generally difficult to synthesize zeolite crystals of adequate size and quality for single crystal XRD structure determinations, and also to load them with controlled amounts of volatile organic sorbates. Hence other techniques capable of providing locations and orientations of guest molecules must be developed.

While X-ray diffraction (XRD) studies of microcrystalline (powder) samples and single crystals of ZSM-5 have yielded the majority of the structural information in these systems, Si MAS NMR has provided critical information such as the number of T-sites, and is very sensitive method for detecting structural changes. Using sorbate-lattice distance information from the solid-state NMR techniques developed in the previous chapters, it should (theoretically) be possible to determine the complete three-dimensional structures of sorbate / zeolite complexes from powder samples.
In this chapter, the results of the preliminary attempts to determine the location and orientation of \( p \)-difluorobenzene molecules in the low-loaded ZSM-5 complex containing ca. four molecules per unit cell (u.c.) are presented. The \( ^1H \cdot ^{29}Si \) and \( ^{19}F \cdot ^{29}Si \) heteronuclear dipolar couplings were probed using CP, REDOR, and TEDOR experiments. Possible sorption sites which were consistent with these data were then determined.

6.1.1 Framework Structure of MFI-type Zeolites

MFI-type zeolites include ZSM-5 which contains Si and Al in varying ratios from about 50 through to the purely siliceous form known as silicalite, as well as various other materials having isomorphous substitution of Al, Si, or both by, for example B or Ti. The MFI framework topology was first determined by Kokotailo et al. from powder X-ray diffraction data, and this was subsequently confirmed by a number of other investigations including several single crystal XRD studies.

The basic building block of the MFI framework is the pentasil unit (Figure 6.1(a)) which consists of eight 5-membered rings. These pentasil units link together by sharing edges to form chains that run parallel to the [001] axis of the unit cell (Figure 6.1(b)). The complete 3-dimensional MFI framework is constructed from sheets of these chains and contains 4-, 5-, 6-, and 10-rings where the neighbouring chains are related by mirror planes. This produces a 3-dimensional channel system formed by two kinds of intersecting channels: sinusoidal (also called zig-zag) channels which run along the [100] axis and straight ones running parallel to [010] as illustrated in Figure 6.1(d). Both types of channels are defined by 10-membered rings which are slightly elliptical (Figure 6.1(c)), and the effective pore dimensions (determined by the oxygen van der Waals radii) are approximately 5.2 \( \times \) 5.8 Å. The exact symmetry of the lattice and the shapes of the channel openings can change with temperature and the presence of guest species such as sorbed organic molecules (see below).
Figure 6.1 Building units, framework topology, and channel structure of the MFI framework. (a) Pentasil basic building unit (BBU) formed by five 8-membered rings. Each vertex represents a T-atom (Si or Al), and oxygens are omitted for clarity. (b) Chains which run parallel to [001] in the framework formed by linking the pentasil BBU's. (c) View down [001] showing sheets formed by joining the chains. The 10-membered ring apertures define the straight channels. Similar sheets are present in the [100] direction. (d) Representation of the channel structure showing the interconnecting straight and sinusoidal (zig-zag) channels. After reference 14.
Because of the nature of the pore system, ZSM-5 possesses very distinct sorption and diffusion properties which are exploited in its industrial applications. The channel size is intermediate between the small pore (8-ring openings, e.g., the LTA framework) and large pore zeolites such as zeolites X and Y (12-ring openings, FAU framework topology). ZSM-5 can adsorb molecules such as p-xylene, but effectively excludes molecules with larger kinetic diameters such as 1,3,5-trimethylbenzene.

6.1.2 Guest- and Temperature-Induced Framework Changes in ZSM-5

6.1.2.1 X-ray Diffraction Studies of ZSM-5 Systems

ZSM-5 has been found to adopt four space groups: three with orthorhombic symmetry: Pnma (12 crystallographically inequivalent T-sites), P212121 (24 T-sites), and Pn21a (24 T-sites); and one having monoclinic P21/n11 symmetry with 24 T-sites. As-synthesized ZSM-5, containing the tetrapropylammonium cation (TPA+) as template, exhibits orthorhombic Pnma symmetry. After calcination to remove the template, the framework shows a reversible phase transition at about 340 K (the precise temperature depends on the Si/Al ratio) and has monoclinic symmetry below and orthorhombic (Pnma) symmetry above the transition temperature.

If certain organic molecules are adsorbed into ZSM-5, the framework symmetry may also change. These changes were observed using powder XRD and 29Si MAS NMR on highly crystalline, siliceous ZSM-5 samples. Only four different sorbed molecules in ZSM-5 have been studied by single crystal diffraction studies to date: p-xylene, p-dichlorobenzene, p-nitroaniline, and naphthalene. Details of the space groups and locations of the sorbed molecules determined from these single crystal studies are summarized in Table 6.1.

While structure refinements from powder diffraction data have been carried out for ZSM-5 containing p-xylene, p-dichlorobenzene, naphthalene, and several other...
Table 6.1 Space groups and numbers of T-sites for several ZSM-5 structures as determined by single crystal X-ray diffraction. For those structures where organic guest species are present, the number of molecules per unit cell and their locations are given.

<table>
<thead>
<tr>
<th>Structure&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>reference</th>
<th>Temp. (K)</th>
<th>Space Group</th>
<th>Number of T-sites</th>
<th>Guest Location&lt;sup&gt;(b)&lt;/sup&gt; (number / u.c.)</th>
<th>Comments&lt;sup&gt;(c)&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>MONO</td>
<td>18</td>
<td>293</td>
<td><em>P</em> 2&lt;sub&gt;1&lt;/sub&gt;/n. I&lt;sup&gt;(d)&lt;/sup&gt;</td>
<td>24</td>
<td>-</td>
<td>crystal exhibits domain twinning</td>
</tr>
<tr>
<td>HTORT</td>
<td>17</td>
<td>350</td>
<td><em>Pnma</em></td>
<td>12</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>TPAORT</td>
<td>16</td>
<td>293</td>
<td><em>Pnma</em></td>
<td>12</td>
<td>intersection (4)</td>
<td>TPA&lt;sup&gt;+&lt;/sup&gt; disordered</td>
</tr>
<tr>
<td>HLPXY</td>
<td>3</td>
<td>293</td>
<td><em>P</em> 2&lt;sub&gt;1&lt;/sub&gt;2&lt;sub&gt;1&lt;/sub&gt;2&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;(e)&lt;/sup&gt;</td>
<td>24</td>
<td>intersection (4) zig-zag (4)</td>
<td>unrestrained anisotropic refinement of all atoms</td>
</tr>
<tr>
<td>HLPDCB</td>
<td>4</td>
<td>293</td>
<td><em>P</em> 2&lt;sub&gt;1&lt;/sub&gt;2&lt;sub&gt;1&lt;/sub&gt;2&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;(e)&lt;/sup&gt;</td>
<td>24</td>
<td>intersection (4) zig-zag (4)</td>
<td>unrestrained anisotropic refinement of all atoms</td>
</tr>
<tr>
<td>LLPDCB</td>
<td>5</td>
<td>293</td>
<td><em>Pnma</em></td>
<td>12</td>
<td>intersection (2.6)</td>
<td>rigid p-dichlorobenzene individual isotropic parms.</td>
</tr>
<tr>
<td>LLPNA</td>
<td>6</td>
<td>293</td>
<td><em>Pnma</em></td>
<td>12</td>
<td>intersection (4)</td>
<td>rigid p-nitroaniline with individual isotropic parms.</td>
</tr>
<tr>
<td>LLPXY&lt;sup&gt;this work&lt;/sup&gt; 9</td>
<td>180</td>
<td>293</td>
<td><em>Pnma</em></td>
<td>12</td>
<td>intersection (4)</td>
<td>framework restraints, rigid p-nitroaniline, isotropic parameters</td>
</tr>
<tr>
<td>NAPH</td>
<td>8</td>
<td>293</td>
<td><em>Pnma</em></td>
<td>12</td>
<td>intersection (3.7)</td>
<td>rigid naphthalene with anisotropic parameters</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> MONO: monoclinic phase of empty (calcined) ZSM-5. HTORT: high temperature orthorhombic phase of empty (calcined) ZSM-5. TPAORT: as-synthesized ZSM-5 containing tetra-propylammonium ions (TPA<sup>+</sup>). HLPXY: high-loaded p-xylene. HLPDCB: high-loaded p-dichlorobenzene. LLPDCB: low-loaded p-dichlorobenzene. LLPNA: low-loaded p-nitroaniline. LLPXY: low-loaded p-xylene /u.c. NAPH: loaded with naphthalene. <sup>(b)</sup> Intersection: in straight channel at intersection with zig-zag channel. Zig-zag: in sinusoidal channel. <sup>(c)</sup> Anisotropic and isotropic refer to the atomic displacement factors. <sup>(d)</sup> Non-standard space group to allow direct comparison with *Pnma* ZSM-5 structures (symmetry operators: x, y, z; -x, -y, -z; 0.5+x, 0.5-y, 0.5-z; 0.5-x, 0.5+y, 0.5+z). <sup>(e)</sup> Origin shifted to (0, 0, 0.25) to allow direct comparison with other *Pnma* ZSM-5 structures. The symmetry operators become: x, y, z; 0.5+x, 0.5-y, 0.5-z; -x, 0.5+y, -z; 0.5-x, -y, 0.5+z. <sup>(f)</sup> Related to *Pnma* by removal of the centre of symmetry which results in a loss of the mirror plane at y = 0.25.
sorbates subsequent single crystal diffraction studies showed that the sorbate location(s) proposed from the powder studies were not always correct.

6.1.2.2 $^{29}$Si NMR Studies of ZSM-5 Systems

As discussed previously, the $^{29}$Si MAS NMR spectra of highly crystalline, purely siliceous zeolite systems can be very diagnostic of the lattice structures (and symmetries) in terms of the local environments of the Si atoms. For example, subtle changes in the average Si(OSi)$_4$ angles by as little 0.2$^\circ$ can be detected as a $^{29}$Si chemical shift difference of about 0.1 ppm, which is readily observable. The temperature-induced phase transition from monoclinic to orthorhombic symmetry is clearly observed in the $^{29}$Si MAS NMR spectra of highly siliceous ZSM-5 as seen in Figures 6.2(a) and (c). Two-dimensional $^{29}$Si COSY and INADEQUATE experiments were used to assign the individual $^{29}$Si NMR resonances indicated in these figures.

Distinct changes in the $^{29}$Si MAS NMR spectra are also observed upon sorption of several organic molecules including $p$-xylene, pyridine, benzene, dimethylsulfoxide (DMSO), acetylacetone, $p$-chlorotoluene (Figures 6.2-6.4). These changes are reversible (e.g. by calcination to remove the sorbate), and occur at ambient temperatures. However, no changes are seen when attempts are made to adsorb $o$-xylene, $m$-xylene, octane, cyclohexane, durene, or ethylcyclohexane. This indicates that the framework symmetry is maintained and it is only the local framework symmetry and geometry which is altered. This is because these molecules are too small to alter the structure or are excluded. Similar temperature and sorbate induced changes have been observed for ZSM-11, but have not been seen for other highly siliceous zeolites (e.g. mordenite, omega, ZSM-23, and others), confirming that the observed changes are not caused by general susceptibility effects of the sorbed organic molecules in the cavities.

For the ZSM-5/sorbate systems where changes are seen, the nature of the lattice distortions seems to be relatively characteristic of the nature of the sorbed molecule (Figure 6.3),
Figure 6.2 High resolution $^{29}$Si MAS NMR spectra of highly siliceous ZSM-5 showing changes that occur with temperature or loading with $p$-xylene. (a) Empty ZSM-5 at 300 K (monoclinic, $P2_1/n.1.1$ phase). (b) ZSM-5 loaded with 2 molecules $p$-xylene per u.c. at 300 K (orthorhombic, $Pnma$ phase). (c) Empty ZSM-5 at 403 K (orthorhombic, $Pnma$ phase). (b) ZSM-5 loaded with 8 molecules $p$-xylene per u.c. at 300 K (orthorhombic, $P2_12_12_1$ phase). The numbers indicate the assignments to specific T-sites from INADEQUATE experiments. After reference 38.
Figure 6.3 High resolution $^{29}$Si MAS NMR spectra of highly siliceous ZSM-5 loaded with selected organic molecules: (a) pyridine (35 μL/250 mg); (b) p-xylene (10 μL/250 mg); (c) dimethylsulfoxide (40 μL/250 mg); (d) acetylacetone (20 μL/250 mg); (e) benzene (25 μL/250 mg); and (f) toluene (24 μL/250 mg). All spectra recorded at room temperature at 79.495 MHz with 7 s recycle delay. After reference 40.
Figure 6.4 High resolution $^{29}$Si MAS NMR spectra of highly siliceous ZSM-5 loaded with ca. 4 molecules per u.c. of: (a) $p$-chlorobenzene, (b) $p$-chlorotoluene, and (c) $p$-xylene. The spectra recorded at ambient temperature. After reference 20.
and the observed changes are usually also affected by the precise loading and temperature.\textsuperscript{20,22,40}

In some cases however, very similar \textsuperscript{29}Si MAS NMR spectra are obtained with different molecules, indicating that the lattice geometries are closely related. For example the low-loaded forms of ZSM-5 containing equal numbers of sorbed \textit{p}-xylene, \textit{p}-chlorotoluene, or \textit{p}-dichlorobenzene only exhibit minor differences (Figure 6.4). From these spectra it was concluded that the locations of the molecules would likely be very similar (CH\textsubscript{3} is sterically similar to Cl and thus the size and shape of these molecules is comparable).\textsuperscript{20} This prediction has since been confirmed by single crystal XRD studies.\textsuperscript{3,5,9}

Fyfe and co-workers determined phase diagrams for highly siliceous ZSM-5 containing various amounts of sorbed \textit{p}-xylene and \textit{p}-dichlorobenzene at temperatures ranging from 293 to 393 K using \textsuperscript{29}Si MAS NMR.\textsuperscript{20,42} The \textsuperscript{29}Si MAS NMR spectra showed that the temperature at which the phase transition between monoclinic and orthorhombic symmetry occurred was dependent on the precise loading and temperature. Furthermore, at certain loadings and temperatures a mixture of the two phases was present and it was possible to determine the fraction of each phase from the \textsuperscript{29}Si MAS NMR spectra (Figure 6.5).\textsuperscript{20}

In attempts to assign the \textsuperscript{29}Si resonances to specific T-sites within the framework based on the observed \textsuperscript{29}Si chemical shifts, various correlations based on the structural geometrical parameters of the T-sites have been proposed.\textsuperscript{37,43-50} These are discussed further in Chapter 8. However, reliance on these correlations can result in erroneous assignments,\textsuperscript{26,37,51} and at present the only reliable methods for assigning the \textsuperscript{29}Si NMR resonances to specific T-sites are the two-dimensional homonuclear NMR correlation experiments such as COSY and INADEQUATE.\textsuperscript{26,38}

6.1.3 Other Techniques for Locating Sorbates in the ZSM-5 Framework
6.1.3.1 Predictions of Sorbate Locations from Energy Minimization Calculations

Several groups have proposed sorption sites of organic molecules within the channels of zeolites from energy minimization calculations.\textsuperscript{10,12,32-35} For example, based on calculated van der
Figure 6.5 Phase diagram for highly siliceous ZSM-5 loaded with p-xylene from $^{29}$Si spectra.
(a) Three-dimensional surface of the effects of the concentration of p-xylene and temperature. The percentage of the orthorhombic Pnma phase present is indicated on the vertical axis. (b) Two-dimensional projection of part (a) showing the relationship of the orthorhombic (Pnma, 12 T-sites) and monoclinic (P$2_1$/n.1.1, 24 T-sites) phases with varying temperature and concentration of p-xylene. After reference 20.
Waals interactions between the hydrocarbon and the zeolite framework and between the hydrocarbon molecules themselves, the most energetically favourable sorption sites for p-xylene at loadings up to 4 molecules/u.c. in silicalite were found to be at the channel intersections with the methyl-methyl axes lying along the straight channel. When the p-xylene occupies only the channel intersections, the van der Waals interactions between adjacent molecules are small, and the major contribution comes from framework-oxygen / p-xylene-hydrogen interactions. Other researchers have reported similar locations. Sorption sites in the zig-zag channel and in the straight channel between the channel intersections have also been found for different sorbates (e.g. alkanes), and when higher sorbate loadings were assumed. Sorbate-sorbate interactions may be significant in some cases, and should be considered, especially at higher sorbate concentrations.

In the overwhelming majority of these calculations the framework has been kept rigid, and the sorbate geometry is usually maintained as a semi-rigid group having some pre-optimized conformation. The locations determined by these techniques are dependent on the potential functions and calculation technique used, and there is not always complete agreement between the various calculations. Furthermore, there seems to be a dynamic interaction between the organic molecules and the framework because the exact framework geometry adopted is related to the nature of the sorbate present, thus the orientations and locations determined from calculations are sensitive to the atomic coordinates used for the framework atoms.

6.1.3.2 Predictions of Sorbate Locations from Solid-State NMR Experiments

Recently Fyfe and co-workers have investigated the location of p-xylene in ZSM-5 with several solid-state NMR techniques. Using selectively deuterated p-xylenes (deuterated at the ring or methyl groups), the locations of the sorbate molecules at a loading of 3, 6, and 8 molecules/u.c. were determined. The inverse of the $T_{CP}$ values obtained from fitting of the $^1H$-$^{29}Si$ CP MAS data were plotted vs. the calculated $^{29}Si$ heteronuclear second moments. The
position of the \( p \)-xylene molecules was systematically varied until a good linear correlation was found. Both the framework and the \( p \)-xylene molecules (idealized geometry) were kept rigid during these calculations. The framework symmetries and coordinates used were those reported for the single crystal XRD determinations of the low-loaded \( p \)-dichlorobenzene complex,\(^5\) and the high-loaded form of \( p \)-xylene in ZSM-5.\(^3\)

Because \( 1/T_{CP} \) is directly proportional to the \(^1\)H-\(^{29}\)Si heteronuclear second moment (Eq. 3.16), a linear correlation which passes through the origin should be obtained. However the linear fit determined from the \( 1/T_{CP} \) vs. \( M_2(\text{\(^1\)H-\(^{29}\)Si}) \) data for the high-loaded complex (i.e., containing 8 molecules/u.c.) at room temperature had a positive \( y \)-intercept.\(^57,58\) The cause of this disagreement was determined to be sorbate motions on the time scale (tens of milliseconds) of the CP experiment. These motions were detected by \(^{13}\)C spin-diffusion measurements on \( p \)-xylene with a \(^{13}\)C label on one of the methyl groups.\(^58\) Lowering the temperature to 273 K or below reduced the diffusion sufficiently that the regression behaved exactly as expected. The final locations and orientations found for the \( p \)-xylene molecules in the straight and zig-zag channels from these experiments were in excellent agreement with those reported for the single crystal XRD determined structure, validating the general approach.\(^5\)

These techniques were then applied to the low-loaded \( p \)-xylene / ZSM-5 complex where the sorbate location was not reliably known prior to beginning the NMR experiments. Static \(^2\)D NMR experiments indicated that the sorbate rings were undergoing 180° ring-flips about the methyl-methyl axis at the temperatures used, and these motions were included in the second moment calculations. In this case, temperatures below \( ca. \) 215 K were required to reduce the molecular motions sufficiently to obtain a zero intercept.\(^59\) The \( p \)-xylenes were located at the channel intersections with the methyl-methyl axis along the straight channel, in agreement with the previous predictions.\(^10,56\) More importantly, the sorbate location and orientation proposed from the NMR data were very close to that found by a subsequent single crystal X-ray diffraction structure determination carried out as part of the present work (Chapter 8).\(^9\) The success of these
investigations indicates that analysis of CP data can be used to obtain reliable information about
the location of sorbates within the ZSM-5 framework, provided that the temperature is low
enough to minimize molecular diffusion. In the best cases it is possible to obtain the precise
position and orientation of the guest molecule. In the present chapter, preliminary solid-state
NMR studies of the low-loaded p-difluorobenzene / ZSM-5 complex are presented.

6.2 MATERIALS AND METHODS

6.2.1 Sample Preparation and Sorbate Loading

Crystalline, completely siliceous ZSM-5 was kindly provided by Ms. G.E. Barlow, The
University of Guelph. Freshly calcined ZSM-5 (500 mg) was loaded into 5 mL glass ampoules.
To this 36 µL of 1,4-difluorobenzene (Aldrich, 99 %) or 1,4-difluorobenzene-d₄ (Aldrich 98
atom % D) was added (corresponding to a loading of 4 molecules/u.c.) using a micro-syringe.
The sample was cooled by immersion in liquid nitrogen, and the ampoule sealed with a flame.
The sample was stored at room temperature for several days to ensure an equilibrium loading had
been attained before loading the rotors for the NMR experiments. The loading of the ZSM-5
powder was verified by thermal gravimetric analysis (TGA) and ²⁹Si MAS NMR. The TGA
measurements were performed on TA Instruments TGA 51 Thermogravimetric Analyzer using a
temperature ramp of 10 °C/min. from room temperature to 600 °C under flowing nitrogen gas.
The samples showed weight losses corresponding to 3.9 (±0.3) molecules/u.c. 'H-²⁹Si, ¹⁹F-²⁹Si
CP, and ²⁹Si MAS NMR experiments confirmed that the samples contained sorbed p-
difluorobenzene.

6.2.2 NMR Experiments

In order to minimize the molecular motions of the sorbate (which can adversely affect
the dipolar-based experiments such as CP, REDOR and TEDOR), the NMR experiments were
performed at low temperatures using the apparatus described in Chapter 2 (Figure 2.1). Initially,
experiments were performed using nitrogen as the drive gas rather than air to prevent formation of ice within the probe, however it was discovered that the nitrogen replaced the molecular oxygen present within the sample. This process was gradual (occurring over a period of 12 hours or longer), and had a direct affect on the low temperature NMR experiments. As the concentration of oxygen within the rotor was reduced, the $^{29}$Si relaxation times increased dramatically. For example, at 240 K the $^{29}$Si $T_1$ relaxation times increased from ca. 2 s to greater than 35 s after the sample had been cooled for 24 hours using nitrogen gas to spin the rotor.

This problem was solved by utilizing air as the drive gas. The air was dried by passing it through several filters and a drying column (Drierite) filled with freshly calcined 5Å zeolite A pellets and an indicator material which changed colour when wet. After less than one hour using air instead of nitrogen, the $^{29}$Si $T_1$ was about 2 s again. Similar changes were seen for the $^{19}$F and $^1$H relaxation times; at 235 K the $^{19}$F $T_1$ increased from 1.5 to 10 s, while the $^1$H $T_1$ increased from 45 ms to 4.5 s if nitrogen was used. The spin-lattice relaxation times also increased with increasing temperature: from 80 ms to 105 ms for $^{19}$F, and from ca. 2 s to about 4 s for $^{29}$Si as the temperature was changed from 293 to 310 K. The $^{29}$Si spin-spin relaxation times were 110-225 ms at 293 K and 40-150 ms at 240 K.

Temperatures used for the INADEQUATE, CP, REDOR and TEDOR experiments were selected to obtain the maximum number of resonances in the $^{29}$Si MAS NMR spectra. The need to maintain a stable temperature and spinning speed for an extended time (> 2 days) was also considered. The pulse and automation programs used to acquire the NMR data are listed in Appendix B. To minimize the effect of drift in the external magnetic field, the INADEQUATE experiments were performed as a series of (12-16 h) experiments which were then co-added. CP-INADEQUATE experiments which employed an initial polarization transfer from protons on the $p$-difluorobenzene were also performed. The fixed delay in the INADEQUATE pulse sequence was set to 15 or 16 ms, following the typical values used for similar experiments reported in references 26 and 38.
The WIN-NMR software\textsuperscript{59} was used to perform the Fourier transformations, phase and baseline corrections of the NMR data. The real mode spectra were then exported using a JCAMP-DX format.\textsuperscript{60} Curve-fitting of the spectra was achieved using the program Grams-386.\textsuperscript{61} Quantitative $^{29}\text{Si}$ NMR spectra were fitted to determine the appropriate parameters (FWHH, chemical shift) for the individual Lorentzian curves, and these parameters were then used for curve-fitting the spectra from CP MAS experiments.

Fitting of the variable contact time CP data to determine $T_{CP}$ values was performed using non linear least squares regression analysis in the Mathematica programming environment\textsuperscript{62} as described in Appendix C.

### 6.2.3 Calculations to Determine Sorbate Locations and Orientations from CP Data

Two computer programs were written to analyze the data from the $^{1}\text{H}-^{29}\text{Si}$ and $^{19}\text{F}-^{29}\text{Si}$ CP experiments. The first of these (CPF9.PAS) calculated the static heteronuclear second moments, while the second program (CPH9.PAS) assumed that the sorbate molecules were undergoing 180° ring-flips about the F-F axis on the timescale of the experiments, and calculated the $M_2$ values using the approach reported by Michel \textit{et al.}\textsuperscript{63} as described in Appendix D. Only F-Si (or H-Si) distances less than 8 Å were used in the second moment analysis, except when the ring flips were assumed, in which case both sites that the H atoms occupied during the motion were included.

The programs moved (and rotated) the sorbate molecule systematically through the channel system of the ZSM-5 framework and performed linear regression analysis of the $1/T_{CP}$ values vs. the calculated second moments for each location and orientation. Initial calculations to determine potential sorption sites used a fairly coarse step size for the translations and rotations (0.25 Å and 15° respectively), in order to sample a larger space within the channel system. Checks were also made to ensure that the molecules did not get too close ($< 2$ Å) to the framework atoms. Calculations were then run using smaller step sizes (0.1 Å and 5°) for the
rotations and translations over the region of interest. A typical calculation required in excess of 750,000 iterations, and took more than 48 hours to run. Any sorbate positions and orientations found which had acceptable regression coefficients ($R^2$) were output. Further details of the algorithms used in these programs and a sample input file are presented in Appendix E.

The ZSM-5 framework was assumed to be rigid with monoclinic ($P2_1/n.1.1$) symmetry as deduced from the chemical shifts in the $^{29}$Si MAS NMR spectra. The fractional atomic coordinates and cell parameters utilized were those reported$^{18}$ for the single crystal XRD structure of calcined ZSM-5 at room temperature, as this has the correct space group symmetry. The $p$-difluorobenzene molecules were defined as rigid units having an idealized geometry: the (planar) aromatic ring was described as a regular hexagon with C–C bond lengths of 1.392 Å and interior C–C–C angles of 60°, and the C–H and C–F bond lengths were fixed at 1.080 Å and 1.328 Å respectively.

The molecules were placed in the straight channels at the channel intersections (one per intersection) with the F-F axes aligned parallel to the $b$ axis and plane of the aromatic ring in the $x$-$y$ plane. The parent molecule was positioned with the ring centroid at fractional coordinates of (0.5, 0.25, 0.0), and all other sorbate molecules in the central unit cell and surrounding 26 unit cells were generated from this by appropriate symmetry operations. The symmetry operators (general positions) for the non-standard space group $P2_1/n.1.1$ are: $^{64}$ $x$, $y$, $z$; 0.5+$x$, 0.5-$y$, 0.5-$z$; $-x$, $-y$, $-z$; 0.5-$x$, 0.5+$y$, 0.5+$z$. However, to ensure the sorbate molecules remained intact after applying translations, rotations and the necessary symmetry operations to generate a complete unit cell, the following modified symmetry operators were used: $x$, $y$, $z$; 0.5+$x$, 0.5-$y$, 0.5-$z$; $-x$, $-y$, $-z$; 0.5-$x$, 0.5+$y$, 0.5+$z$. Figures of the solutions found were generated using ORTEP-3 for Windows.$^{65}$ Some geometrical analysis was also checked using the PLATON-98 software.$^{66}$
6.3 RESULTS AND DISCUSSION

6.3.1 1-D $^{19}$F and $^{29}$Si MAS NMR

1-D $^{19}$F and $^{29}$Si MAS (with decoupling) NMR data were collected at 5 degree intervals from 215 K to 300 K. The $^{19}$F MAS spectra showed a series of spinning sidebands at the spinning speeds used (Figure 6.6). The isotropic chemical shift was -128.8 ppm.

At temperatures above ca. 293 K, the $^{29}$Si MAS NMR spectra showed 12 resonances, and the chemical shifts indicated that the ZSM-5 framework had orthorhombic $Pnma$ symmetry (Figures 6.7(a,b)). This phase has been reported for several other low-loaded sorbate / ZSM-5 complexes. However, on cooling below ambient temperature, the appearance of the spectrum changed dramatically. The most obvious change was the appearance of a new resonance at -109.8 ppm, and also 4 new peaks in the region -114 to -117 ppm (Figure 6.7). The resonance at -109.8 ppm is characteristic of the monoclinic $P2_1/n.1.1.$ phase. At lower temperatures, the spectrum was very similar to that observed for the empty ZSM-5 at room temperature (Figures 6.7(k)). It was concluded that a portion of the sample had undergone a phase transition from orthorhombic to monoclinic symmetry. Inspection of the spectra obtained for temperatures below 290 K showed a gradual increase in the intensities of these additional resonances relative to those assigned to the orthorhombic phase. The resonance at -117 ppm is diagnostic of the orthorhombic phase, and below about 260 K, this peak was no longer observed, indicating the sample had completely transformed to monoclinic symmetry.

The precise $^{29}$Si chemical shifts varied slightly with temperature, and the temperature at which the phase transition was complete was also found to depend on the concentration of $p$-difluorobenzene. At lower loadings, the transformation occurred at higher temperatures, in agreement with the behavior reported for the low-loaded $p$-xylene- and $p$-dichlorobenzene / ZSM-5 complexes. The low-temperature (monoclinic) spectra could be deconvoluted in terms of up to 20 Lorentzian curves (Figure 6.8). This phase transition from orthorhombic to monoclinic symmetry was completely reversible, and was subsequently confirmed by powder X-
Figure 6.6 $^{19}$F MAS NMR spectra of $p$-difluorobenzene in ZSM-5 at the temperatures indicated. 20 transients were recorded with a recycle delay of 5 s and spinning speeds of: (a) 3.12 kHz, (b) 3.07 kHz, (c) 3.03 kHz, and (d) 3.20 kHz. Spinning sidebands are marked "*".
Figure 6.7 $^{29}$Si MAS NMR spectra of purely siliceous ZSM-5 loaded with ca. 4 molecules of $p$-difluorobenzene/u.c recorded at the temperatures indicated using a recycle delay of 20 s. 'Ortho' and 'Mono' label resonances which are diagnostic of the orthorhombic (Pnma) and monoclinic (P2$_1$/n.1.1) phases, respectively. The spectrum of the empty (monoclinic) ZSM-5 at 295 K is shown for comparison (k).
Figure 6.7 (continued) $^{29}$Si MAS NMR spectra of purely siliceous ZSM-5 loaded with ca. 4 molecules of $p$-difluorobenzene/u.c recorded at the temperatures indicated using a recycle delay of 20 s. 'Ortho' and 'Mono' label resonances which are diagnostic of the orthorhombic (Pnma) and monoclinic (P2$_1$/n.1.1) phases, respectively. The spectrum of the empty (monoclinic) ZSM-5 at 295 K is shown for comparison (k).
Figure 6.8 MAS NMR spectra of the low-loaded $p$-difluorobenzene / ZSM-5 complex. (a) Quantitative $^{29}$Si MAS spectrum and fit obtained (b) by deconvolution in terms of individual Lorentzian curves (c). CP MAS spectra obtained using 20 ms cross polarization from: $^1$H (d), and $^{19}$F (e). The temperatures and tentative assignments of the resonances to specific T-sites are indicated.
ray diffraction experiments (see Chapter 7). Although the framework symmetry at low
temperatures is the same as that observed for empty ZSM-5, the p-difluorobenzene molecules
remain inside the ZSM-5 framework during and after the phase transition. This was confirmed by
successful polarization transfer from $^1\text{H}$ and $^{19}\text{F}$ in CP experiments (see below).

### 6.3.2 INADEQUATE Experiments

It is essential to know the assignments of the different $^{29}\text{Si}$ resonances to specific T-sites
if information about the positions of guest molecules within zeolites is to be obtained using NMR
techniques based on the dipolar interactions between the sorbed molecules and the silicon atoms
in the framework. In order to assign the resonances in the $^{29}\text{Si}$ NMR spectra, a series of 2-D
INADEQUATE and 2-D CP-INADEQUATE experiments were performed at temperatures of
235 K, 245 K and 250 K. These temperatures were selected because the 1-D spectra showed at
least 17 well resolved resonances, some of which had chemical shifts that changed considerably
between these temperatures. It was thought that 2-D spectra obtained at these three temperatures
would provide the best possible chance of achieving a complete assignment. However, due to the
variation in the relaxation times induced by spinning with nitrogen gas, good quality
INADEQUATE spectra were only obtained at 245 K when air was used. A contour plot of the
CP INADEQUATE acquired at 245 K is presented in Figure 6.9.

The monoclinic phase of ZSM-5 having $P2_1/n11$ symmetry contains 24
crystallographically inequivalent T-sites, and thus represents one of the most complicated of the
known zeolite frameworks. The connectivity list for the T-sites (based on the single crystal
structure$^{18}$) is given in Table F.1 (Appendix F). 48 different $^{29}\text{Si}$-$^{29}\text{Si}$ connectivities are present
and should theoretically be observed in a 2-D INADEQUATE spectrum. However, there are no
self-connectivities, and even when the second coordination sphere of T-atoms (ignoring oxygens)
is considered, no T-site has a unique connectivity pattern. This makes it difficult to find a
suitable starting point to make the assignment.
Figure 6.9 Contour plot of a CP-INADEQUATE experiment on ZSM-5 loaded with 4 molecules/u.c. of p-difluorobenzene at 245 K with a 1-D $^1$H-$^{29}$Si CP MAS spectrum above. 48 experiments with 1120 scans in each experiment were carried out using a recycle delay of 3 s for a total experiment time of ca. 48 h. A spectral width of 1000 Hz, contact time of 35 ms, fixed delay of 16 ms and 256 real data points were used. Sine-bell apodization and a power calculation were used for the data processing.
Due to the close similarities between the $^{29}\text{Si}$ MAS NMR spectrum of the empty (monoclinic) ZSM-5 (for which a complete assignment has been published$^{26}$) and that observed for the $p$-difluorobenzene / ZSM-5 complex at low temperatures, it was felt that the previous assignment provided a good starting point. Assuming that the differences between the T-sites would be maintained in the low-temperature monoclinic form, the lowest field resonance (at ca. -109.5 ppm) was tentatively assigned to Si-21, and the highest field resonance at ca. -117.1 ppm, to Si-8.

From these starting points a partial assignment of the spectrum was possible (Figure 6.9). The assignment is self consistent but incomplete because there is considerable peak overlap in the center region of the 1-D spectrum. There is good internal consistency in the assignment of the best resolved peaks (i.e. the highest and lowest-field resonances), and all of the expected connectivities between these sites are clearly observed. For example Si-5 is connected to Si-11, which is connected to Si-10, and silicons 8, 10 and 21 are all connected to Si-9 as expected from the framework connectivities. At the present time this assignment is thought to be correct.

An important difference from the empty monoclinic ZSM-5 at 300 K, is the interchange of the resonances assigned to Si-14 and Si-16; at 245 K silicon 14 is to high field of Si-16 in the $^{29}\text{Si}$ MAS NMR spectrum of the $p$-difluorobenzene / ZSM-5 complex. The silicons in four-membered rings (T-sites 9, 10, 21 and 22) are expected to occur at lower field based on correlations between $^{29}\text{Si}$ chemical shifts and the geometrical parameters such as Si-O-Si bond angles and Si-Si distances.$^{37}$ For the resonances which have been assigned, there is also a reasonable correlation between the $^{29}\text{Si}$ chemical shifts and the mean Si-Si distances which supports the correctness of the assignment.$^{26}$

### 6.3.3 $^1\text{H}$-$^{29}\text{Si}$ Cross Polarization Experiments

Figure 6.8(d) shows $^1\text{H}$-$^{29}\text{Si}$ CP MAS spectrum of the low-loaded $p$-difluorobenzene / ZSM-5 complex obtained using a 20 ms contact time at 230 K. Comparison with the quantitative
$^{29}$Si MAS NMR spectrum (Figure 6.8(a)) reveals that the intensities of the resonances in the CP spectrum are no longer equal. For example, the signals for silicons 11 and 14 are almost twice as intense as for Si-16. Also at 230 K, the resonances assigned to Si-10 and Si-23 overlap with other peaks and thus there are only six well resolved resonances. A series of CP experiments were acquired as a function of the contact time, and deconvoluted in terms of 18 individual Lorentzian curves. Figure 6.10 shows a plot of the intensities of the 6 outermost (best resolved) T-sites as a function of the contact time. The different T-sites seem to be divided into three groups. Silicons 21 and 5 show the most rapid intensity increase as a function of contact time and are thus the most efficiently polarized, while Si-11, Si-14 and Si-8 show less efficient polarization, and Si-16 shows quite inefficient polarization. From this behavior it is clear that silicons 21 and 5 are closer to the $^1$H polarization source than silicons 11, 14 and 8, while Si-16 is relatively far from any $^1$H nuclei. Si-16 is located in the zig-zag channel while those silicons with largest polarization following CP are in the straight channel. Because the $^1$H nuclei used as the source of the polarization are on the aromatic rings, the $p$-difluorobenzene molecules must be located somewhere within the straight channels.

The $T_{CP}$ values determined from nonlinear least squares regression analysis of this data to Eq. 3.15 (with $T_{1p}(^1$H) held constant at 110 ms) are listed in Table 6.2. Silicons which have protons in close proximity will have the smaller $T_{CP}$ values than those which are far from the sorbate. The CP curves calculated using these time constants are overlaid on the experimental data in Figure 6.10. Using these $T_{CP}$ values and assuming a static sorbate molecule, the best solution found from analysis with the program CPF9.PAS had a correlation coefficient, $R^2$, of 0.991, with a slope of $3.092 \times 10^{-4}$, and a y-intercept of 45.91. The second moments calculated for this solution are listed in Table 6.2, and the parameters defining the translations and rotations applied are given in Table 6.3. Figure 6.11(a) shows the highly linear correlation found between the experimental $1/T_{CP}$ values and the (static) second moments calculated for this solution.
Figure 6.10  Intensities of the \textsuperscript{1}H-\textsuperscript{29}Si CP MAS NMR signals as a function of the contact time at 230 K for ZSM-5 loaded with ca. 4 molecules of \textit{p}-difluorobenzene per u.c. The curves were obtained from nonlinear least squares fitting of the data to Eq. 3.15 with $T_{1p}(^{1}H)$ fixed at 110 ms.

Table 6.2  Experimental and calculated parameters related to the \textsuperscript{1}H-\textsuperscript{29}Si cross polarization experiments on the low-loaded \textit{p}-difluorobenzene / ZSM-5 complex at 230 K.

<table>
<thead>
<tr>
<th>T-site</th>
<th>Chemical Shift (ppm)$^{(a)}$</th>
<th>$T_{CP}$ (ms)$^{(b)}$</th>
<th>$M_2(^{1}H-^{29}Si)$ (Hz$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Static$^{(c)}$</td>
</tr>
<tr>
<td>Si 21</td>
<td>-109.5</td>
<td>15.703</td>
<td>59408</td>
</tr>
<tr>
<td>Si 5</td>
<td>-110.7</td>
<td>16.943</td>
<td>40903</td>
</tr>
<tr>
<td>Si 11</td>
<td>-114.9</td>
<td>19.061</td>
<td>20264</td>
</tr>
<tr>
<td>Si 16</td>
<td>-115.1</td>
<td>21.248</td>
<td>5914</td>
</tr>
<tr>
<td>Si 14</td>
<td>-116.1</td>
<td>17.647</td>
<td>34539</td>
</tr>
<tr>
<td>Si 8</td>
<td>-117.1</td>
<td>18.209</td>
<td>27551</td>
</tr>
</tbody>
</table>

$^{(a)}$ Referenced to TMS.  $^{(b)}$ Calculated using nonlinear least squares fitting to Eq. 3.15 with $T_{1p}(^{1}H)$ fixed at 110 ms.  $^{(c)}$ Calculated using Si-H distances up to 8 Å for the sorbate locations described by the translations and rotations given in Table 6.3.
Table 6.3 Results of fitting cross polarization data for the low-loaded $p$-difluorobenzene / ZSM-5 complex at low temperature.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^1$H-$^{29}$Si CP</th>
<th>$^{19}$F-$^{29}$Si CP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculation Type</td>
<td>Static</td>
<td>$180^\circ$ Ring Flips</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>230</td>
<td>230</td>
</tr>
<tr>
<td>Number of Points</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.991</td>
<td>0.966</td>
</tr>
<tr>
<td>Slope</td>
<td>$3.092 \times 10^{-4}$</td>
<td>$5.483 \times 10^{-4}$</td>
</tr>
<tr>
<td>Intercept$^{(a)}$</td>
<td>45.91</td>
<td>45.24</td>
</tr>
<tr>
<td>$\Delta X$ (Å)$^{(b)}$</td>
<td>-0.3</td>
<td>-0.2</td>
</tr>
<tr>
<td>$\Delta Y$ (Å)$^{(b)}$</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>$\Delta Z$ (Å)$^{(b)}$</td>
<td>-0.4</td>
<td>-0.5</td>
</tr>
<tr>
<td>$\phi$ (°)$^{(c)}$</td>
<td>-40</td>
<td>-60</td>
</tr>
<tr>
<td>$\theta$ (°)$^{(c)}$</td>
<td>-40</td>
<td>-40</td>
</tr>
<tr>
<td>$\psi$ (°)$^{(c)}$</td>
<td>-25</td>
<td>-20</td>
</tr>
</tbody>
</table>

$^{(a)}$ Y axis intercept. $^{(b)}$ Translations along the $a$ ($\Delta X$), $b$ ($\Delta Y$), or $c$ ($\Delta Z$) axes from the chosen starting position at the channel intersection in centre of straight channel (10.0535 Å, 4.96941 Å, -0.05811 Å). $^{(c)}$ Euler angles defining rotation from starting orientation with aromatic ring in the $x$-$y$ plane, and F-F axis parallel to $b$ axis.
Figure 6.11 Best linear fits of $1/T_{CP}$ vs. calculated $M_2(^1\text{H}^{29}\text{Si})$ values found from analysis of the $^1\text{H}^{29}\text{Si}$ CP MAS data recorded at 230 K assuming the $p$-difluorobenzene molecules were static (a), or undergoing 180° ring-flips about the F-F axis (b). See Table 6.3 for parameters.
The molecule was found to be shifted slightly from the center of the straight channel (0.3 Å along [100] and 0.4 Å along [001]) and was oriented so that the plane of the aromatic ring was almost parallel to the major axis of the elliptically distorted 10-ring (Figure 6.12). The molecule was also twisted slightly away from the b axis. However, the most striking difference between the orientation found from this analysis and those reported for other sorbates in the straight channels of ZSM-5, is the rotation of the ring by 40° so that the fluorine atoms point towards the openings of the zig-zag channels rather than being parallel to [010] as can be clearly seen in Figure 6.13(b). The fractional atomic coordinates for the sorbate atoms for this solution are listed in Table F.2 (Appendix F). In this location Si-16 has only three 1H nuclei within an 8 Å radius sphere, and these are all more than 7.1 Å away. Conversely Si-21 has six protons within 8 Å three of which are closer than 6 Å, and Si-5 also has two protons closer than 4.6 Å.

A possible reason why the molecules adopt this orientation within the channels is to minimize the repulsive fluorine-fluorine and fluorine-oxygen interactions. Considering the orientations which are permitted by steric restriction between the sorbate and framework atoms, the fluorine-fluorine distances have been maximized. For the best solution found, the distance between F atoms on adjacent rings in the straight channel is 10.0 Å, and the closest F-F distance between molecules in neighbouring channels is 8.31 Å. This arrangement may also explain why loadings of more than 4 molecule/u.c. were not obtained at ambient temperature and pressure, even when excess p-difluorobenzene was used. If more than 4 molecules/u.c. were present, some molecules would need to be in the zig-zag channels, and this would prevent the molecules in the straight channels from having their fluorine atoms near the openings of the zig-zag channels.

When 180° ring-flips about the F-F axis were included in the 1H-29Si heteronuclear second moment calculations, the best solution \( R^2 = 0.966 \) had very similar location and orientation of the p-difluorobenzene as seen from a comparison of the parameters for the two solutions listed in Table 6.3. The correlation obtained for the \( 1/T_{CP} \) vs. \( M_2 \) in this case is shown in Figure 6.11(b), which again does not pass through the origin. For this solution, the closest F-F
Figure 6.12 View down [010] showing location and orientation of $p$-difluorobenzene in ZSM-5 found from fitting of $^1H$-$^{29}Si$ cross polarization data at 230 K.
Figure 6.13 Location and orientation of the \( p \)-difluorobenzene molecules in ZSM-5 found from analysis of \(^1\)H-\(^{29}\)Si CP data acquired at 230 K: Views along the straight channel (a), and into the zig-zag channel (b) show the spatial relationship of the sorbate atoms to the different Si atoms (T-sites).
distances between molecules in the same channel and those in adjacent channels are 10.2 Å and 8.1 Å respectively.

Figures 6.13 shows views down the straight channel and into the zig-zag channel for the orientation and location found from the fitting assuming stationary molecules. In these figures, the proximity of the sorbate protons the different T-sites is seen. There are no $^1$H nuclei close to Si-16, while silicons 21 and 5 have several protons in close proximity, as expected from the general qualitative trends in the CP intensities as a function of contact time.

The regression lines found in these experiments had large y-intercepts which from the previous work on the $p$-xylene / ZSM-5 systems, probably indicates that the $p$-difluorobenzene molecules are still undergoing some slow diffusion along the channels on the time scale of the CP experiments at 230 K. Furthermore, the reliability of the assignment of the $^{29}$Si resonances from the INADEQUATE experiments is not confirmed at the present time, and only six from the possible 24 T-sites were included in the analysis. For these reasons the location and orientation found from fitting of the $^1$H-$^{29}$Si CP data at 230 K should be viewed as tentative, and preliminary at this time.

As a check of the location found from the $^1$H-$^{29}$Si, a series of $^1$F-$^{29}$Si variable contact time experiments were also performed at low temperatures. These results are presented in the next section.

6.3.4 $^{19}$F-$^{29}$Si Cross Polarization Experiments

Samples of purely siliceous ZSM-5 containing ca. 4 molecules/u.c. $p$-difluorobenzene-$d_4$ were used for the $^{19}$F-$^{29}$Si cross polarization experiments to avoid possible complications from $^1$H-$^{19}$F dipolar interactions. Variable contact time CP experiments were performed at 235 K, 240 K, 245 K and 250 K. Figure 6.9(e) shows a $^{19}$F-$^{29}$Si CP MAS spectrum obtained using a 20 ms contact time at 235 K. Again the peak assigned to Si-16 shows relatively low intensity, and is thus far from the $^{19}$F nuclei. Conversely, the peak assigned to Si-8 is very intense, and Si-14 and
Si-21 are also relatively strong indicating that silicons in these T-sites must have \(^{19}\text{F}\) nuclei in close proximity. Because the resonance assigned to Si-23 is better separated than at 230 K, data from this peak was also used.

Figure 6.14 shows a plot of the intensities of the 7 outermost (best resolved) T-sites as a function of the contact time. Again, the different T-sites seem to be divided into three groups. Silicon 8 shows the most rapid intensity increase as a function of contact time, Si-16 shows relatively inefficient polarization, and the other 5 silicons show intermediate degrees of polarization transfer. From this behavior it is clear that the \(^{19}\text{F}\) nuclei in the sorbate molecules are close to Si-8, and that silicons 14 and 21 are also closer to fluorine atoms than the other silicons. Again these observations are consistent with the \(p\)-difluorobenzene molecules being located somewhere within the straight channel.

There is no obvious decay seen in the data up to the 55 ms contact time used, which indicates that \(T_{1\rho}(^{19}\text{F})\) is quite long. The \(T_{\text{CP}}\) values determined from nonlinear least squares regression analysis of this data to Eq. 3.15 (with \(T_{1\rho}(^{19}\text{F})\) held constant at 1800 ms) are listed in Table 6.4. The CP curves calculated using these time constants are overlaid on the experimental data in Figure 6.14, and although there is agreement between the calculated and experimental data the fits are not as good as for the \(^1\text{H}-^{29}\text{Si}\) CP data.

Using these \(T_{\text{CP}}\) values and assuming a static sorbate molecule, the best solutions found from analysis with the program \textit{CPF9.PAS} had \(R^2 = 0.962\), a slope of \(3.908 \times 10^{-3}\), and a y-intercept of 54.79 (Figure 6.15). In this case there was a family of solutions having the same parameters for the correlations. For all of these solutions the ring centroid was shifted from the center of the straight (by 0.4 Å along [010] and 0.4 Å down [001]) but different rotational angles were found. This is precisely the behavior expected because any orientation of the aromatic ring plane about the F-F axis will leave the Si-F distances (and hence the \(^{19}\text{F}-^{29}\text{Si}\) heteronuclear second moments) unchanged.
Figure 6.14 Intensities of the $^{19}$F-$^{29}$Si CP MAS NMR signals as a function of the contact time at 235 K for the ZSM-5 loaded with ca. 4 molecules of $\alpha$-difluorobenzene-$d_4$ per u.c. The curves were obtained from nonlinear least squares fitting of the data to Eq. 3.15 with $T_{1p}^{(19F)}$ fixed at 1800 ms.

Figure 6.15 Best linear fit of $1/T_{CP}$ vs. calculated $M_2^{(19F-29Si)}$ values found from analysis of the $^{19}$F-$^{29}$Si CP MAS data recorded at 235 K. See Table 6.3 for parameters.
Table 6.4 Experimental and calculated parameters related to the $^{19}\text{F}-^{29}\text{Si}$ cross polarization experiments on the low-loaded $p$-difluorobenzene / ZSM-5 complex at 235 K.

<table>
<thead>
<tr>
<th>T-site</th>
<th>Chemical Shift (ppm)$^a$</th>
<th>$T_{\text{CP}}$ (ms)$^b$</th>
<th>$M_R(^{19}\text{F}-^{29}\text{Si})$ (Hz$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si 21</td>
<td>-109.5</td>
<td>9.674</td>
<td>12134</td>
</tr>
<tr>
<td>Si 5</td>
<td>-110.8</td>
<td>10.248</td>
<td>11194</td>
</tr>
<tr>
<td>Si 23</td>
<td>-114.5</td>
<td>10.341</td>
<td>9424</td>
</tr>
<tr>
<td>Si 11</td>
<td>-115.0</td>
<td>11.149</td>
<td>8722</td>
</tr>
<tr>
<td>Si 16</td>
<td>-115.2</td>
<td>15.566</td>
<td>2846</td>
</tr>
<tr>
<td>Si 14</td>
<td>-116.1</td>
<td>10.271</td>
<td>11441</td>
</tr>
<tr>
<td>Si 8</td>
<td>-117.1</td>
<td>9.766</td>
<td>12758</td>
</tr>
</tbody>
</table>

$^a$ Referenced to TMS. $^b$ Calculated using nonlinear least squares fitting to Eq. 3.15 with $T_{1p}(^{19}\text{F})$ fixed at 1800 ms. $^c$ Calculated using Si-F distances up to 8 Å for translations and rotations given in Table 6.3.
However, as seen from comparison of the translation and rotation parameters in Table 6.3, this solution corresponds to a position and orientation of the organic molecules which is significantly different from those found for the $^1\text{H}^{29}\text{Si}$ CP data. The molecule has the fluorine-fluorine axis parallel with the straight channel as shown in Figure 6.16. This position and orientation is very similar to those found for the two other low-loaded sorbate / ZSM-5 complexes whose structures are known.\textsuperscript{55} When the sorbates are at this location, the fluorine-fluorine distances between adjacent molecules in straight channel is reduced to 5.7 Å. The closest F-F distance between fluorines in neighbouring channels is 11.7 Å. Table 6.4 summarizes the second moments calculated for one of these (equivalent) solutions, and the fractional atomic coordinates for the sorbate atoms are listed in Table F.3 (Appendix F).

As seen from Figure 6.15, the large $y$-intercept and lower $R^2$ are a primarily due to the large displacements seen for the Si-10 and Si-16 from the overall correlation trend. This may be a result of the overlap of the resonance corresponding to Si-10 with another peak, which would affect the intensity determined from curve fitting since there may have been a significant contribution from the next (unassigned) resonance and the $T_{\text{CP}}$ value obtained would be incorrect. Slow diffusion occurring on the time scale of tens of milliseconds will also affect the CP experiments, and the large $y$-intercepts tend to indicate that such motions are present.

Another possibility is that there are too few $^{19}\text{F}$ nuclei to fulfill the assumptions of adequate (strong) $^{19}\text{F} - ^{19}\text{F}$ dipolar interactions (which mean that the fluorines can be treated as a large spin reservoir) required for Eq. 3.15 to be valid.\textsuperscript{67} In fact, there may be oscillatory behavior in the variable contact time CP data which indicates the system might be more appropriately described in terms of an $I_N S$ spin system with $N$ small. In the case of the $^1\text{H}^{29}\text{Si}$ CP experiments this is less of a concern because the are more protons (twice the number of fluorines), and they are much closer to one another.
Figure 6.16 View down [010] showing location and orientation of $p$-difluorobenzene in ZSM-5 found from fitting of $^{19}\text{F}$-$^{29}\text{Si}$ cross polarization data at 235 K.
6.3.5 $^{19}$F-$^{29}$Si REDOR and TEDOR Experiments

A series of REDOR and TEDOR experiments were also performed at 240 K, and the results indicate that both experiments are viable. However these were all affected by the variation of the relaxation times caused by the gradual replacement of the oxygen gas in the sample by nitrogen described above. In addition the positive $y$-intercepts found for the correlations between $1/T_{CP}$ vs. the calculated heteronuclear second moments indicated that slow diffusions were still occurring at 240 K which would also affect the REDOR and TEDOR experiments and they were not analyzed in detail.

Although the spin system could not be considered to be composed of completely isolated $^{19}$F-$^{29}$Si spin pairs, the low loading did minimize the number of dipolar $^{19}$F-$^{29}$Si interactions within an 8 Å radius of any of the T-sites. It was hoped that the positions and orientations found for the $p$-difluorobenzene molecules from analysis of the cross polarization experiments could provide a good starting model of the spin-system as required for the multi-spin REDOR and TEDOR calculations (see Chapter 3).

6.4 SUMMARY AND CONCLUSIONS

Loading ZSM-5 with 4 molecules of $p$-difluorobenzene per unit cell caused the framework to change from monoclinic ($P2_1/n$ $I$ $I$ symmetry, 24 T-sites) to a phase having 12 T-sites at temperatures above ca. 293 K. From the appearance of the $^{29}$Si MAS NMR spectra the orthorhombic $Pnma$ symmetry is proposed for this phase. This orthorhombic phase has been reported previously for three other low-loaded, para-disubstituted aromatic / ZSM-5 complexes. Loadings higher than 4 molecules/u.c. were not obtained for samples prepared with excess $p$-difluorobenzene at ambient pressure and temperature.

Cooling the sample below 290 K resulted in a transformation back to a phase having 24 T-sites, which was maintained to the lowest temperature accessible (215 K). The $^{29}$Si NMR chemical shifts observed for this phase indicated that it was almost identical to the monoclinic
P2/n 1.1 phase adopted by the empty ZSM-5 framework at temperatures below ca. 340 K. The success of $^1$H-$^{29}$Si and $^{19}$F-$^{29}$Si polarization transfer observed during Hartmann-Hahn CP experiments provided unambiguous evidence that the sorbate molecules remained within the ZSM-5 channel system during, and after, this phase transition. It is anticipated that the transformation to monoclinic symmetry for the ZSM-5 framework observed in the present case may also occur in other sorbate / ZSM-5 systems at low temperatures.

The general location of the sorbed p-difluorobenzene molecules was determined to be in the straight channels at the intersection with the sinusoidal channels. However, the precise position and orientation could not be unambiguously determined from these initial studies. Two different orientations were found from analysis of the $^1$H-$^{29}$Si and $^{19}$F-$^{29}$Si CP MAS NMR data. Fitting of the $^1$H-$^{29}$Si CP data acquired at 230 K yielded a very good linear correlation for the experimental $1/T_C$ values versus the calculated $^1$H-$^{29}$Si heteronuclear second moments when the p-difluorobenzene molecules were oriented so that the fluorine atoms were pointing towards the openings of the zig-zag channels and the plane of the aromatic ring was at an angle which corresponded closely to the longest cross-channel dimension of the straight channel. A much poorer linear correlation was obtained from calculations utilizing the $^{19}$F-$^{29}$Si CP data acquired at 235 K, with the best solution(s) found when the fluorine-fluorine axis was parallel to [010]. This orientation is in accord with that previously observed for the other low-loaded ZSM-5 / sorbate complexes. Unfortunately, the $^{19}$F-$^{29}$Si experiments cannot provide any information about the orientation of the plane of the aromatic ring relative to the crystallographic axes. This is because the ring can rotate freely about the F-F axis without affecting the F-Si distances. In both cases the molecule centroid was shifted slightly from the center of the straight channel.

When sorbate molecules are present the 10-rings defining the channels containing the sorbate distort to become more elliptical, presumably in order to better accommodate the guest molecules.\cite{5,5,9} In the present work, as in most of the previous investigations to determine preferred sorption sites of guests in the zeolite channel systems from theoretical calculations (e.g.
energy minimizations), the framework geometry was selected and kept rigid. However the
precise geometry of the framework (and the channel shapes) is known to vary with different
sorbates, and the chosen framework geometry may not accurately reflect the real structure,
which may affect the exact position and orientation found for the sorbed molecules.

Additional 2-D INADEQUATE experiments are required (including several at different
temperatures) in order to assign all of the resonances in the $^{29}$Si MAS NMR spectra, and in
addition, these preliminary results indicate that experiments need to be done at lower
temperatures to slow the rate of the diffusions within the channels.

Detailed investigations of powder X-ray data and $^{29}$Si MAS NMR data are invaluable
aids to determining the possible symmetry, number of crystallographically inequivalent T-sites,
and space group, as well as the temperature and loadings at which any changes occur, and if
possible should be obtained prior to single crystal studies.

Recent NMR investigations of the low-loaded $p$-xylene / ZSM-5 complex have been
utilized to predict the sorbate location and orientation, and the solution found to correspond
closely to that determined by the subsequent single crystal XRD structure determination (Chapter
8), thus proving the feasibility, and reliability of these NMR techniques to accurately locate the
guests within the channels of zeolites. In the next chapter, the results of the preliminary powder
X-ray diffraction studies undertaken to verify the space group symmetries and unit cell
parameters of the two phases observed for the low-loaded $p$-difluorobenzene in ZSM-5 are
presented.
REFERENCES FOR CHAPTER 6


9 Single crystal XRD structure of low-loaded p-xylene/ZSM-5 complex. See Chapter 8.


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CHAPTER 7

PRELIMINARY POWDER X-RAY DIFFRACTION
INVESTIGATIONS OF THE LOW-LOADED PARA-
DIFLUOROBENZENE / ZSM-5 COMPLEX

7.1 INTRODUCTION

As discussed in Chapter 6, single crystal diffraction experiments (where feasible) would provide an incisive check on the correctness of guest-host structures predicted by NMR. Powder diffraction data acquired with both synchrotron and conventional X-ray sources has provided information about the unit cell parameters, framework symmetry, and phase transitions in ZSM-5. In a few cases, the location and orientation of sorbed guest species within the framework channels have been proposed from fitting of powder diffraction data. However, although refinement of these structures is possible, the small amount of literature data indicate that these are very complex systems. X-ray diffraction studies were initiated for the low-loaded para-difluorobenzene / ZSM-5 complex and the progress to date is presented in this chapter.

$^{29}$Si MAS NMR can provide complementary information such as the number of T-sites which greatly assists the space group determination. Details of the MFI framework structure, and previous investigations of the guest- and temperature-induced changes in the framework by X-ray powder diffraction and $^{29}$Si MAS NMR are discussed in Chapter 6.

For the ZSM-5 / sorbate systems where changes are seen, the lattice distortions seem to be reasonably characteristic of the nature of the sorbed molecule. In some cases however, very similar $^{29}$Si MAS NMR spectra are obtained with different molecules, indicating that the lattice
geometries are closely related. It may be that the locations of the molecules in these cases are similar, but this has only been verified for three systems to date (including the low-loaded form of p-xylene in ZSM-5 described in Chapter 8). As-synthesized ZSM-5 has \textit{Pnma} symmetry (12 T-sites),\textsuperscript{19,20} which is transformed to monoclinic symmetry following calcination to remove the templating species.\textsuperscript{1,21} Loading the calcined (empty) ZSM-5 framework with more than two, but less than four, molecules of p-xylene per unit cell (u.c.) brings about a transformation from monoclinic \textit{P2}_1/\textit{n}.\textit{l}.\textit{l} (with 24 T-sites) to orthorhombic \textit{Pnma} symmetry.\textsuperscript{22,23} The symmetry of the empty framework also changes to \textit{Pnma} symmetry at temperatures above about 340 K.\textsuperscript{22,24} Increasing the loading to between 6 and 8 molecules/u.c. induces a further change to \textit{P2}_1/\textit{2}_1/\textit{2}_1 symmetry which has 24 inequivalent T-sites.\textsuperscript{14,22} These transformations are reversible, and sorbates other than p-xylene may induce similar structural transformations.\textsuperscript{1,7,8}

Figure 7.1(a) shows a view along the zig-zag channel of the orthorhombic (\textit{Pnma}) phase of ZSM-5. For the empty ZSM-5 framework, the small increase in the cell angle (typically from 90° to 90.3-90.7°) changes the shape of the unit cell. This results in the removal of the symmetry elements such as the mirror planes parallel to the \textit{b} axis which bisect the sinusoidal channel in the orthorhombic phase (Figures 7.1(a) and (c)). The change to monoclinic symmetry is also associated with small displacive transformations of the framework atoms, although the framework topology is maintained.

Overall, the X-ray diffraction patterns of the orthorhombic and monoclinic phases are quite similar. However there are small (but characteristic) differences which can be detected provided the samples are of high crystallinity. When the cell angles are all 90° (as is the case for orthorhombic symmetry), certain reflections will overlap. For example, the reflections with Miller indices \((h\ k\ l)\) of (-3 1 3) and (3 1 3) are coincident and occur at approximately 24.4° 2θ in the orthorhombic phase \((a \approx 20.1\ \text{Å}, b \approx 19.9\ \text{Å}, c \approx 13.3\ \text{Å})\). When \(β\) becomes larger than 90° (monoclinic \textit{P1.2}_1/\textit{n}.\textit{l} phase), these reflections are no longer equivalent, and they are observed
Figure 7.1 View along the zig-zag channels of ZSM-5 for structures having different symmetries: (a) orthorhombic Pnma symmetry, (b) monoclinic P2₁/n1.1 symmetry with domain twinning, and (c) ideal monoclinic P2₁/n1.1 symmetry without twinning. The size of the twin domains was estimated to be approximately 50 unit cells (ca. 1000 Å). After reference 21.
as independent peaks in the powder pattern at about 24.3° and 24.6° 2θ respectively. Similar behavior is seen for other pairs of reflections, with the most obvious being those centered at ca. 11.9°, 15.5°, and 28.5° 2θ. The separation of the diffraction peaks into these “doublets” will increase with increasing 2θ and also as the deviation of the cell angle from 90° becomes larger. The observation of such “doublets” is usually taken as evidence that the sample has monoclinic symmetry.

The presence of ordered guest species within the channels of the ZSM-5 has a relatively small effect on the appearance of the powder XRD patterns, unless the loading is sufficient to bring about a change of symmetry. The major differences between the patterns for the empty framework and a sorbate-containing sample with the same overall symmetry are usually only detected as small changes in the relative intensities of the reflections below about 30° 2θ, and may be associated with slight peak shifts due to changes in the cell dimensions. In general however, these changes are significant (and measurable), particularly the intensity changes for the lowest angle reflections due to the presence of sorbed organic guest.

For purely siliceous ZSM-5, both powder XRD and ²⁹Si MAS NMR can be used to distinguish between monoclinic and orthorhombic symmetry. However only NMR can be used to determine whether the orthorhombic symmetry is Pnma or P2₁2₁2₁ since the number of T-sites and chemical shifts in the ²⁹Si MAS NMR spectra are diagnostic. Exceptions may arise if the variations in the local framework geometry are not large enough to be observed in the NMR spectrum, or if the unique cell angle is very close to 90° in the monoclinic phase.

For the monoclinic phase, the single crystal X-ray refinement reported in the literature was performed using the non-standard setting P2₁/n.1.1 rather than P1.2₁/n.1. The use of P2₁/n.1.1 ensures that the straight channels are aligned along the b axis, rather than a, which permits direct comparisons with the orthorhombic structures. P2₁/n.1.1 symmetry with cell
constants \( a = 20.107 \, \text{Å}, \quad b = 19.879 \, \text{Å}, \quad c = 13.369 \, \text{Å}, \quad \text{and} \quad \alpha = 90.67^\circ \) is equivalent to the standard setting \( P1_21_12 \) with \( a = 19.879 \, \text{Å}, \quad b = 20.107 \, \text{Å}, \quad c = 13.369 \, \text{Å}, \quad \text{and} \quad \beta = 90.67^\circ \).

An additional complication for the monoclinic phase is the (apparently intrinsic) domain twinning which was observed by van Koningsveld \textit{et al.} in their single crystal investigations of calcined ZSM-5 at room temperature.\(^2\) They determined that the monoclinic phase consists of an aggregate of monoclinic twin domains with domain sizes of the order of 1000 Å. A representation of the monoclinic framework structure in the presence of these twin domains is reproduced in Figure 7.1(b). An "ideal" single-domain monoclinic crystal without twinning present is shown in Figure 7.1(c) for comparison.

This chapter presents the results of preliminary X-ray diffraction studies on the low-loaded \( p \)-difluorobenzene / ZSM-5 complex. Powder XRD data were collected on a ZSM-5 sample loaded with approximately four molecules of \( p \)-difluorobenzene/u.c. at several temperatures, and also for a sample of the empty (calcined) ZSM-5 at room temperature. The cell constants and space group for calcined ZSM-5 are well established,\(^1,21\) and provided a check of the analysis technique, before it was applied to fit the \( p \)-difluorobenzene / ZSM-5 data.

### 7.2 MATERIALS AND METHODS

#### 7.2.1 Sample Preparation and Data Collection

Highly crystalline, purely siliceous ZSM-5 powder identical to that used for the NMR experiments was calcined at 825 K immediately prior to use. After cooling to room temperature it was loaded into 0.7 mm diameter glass capillaries specifically designed for X-ray use. One sample was sealed directly and a measured amount of \( p \)-difluorobenzene (corresponding to 4 molecules/u.c.) was added to another before freezing in liquid nitrogen and flame sealing. These samples are referred to as "calcined" and "DFB" respectively in the following discussion.

Powder XRD patterns were acquired with the assistance of Dr. Bernd Marler using a Siemens D5000 system at the Institute of Mineralogy, Ruhr-Universität Bochum, Germany. The
diffractometer was operated in a modified Debye-Scherrer transmission geometry using monochromatized Cu $K_a$ radiation ($\lambda = 1.540598 \text{ Å}$) with a position sensitive detector. The sealed capillary containing the sample was rotated to reduce preferred orientation effects and a step-scanning mode was used to produce more accurate diffraction line profiles.

For both the calcined ZSM-5 and the sample loaded with $p$-difluorobenzene, data were recorded over the range 6.0–40.0° 29 with a step size of 0.007772° at room temperature (293 K). Four individual scans (ca. six hours / scan) were co-added to obtain the final powder patterns. The difluorobenzene-containing sample was then cooled using a stream of cold air. The air was cooled by passing it through a 0.5 m length of coiled copper tubing immersed in a vacuum dewar filled with dry ice. The cold air was directed onto the capillary through an insulated transfer tube. A series of scans over the range 21–27° 29 (step size 0.007772° 29) were acquired at approximately 10 minute increments (ca. 1 minute scan time) during the cooling from room temperature. After cooling for about one hour, the temperature of the air stream stabilized at approximately 260 K and data (4 scans) were collected over the range 6.0–40.0° 29 (0.007772° steps).

The powder patterns were baseline corrected using the GRAMS-386 software package and converted to ASCII-format files with the appropriate header information for the analysis program.

7.2.2 Fitting of Reflection Data

Analyses and fitting of the XRD data were done using the AJUST program running on an IBM-compatible PC with the MS DOS operating system. The program allowed selection of the crystal system, as well as the reflection conditions to define the space group. The input file contained information about the sample geometry (capillary), wavelength of the X-ray radiation used, the 2θ range (and step size), initial values for the various parameters which could be
optimized by the least squares fitting, and “flags” for each parameter which indicated whether
the specific parameter was to be varied or held fixed during the refinement cycles.

The Voigt function is a convolution of Lorentzian ($L$) and Gaussian ($G$) functions which
has been shown to describe the experimental peak profiles in X-ray diffraction data quite well.$^{29}$
Although an analytical form exists for the Voigt function, this is usually approximated as a
c pseudo-Voigt function to reduce calculation times.$^{29}$ AJUST implements a pseudo-Voigt function
to model the diffraction lineshapes with a weighted sum of the two lineshape functions $L$ and $G$
described by Eq. 7.1.

$$pV = \eta L + (1 - \eta)G$$  \hspace{1cm} 7.1

Here $\eta$ is the mixing parameter describing the weighting of the Gaussian and Lorentzian
contributions to the final peak profile. The full-widths at half-height for the diffraction ($W_L$ and
$W_G$ for the Lorentzian and Gaussian contributions, respectively) have a dependence on the
scattering angle $\theta$ which are modeled as:$^{27}$

$$W_L = \sqrt{w_1 + w_2 \tan \theta + w_2 \tan^2 \theta}$$  \hspace{1cm} 7.2

and

$$W_G = w_x \tan \theta + (w_y / \cos \theta)$$  \hspace{1cm} 7.3

In addition to a zero correction (linear shift of all $2\theta$ values), an asymmetry function was
applied to the peaks up to $20^\circ 2\theta$ to account for the diffractometer and sample-induced effects
(absorption, unfocussed X-ray beam, etc.). Up to 12 parameters were refined: the cell constants
($a$, $b$, $c$, and the unique angle $\beta$ if monoclinic symmetry was assumed), the lineshape
contributions ($w_1$, $w_2$, $w_3$, $w_x$, and $w_y$), an asymmetry parameter, a zero correction, and a scale
factor to match observed and calculated intensities. The variable for transparency correction (to
account for absorption effects etc.) was fixed at 0.0 in all cases, and other cell angles were held
constant at $90^\circ$. During the early stages of a refinement, several of the parameters were held fixed
(e.g. lineshape parameters) while the cell constants were refined. As the refinement proceeded (and the \( R_{wp} \) decreased), the other variable parameters were progressively included in the fitting. In the final cycles all of the parameters were refined.

The weighted pattern residual ('R' factor) \( R_{wp} \) used is defined in Eq. 7.4. \( R_{wp} \) provides a numerical criterion for following the progress of the refinement as well as a measure of the "goodness of fit" between the calculated and observed patterns.\(^{30}\)

\[
R_{wp} = \sqrt{\frac{\sum w_i [y_i(\text{obs}) - y_i(\text{calc})]^2}{\sum w_i [y_i(\text{obs})]^2}}
\]

7.4

Here \( y_i \) is the intensity at the \( i \)th position in the profile, \( \text{obs} \) and \( \text{calc} \) refer to the observed and calculated intensities respectively, and \( w_i \) is the weight assigned to the intensity observed at the \( i \)th step. A smaller value of \( R_{wp} \) indicates a smaller deviation between the observed and calculated patterns, and a better "fit". From a purely mathematical point of view, \( R_{wp} \) is the most meaningful of the possible \( R \) factors because the numerator is the residual being minimized, and thus it also reflects the progress of the refinement.\(^{30}\)

7.3 RESULTS AND DISCUSSION

7.3.1 Phase Transitions on Cooling

The \( ^{29} \text{Si} \) MAS NMR spectra acquired in the investigations of purely siliceous ZSM-5 loaded with 4 molecules/u.c. of \( p \)-difluorobenzene were presented in Chapter 6. At temperatures above 293 K a spectrum characteristic of orthorhombic \( Pnma \) symmetry with 12 resonances was observed (Figures 6.7(a,b)). Below about 260 K, the appearance of the spectrum and chemical shifts were very similar, but not identical, to those seen for empty ZSM-5, which is known to be monoclinic with \( P2_1/n 1.1 \) symmetry (Figures 6.7(g-j)). At intermediate temperatures, a mixture of the two phases was detected (Figures 6.7(d-f)). The exact temperature of the (assumed)
orthorhombic to monoclinic transformation was found to depend on the precise sorbate loading, but was completely reversible.

This phase transition for the DFB sample was followed as the temperature was lowered from room temperature by recording XRD powder patterns over the region 22.5° to 25.0° 2θ every 10 minutes after cooling was initiated. This 2θ range was chosen because it included the region around 24.5° 2θ where a characteristic monoclinic "doublet" should be clearly resolved if lower temperatures induced a phase transformation from orthorhombic to monoclinic symmetry as predicted from the NMR studies.

Selected diffraction patterns obtained during this experiment are reproduced in Figure 7.2. Of particular interest is the number of peaks in the region from ca. 24.2-24.7° 2θ. At 293 K a single peak centered at 24.45° 2θ was clearly seen (Figure 7.2(a)). After cooling for 10 minutes the appearance of the powder pattern changed considerably, and the doublet (peaks at 24.3° and 24.6° 2θ) expected for the monoclinic symmetry appeared (Figure 7.2(b)). In addition, a new reflection centered at 23.4° became visible. These observations indicated that the sample was a mixture of two phases. There was certainly a temperature gradient across the sample, but this was not the only reason for the coexistence of the two phases. Similar two-phase samples were also detected in the NMR experiments where the temperature gradient was minimized by holding the sample at a constant temperature for an extended period of time. Also, in the NMR investigations the temperature range studied was considerably larger (230-300 K). It was therefore concluded that either the size of the individual crystals determined the temperature at which the phase transformation occurred, or that domains of each symmetry were present within individual crystals.

As the cooling continued, a general decrease in the intensities of reflections assigned to the orthorhombic Pnma phase, and an associated increase in those for the monoclinic symmetry, was observed. After cooling for 40 minutes the orthorhombic reflections were no longer detected (Figure 7.2(c)). The temperature of the air stream had stabilized at 260 K by this time, and after
Figure 7.2 Powder X-ray diffraction patterns of ZSM-5 loaded with 4 molecules per unit cell of \( p \)-difluorobenzene (DFB) showing the transformation, (a) to (d), from orthorhombic \( Pnma \) to monoclinic \( P1.2_1/n.1 \) symmetry observed as the sample was cooled from 293 K to 260 K. The pattern for the calcined (empty) ZSM-5 at 293 K (monoclinic \( P1.2_1/n.1 \) symmetry) is shown for comparison in (e).
allowing an additional 20 minutes for the sample to reach an equilibrium temperature, a series of four scans over the range 6-40° 2θ (step size 0.007772°, ca. 6 hours / scan) were recorded.

Comparison of the patterns recorded for the DFB sample after more than 40 minutes cooling (Figure 7.2(d)), with that obtained for the calcined ZSM-5 at room temperature (Figure 7.2(e)), shows that the patterns are almost indistinguishable in the 22.5-25.0° 2θ region. This indicates that the DFB sample almost certainly has the same (monoclinic) symmetry as the empty ZSM-5 at low-temperatures.

The powder patterns recorded over the ranges 7.0-40.0° 2θ for the calcined (T=293 K), and p-difluorobenzene loaded ZSM-5 (at T=293K and 260 K) are presented in Figure 7.3. Inspection of these diffraction patterns reveals a direct correspondence between those recorded for the calcined and low temperature difluorobenzene-loaded samples, again supporting the monoclinic symmetry postulated for the DFB sample at low temperatures from the 29Si MAS NMR studies.

At room temperature, the absence of the “doublet” reflections at ca. 8.5°, 24.4°, and 28.5° 2θ (as well as other differences) for the difluorobenzene-loaded sample, indicates that the symmetry is orthorhombic. Because only 12 resonances are observed in the 29Si NMR spectrum above ca. 293 K, the framework symmetry may be unambiguously described as Pnma rather than P212121. Theoretically, it is also possible that monoclinic symmetry is maintained, but that all of the cell angles are 90° (or at least very close to 90°). However, such a change would essentially make the framework virtually identical to that having truly orthorhombic symmetry, and it would be impossible to distinguish between these.

The fitting of the powder diffraction data for the calcined ZSM-5 and the DFB samples recorded at 293 K and 260 K undertaken and to determine the cell constants, and verify the symmetries of the two phases, is described in the following sections. For clarity the three samples are discussed separately.
Figure 7.3 Powder X-ray diffraction patterns (7.0-22.5° 2θ) of ZSM-5 loaded with 4 molecules/u.c of p-difluorobenzene at 293 K (a), and 260 K (b). The pattern recorded for calcined (empty) ZSM-5 at 293 K is shown for comparison (c). Vertical scaling has been applied to match the intensities of the reflection at 7.8° 2θ. No baseline corrections have been applied.
Figure 7.3 (continued) Powder X-ray diffraction patterns (22.5-40.0° 2θ) of ZSM-5 loaded with 4 molecules/u.c of p-difluorobenzene at 293 K (a), and 260 K (b). The pattern recorded for calcined (empty) ZSM-5 at 293 K is shown for comparison (c). Vertical scaling has been applied to match the intensities of the reflection at 7.8° 2θ. No baseline corrections have been applied.
7.3.2 Empty ZSM-5 at 293 K

An ideal polycrystalline material or powder is an ensemble of a very large number of randomly orientated crystals. The correct unit cell parameters and information regarding the possible space groups may not be always be readily determined from a twinned single crystal. In a powder sample however, each of the twin domains scatters the X-ray radiation slightly differently, and effectively produces a “more random” orientation of the crystallites. Such a system will therefore approximate a “perfect” powder sample more closely. For these reasons, the problems in data analysis of domain twinning which affect the single crystal data for the monoclinic phase are avoided when powder X-ray diffraction data is used.

The powder XRD data recorded for the calcined ZSM-5 at 293 K were successfully refined to \( R_{wp} = 4.71\% \) in \( P1.2/n.1 \), and yielded cell parameters of \( a = 19.8823(4) \) Å, \( b = 20.1085(2) \) Å, \( c = 13.3686(2) \) Å, and \( \beta = 90.537(2)^\circ \). A small zero shift correction of \(-0.021^\circ\) was automatically determined, refined, and applied by the AJUST program during the fitting. Because the standard setting of \( P1.2/n.1 \) (i.e. with \( \beta \) unique) rather than \( P2_1/n.1.1 \) (\( \alpha \) unique) was used, the \( a \) and \( b \) cell dimensions are swapped compared to those reported for single crystal data in the literature. Estimated standard deviations for the cell constants and the lineshape parameters used are listed in Table 7.1. As expected, the estimated standard deviations for the cell parameters are significantly smaller than those reported for the monoclinic single crystal structure (0.002 Å and 0.01°). The cell dimensions of ZSM-5 are known to vary with temperature, and also with the Si/Al content, but the values found from fitting of the XRD data are within the range reported for calcined ZSM-5 in the literature.

The calculated pattern shows excellent agreement with the observed reflection data with only minor differences apparent (Figure 7.4). The major discrepancies are seen for the low angle reflections, and this is primarily due to the inability to exactly match the experimental peak profiles using the pseudo-Voigt lineshape function in this case, even when some peak asymmetry is included. This is clearly seen as “dispersion-type” peaks in the difference pattern (observed -
Table 7.1 Results from the fitting of the ZSM-5 XRD powder data using the program AJUST. The lineshape and zero-shift parameters used are also listed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Empty (calcined)</th>
<th>4 molecules/u.c. p-difluorobenzene</th>
<th>293 K</th>
<th>260 K</th>
<th>293 K</th>
</tr>
</thead>
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<tr>
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<td>293 K</td>
<td>260 K</td>
<td>293 K</td>
<td></td>
<td></td>
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<tr>
<td>Collection time</td>
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<td>24 h</td>
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<td>P1.2/n.l (No. 14)</td>
<td>Pnma (No. 62)</td>
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<td>Rwp (%)</td>
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<td>6.21</td>
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<td>a (Å)</td>
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<td>19.8796 (0.0004)</td>
<td>20.0298 (0.0002)</td>
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<td></td>
</tr>
<tr>
<td>b (Å)</td>
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<td>20.0978 (0.0003)</td>
<td>19.9195 (0.0003)</td>
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<tr>
<td>c (Å)</td>
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<td>13.3651 (0.0003)</td>
<td>13.3776 (0.0003)</td>
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</tr>
<tr>
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<td>90.000</td>
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<td></td>
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<tr>
<td>β (°)</td>
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<td>90.705 (0.002)</td>
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<td></td>
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<tr>
<td>γ (°)</td>
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<td>90.000</td>
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<td>0.999846</td>
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<td>0.000</td>
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<tr>
<td>Asymmetry Coefficient (c)</td>
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<td>0.50215</td>
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<td></td>
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<td>-0.194023</td>
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<td>0.091062</td>
<td>0.098729</td>
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<tr>
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<td>-0.007556</td>
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<tr>
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<td>0.154197</td>
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<td></td>
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</tbody>
</table>

(a) Estimated standard deviations. (b) Parameter held constant during fitting. (c) To match calculated and experimental patterns. (d) Linear shift of all 2θ values. (e) Applied up to 20° 2θ.  

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Figure 7.4 Observed (baseline corrected) and calculated powder X-ray diffraction patterns for calcined (empty) ZSM-5 at 293 K. The acquisition time for the experimental pattern was 24 hours and the calculated pattern ($R_w = 4.71\%$) was obtained using the AJUST program assuming monoclinic $P1.2/n.1$ symmetry with the parameters listed Table 7.1.
calculated). The baseline correction may have also modified the peak profiles slightly.

A small broad peak at ca. 21.8° 2θ was not well fit and was in fact due to small amount of cristobalite in the samples used. Cristobalite is a dense silica phase often present as an impurity in zeolite syntheses. This was not observed in the 29Si NMR spectra because it was only very minor small fraction of the sample, and more importantly, because of the long T1 relaxation times (100's of seconds) which means it was discriminated against with the relatively short recycle delays (of order of 10-20 s) used.

The successful refinement of the lattice parameters for the calcined ZSM-5 sample validates the use of the program AJUST, and the general refinement approach employed. It furnishes values for the cell constants for the purely siliceous ZSM-5 used, and initial values for the peak profile parameters to be used in the other refinements. Furthermore, the low Rwp value indicates a very good fit, and provides a “benchmark” by which the quality of the subsequent refinements for the DFB data may be judged.

7.3.3 DFB / ZSM-5 at 260 K

A total of four scans were acquired for the DFB sample at 260 K. The first two of the 4 six-hour scans recorded with the sample cooled showed only the characteristic monoclinic features, while the third in the series contained reflections for both phases. The fourth and final scan in the series was essentially identical to that recorded for the sample at room temperature. This transformation back to the (proposed) orthorhombic phase was attributed to a gradual warming of the sample as the dry ice sublimed and the cooling became less efficient. Consequently only the first two of the low temperature scans were added and used for the refinement of the low temperature phase. This reduced the signal-to-noise ratio compared with the other two data sets, so it was anticipated that the final Rwp should be slightly higher than that obtained for the calcined ZSM-5.
Comparison of the powder diffraction data recorded for the DFB sample at 260 K (Figure 7.3(b)), with that obtained for the calcined ZSM-5 at room temperature (Figure 7.3(c)) reveals that the relative intensity of many of the reflections below about 25° 2θ is substantially different in the presence of p-difluorobenzene. A vertical intensity scaling has been applied to ensure the peak height of the reflection at ca. 7.8° 2θ is equal for all of the powder patterns in Figure 7.3. The peak intensities have not changed uniformly for all of the reflections; some are almost unchanged (e.g. reflections at 14.7°, 17.6° and 17.8° 2θ), while others exhibit dramatic increases (see peaks in region 10-14° 2θ). If this intensity scaling is disregarded, the patterns are virtually indistinguishable, with the reflections occurring at almost the same 2θ values in both cases.

The sorbate atoms will contribute to the scattering and will affect the intensity of all the reflections. The contribution to the scattering from the sorbate molecules will fall off quite steeply (compared to that for the framework) with increasing 2θ due to significant thermal motions of the sorbate molecules. Because of this, the major intensity differences are expected at lower 2θ angles, as was indeed observed.

Assuming P1.2/n.1 symmetry, the DFB powder data acquired at 260 K refined to a final $R_{wp}$ of 6.82 % using the parameters listed in Table 7.1. Considering the reduced signal to noise ratio for these data, this indicates a very good fit to the experimental pattern. The good agreement between the calculated and observed powder patterns can be seen in Figure 7.5. For the reasons described in section 7.3.2, the largest discrepancies occur in the low angle region (as was also the case for the calcined ZSM-5 data).

The refined cell parameters refined to $a = 19.8796$ Å, $b = 20.0978$ Å, $c = 13.3651$ Å, and $\beta = 90.705°$. The cell dimensions are all slightly smaller than those found for the empty ZSM-5 at 293 K, but the angle $\beta$ has become slightly larger (see Table 7.1). Overall, the unit cell volume was reduced by about 0.1% compared to that of the empty ZSM-5 at 293 K. Similar reductions in
Figure 7.5 Observed (baseline corrected) and calculated powder X-ray diffraction patterns for ZSM-5 loaded with 4 molecules/u.c. of $p$-difluorobenzene at 260 K. The acquisition time for the experimental pattern was 12 hours and the calculated pattern ($R_{wp} = 6.82\%$) was obtained using AJUST assuming monoclinic $P1_21/n.1$ symmetry with the parameters listed Table 7.1.
the unit cell volume are seen for the low-loaded \textit{p}-\textit{xylene},\textsuperscript{23} \textit{p}-dichlorobenzene,\textsuperscript{16} and \textit{p}-
nitroaniline-ZSM-5 complexes at room temperature.\textsuperscript{17,18} However, because low temperature data
was not collected for the calcined ZSM-5, it is unclear whether this contraction is primarily due
to the presence of the sorbed guest molecules, or whether the lower temperature also changes the
unit cell dimensions and angles.

\subsection*{7.3.4 DFB / ZSM-5 at 293 K}

As a check for other cell symmetries, refinements were tried using the reflection
conditions corresponding to \textit{Pnma} and the lower symmetry space group \textit{Pn2}_1\textit{a}, which is related
to \textit{Pnma} by removal of the mirror plane perpendicular to the \textit{b} axis. Because \textit{p}-difluorobenzene
is a centrosymmetric molecule, it was decided that the higher \textit{Pnma} symmetry would more likely
be adopted by the DFB sample above 293 K. The only sorbate / ZSM-5 complex which has been
classified to date (by single crystal XRD techniques) using \textit{Pn2}_1\textit{a} symmetry is ZSM-5 loaded
with 4 molecules/u.c. of \textit{p}-nitroaniline / ZSM-5.\textsuperscript{17}

Using \textit{Pnma} symmetry the data were successfully refined to an \textit{R}_{wp} of 6.21\% using the
lineshape and correction parameters listed in Table 7.1. The angles \textit{\alpha}, \textit{\beta}, and \textit{\gamma} were all fixed at
90° during the fitting and the final cell dimensions obtained are listed in Table 7.1. The unit cell
volume is less than both the empty ZSM-5, and the DFB at 260 K. This was caused by a
reduction in the \textit{a} dimension by almost 0.08 Å, even though \textit{b} and \textit{c} both increased very slightly.

These cell dimensions are in general agreement with those reported for the single
crystal\textsuperscript{16-18,23} and powder refinements\textsuperscript{2-5} of the sorbate / ZSM-5 containing \textit{ca.} 4 molecules/u.c. of
single ring aromatics which exhibit \textit{Pnma} symmetry. An interesting trend in the unit cell volumes
was noted for these systems. The cell volume increases from 5315 Å\textsuperscript{3} when \textit{ca.} 4 molecules/u.c.
of \textit{p}-\textit{xylene} are sorbed,\textsuperscript{23} through 5320 Å\textsuperscript{3} for \textit{p}-\textit{nitroaniline},\textsuperscript{18} to 5324 Å\textsuperscript{3} when \textit{p}-
dichlorobenzene is sorbed.\textsuperscript{16} Although these values will be affected by the exact Si/Al ratio of the
ZSM-5 used\textsuperscript{1} they are perhaps a useful indicator for the strength of the sorbate-framework

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\textbf{Compound} & \textbf{Unit Cell Volume (Å\textsuperscript{3})} & \textbf{Notes} \\
\hline
\textit{p}-\textit{xylene} & 5315 & \\
\textit{p}-\textit{nitroaniline} & 5320 & \\
\textit{p}-dichlorobenzene & 5324 & \\
\hline
\end{tabular}
\caption{Unit Cell Volumes for Sorbate / ZSM-5 Complexes}
\end{table}
interactions (strongest for \( p \)-xylene and decreasing with increasing unit cell volume). Assuming this to be true, the cell volume found for the low-loaded \( p \)-difluorobenzene / ZSM-5 complex having \( Pnma \) symmetry (5339 Å\(^3\)), would suggest that the sorbate-framework interactions are weaker than for the other systems. Fluorine-fluorine and fluorine-oxygen repulsive interactions may contribute to this. Further support for this argument is provided by the relatively high temperature (290 K) below which the \( p \)-difluorobenzene / ZSM-5 complex transforms to monoclinic symmetry.

Although the \( R_{wp} \) value is slightly higher than the benchmark value of 4.71% obtained for the calcined ZSM-5, it is still low enough to support the proposed \( Pnma \) symmetry. As can be seen from inspection of Figure 7.6, the calculated powder pattern shows very good agreement to the experimentally determined XRD data, and with the exception of the broad peak at \( ca. \) 21.8° 2\( \theta \) attributed to the presence of a very small amount of cristobalite in the sample, all of the reflection features are well described.

### 7.4 CONCLUSIONS

Accurate lattice parameters were determined from refinement of the powder X-ray diffraction data collected for calcined ZSM-5 at 293 K, and ZSM-5 loaded with 4 molecules of \( p \)-difluorobenzene/u.c. at 260 and 293 K. The cell parameters are summarized in Table 7.1. The calcined and low temperature DFB data sets were successfully refined in the space group \( P1.2_I/n.1 \), and the room temperature DFB data was satisfactorily refined in \( Pnma \). These XRD refinements complement the NMR investigations into the location and orientations of \( p \)-difluorobenzene molecules in the channels of ZSM-5 at a loading of approximately 4 molecules per unit cell described in Chapter 6. In addition to furnishing accurate cell parameters, fitting of the XRD data provided an independent verification of the framework symmetries proposed from the NMR experiments, and confirmed that the framework adopts two distinct symmetries within the temperature range studied.
Figure 7.6 Observed (baseline corrected) and calculated powder X-ray diffraction patterns for ZSM-5 loaded with 4 molecules/u.c. of p-difluorobenzene at 293 K. The acquisition time for the experimental pattern was 24 hours and the calculated pattern ($R_{wp} = 6.21\%$) was obtained using \textit{AJUST} assuming orthorhombic \textit{Pnma} symmetry with the parameters listed Table 7.1.
Above ca. 293 K, the framework has $Pnma$ symmetry, as has been found for three other low-loaded sorbate / ZSM-5 complexes. At temperatures below about 290 K, the framework symmetry for the low-loaded form of the $p$-difluorobenzene / ZSM-5 complex transforms to monoclinic (space group $P1_{2}1/n$) which is the same symmetry adopted by empty ZSM-5 below 340 K. Unambiguous proof that the $p$-difluorobenzene molecules remain inside the ZSM-5 framework following this phase transition is provided by the successful $^1$H-$^{29}$Si and $^{19}$F-$^{29}$Si cross polarization experiments described in Chapter 6. From these observations it was concluded that the sorbate / framework interactions in this system are somewhat weaker than those in the low-loaded $p$-xylene / ZSM-5 complex which maintains orthorhombic $Pnma$ symmetry to temperatures at least as low as 173 K.

It is predicted that sorbate / ZSM-5 complexes other than the low-loaded form of $p$-difluorobenzene in ZSM-5 studied here may undergo similar orthorhombic to monoclinic transformations at low temperatures. Knowledge of such transitions will be critical if the NMR techniques for locating guest species in the voids of microporous materials described in this thesis are to be successfully applied to other guest / host, sorbate / zeolite systems.

In general, detailed investigations of powder X-ray data and $^{29}$Si MAS NMR data such as those described in this section and in Chapter 6 are invaluable aids for determining the possible crystal system, lattice parameters, the symmetry (space group), and the number of crystallographically inequivalent T-sites. They can furnish information about the temperatures and/or loadings at which structural changes occur. If possible, these techniques should be utilized prior to beginning single crystal studies. Moreover, even in cases where the crystals are twinned or contain aggregates of twin domains, fitting of the powder X-ray diffraction data should still permit the correct unit cell parameters and possible space groups to be determined.

No attempts were made to locate the $p$-difluorobenzene molecules within the ZSM-5 framework from the powder XRD data. However, these investigations have established the space group symmetry; information that will be extremely useful for future single crystal XRD
experiments to determine the location(s) and orientation(s) of p-difluorobenzene molecules in ZSM-5. Several single crystal XRD data sets have been acquired on p-difluorobenzene / ZSM-5 samples prepared using the specially designed apparatus described in Chapter 2 (which permits single zeolite crystals to be loaded with precisely controlled amounts of volatile organic sorbates). Although at this point a complete structure refinement has not been possible using these data sets, (which is not surprising given the complexities of these kinds of systems), the structure of the low-loaded p-xylene / ZSM-5 complex has been determined from single crystal data and this is discussed in Chapter 8.

REFERENCES FOR CHAPTER 7


31 Diaz, A.C; Fyfe, C.A. Personal communication.
CHAPTER 8

STRUCTURE OF THE LOW-LOADED COMPLEX OF PARA-
XYLENE IN ZSM-5 FROM A SINGLE CRYSTAL X-RAY
DIFFRACTION STUDY

8.1 INTRODUCTION

Although it has not been possible to date to fully refine the single crystal XRD data for
the p-difluorobenzene / ZSM-5 complex described in the preceding chapters, the general
concept of using single crystal X-ray diffraction data to check the correctness of the NMR
derived structures has been checked for one other system where a structure had previously been
proposed from NMR experiments identical to those described in Chapter 6. This is the low-
loaded complex of p-xylene in ZSM-5, and the successful refinement of the single crystal XRD
data is described in detail in this chapter.

As discussed in Chapters 1 and 6, there have been several investigations into the changes
which occur in the framework lattice due to the presence of guest species such as sorbed organic
molecules. However, only in a very limited number of cases has the location of the sorbed
organic molecules been reliably determined (e.g. by refinement of single crystal X-ray diffraction
data).\textsuperscript{2,7} Sorption sites have been proposed from theoretical calculations, but these are not always
in agreement with one another, or the X-ray determined structures where these are known.\textsuperscript{4,8,11} In
general, the successful refinement of single crystal X-ray diffraction data from ZSM-5 single
crystals is \textit{not} trivial; there are difficulties in synthesizing single zeolite crystals of adequate size
and quality for single crystal XRD work (twinning is often a problem). At the time the current investigation was undertaken, only six single crystal X-ray diffraction studies of ZSM-5 containing organic sorbates had been reported in the literature.

While X-ray Diffraction (XRD) studies of microcrystalline (powder) samples and single crystals of ZSM-5 have yielded much of the structural information, $^{2,7,12-16}$ $^{29}$Si MAS NMR has also provided critical information. $^{16-22}$ For the ZSM-5 / sorbate systems where changes are seen, the nature of the lattice distortions seems to be relatively characteristic of the nature of the sorbed molecule. $^{19-22}$ In some cases however, very similar $^{29}$Si MAS NMR spectra are obtained with different molecules, indicating that the lattice geometries are closely related. It may be that the locations of the molecules in these cases is very similar, but this has only been verified for two systems to date. $^{2,3}$

The increasing reliance on theoretical calculations to determine the locations of sorbates in these zeolite structures must be tempered by the relatively few accurate structures which have been determined by experiment. Moreover, the calculations rely on molecular forcefields and potential functions “borrowed” from other (often purely organic) systems. $^{25}$ Clearly there is a need to expand the database of dependable structures as a check on the accuracy of the proposed structures and also to improve the reliability of the calculations methods.

This chapter presents the results of the structure refinement for $p$-xylene molecules in the framework of ZSM-5 at a loading of less than four molecules per unit cell using X-ray diffraction data collected from a single crystal at 180 K. Prior to the structure determination reported here, the location and orientations of $p$-xylene molecules in the low-loaded form of ZSM-5 had been proposed from a ‘fit’ of X-ray powder diffraction data, $^{22}$ and also by energy minimization calculations. $^{8,23,26}$ Solid-state NMR experiments including $^1$H-$^{29}$Si CP MAS and $^{13}$C-$^{29}$Si REDOR had recently been completed in this research group to determine the location of the $p$-xylene in ZSM-5 for the low-loaded form by solid state NMR. $^{27}$ The location and orientation found in the present work for $p$-xylene in ZSM-5 by single crystal X-ray diffraction is compared to those
proposed from the previous investigations and those of other sorbate / ZSM-5 complexes determined from single crystal XRD studies reported in the literature.

8.1.1 Single Crystal X-ray Diffraction Studies of ZSM-5 Systems

Following the initial determination of the ZSM-5 framework structure from powder diffraction data by Kokotailo et al.,\(^{12,28}\) several refinements using single crystal X-ray diffraction data on as-synthesized samples were undertaken. Of these, the most accurate structure to date is that by van Koningsveld et al. who were able to locate the templating TPA\(^+\) ion.\(^2\) (the other structure determinations of the as-synthesized materials are discussed in reference 1). The space groups, numbers of crystallographically inequivalent T-sites, as well as the number and general location of guest species present (if any) found from single crystal XRD refinements on ZSM-5 systems are summarized in Table 6.1.

ZSM-5 has been found to adopt four space groups: three with orthorhombic symmetry: \(Pnma\) (12 T-sites), \(P2_12_12_1\) (24 T-sites), and \(Pn2_1a\) (24 T-sites); and one having monoclinic \(P2_1/n\) symmetry with 24 T-sites. Four different sorbed molecules in ZSM-5 have been studied by single crystal diffraction studies to date: \(p\)-xylene,\(^2\) \(p\)-dichlorobenzene,\(^3,4\) \(p\)-nitroaniline,\(^5,6\) and naphthalene.\(^7\) The latter three compounds are all solids at room temperature, allowing the low-loaded (\(\leq 4\) molecules/u.c.) forms to be relatively easily obtained. However in the case of \(p\)-xylene, which is a volatile liquid, only the high-loaded (saturated) complex containing 8 molecules/u.c. had been previously studied by single crystal X-ray diffraction, presumably due to difficulties in controlling the amount of volatile sorbate loaded into a single crystal.

With the exception of the high-loaded \(p\)-xylene / ZSM-5 complex, all of the single crystal X-ray diffraction studies reported for sorbates in ZSM-5 used crystals which were selected from a batch of crystals sufficiently large that controlled amounts of (solid) sorbates could be added by weight. In the case of the high-loaded \(p\)-xylene a single crystal was simply
exposed to excess vapor to obtain a saturated loading. It is assumed that for these studies the
crystals were not loaded in capillaries since this was not discussed in the literature.

Using the specially designed apparatus described in Chapter 2, precise loading of volatile
organic molecules into single crystals of ZSM-5 is now possible. This represents a major advance
in this field and use of this purpose-built equipment will permit the single crystal XRD
investigations of many other previously unobtainable zeolite host-guest systems by X-ray
diffraction, provided single crystals of adequate dimensions and quality are available.

The current availability of image plate and CCD area detectors has dramatically reduced
the minimum crystal size required (from ca. 100 \( \mu m \) to about 20 \( \mu m \)), thus increasing the number
of zeolites for which single crystal studies should be possible. Furthermore, the improved
collection efficiency of these area detectors means that data collection times are reduced from
more than a week to less than 24 hours and low temperature studies are thus quite feasible. In
general, collection of diffraction data at low temperatures results in smaller thermal errors,
reduces the dynamic disorder, and allows more accurate bond distances and angles to be
obtained.

Detailed investigations of powder X-ray data and \(^{29}\)Si MAS NMR data are invaluable
aids to determining the possible crystal system and lattice parameters, the symmetry (space
group), and the number of crystallographically inequivalent T-sites. In addition they can often be
used to determine the temperatures and/or loadings at which structural changes are induced. If
possible, these techniques should be utilized prior to beginning single crystal studies.

8.1.2 Correlations Between \(^{29}\)Si NMR Chemical Shifts and Structural Parameters

As discussed in Chapter 6, the \(^{29}\)Si NMR chemical shift is a very sensitive probe of the
local structure and geometry around the Si nuclei in the T-sites, and this information has been
utilized as aid in selecting the correct space group for structure determination in cases where this
is ambiguous.\(^{17,18}\) In attempts to interpret and assign the \(^{29}\)Si resonances to specific T-sites within
the framework lattice, various correlations based on the structural geometrical parameters of the T-sites have been presented.\textsuperscript{22,29,36} The geometrical parameters from XRD data used for interpreting the \textsuperscript{29}Si MAS NMR spectra of highly siliceous zeolites are: (i) the mean Si–O–Si angle $\alpha_{av}$ and various functions based on this including $\cos \alpha_{av} / \cos(\alpha_{av} - 1)$,\textsuperscript{29,35,36} (ii) the mean Si–Si distance,\textsuperscript{29,30,32} and (iii) The mean Si–O bond length.\textsuperscript{30} The latter is not very sensitive since the Si–O distances show little variation in siliceous zeolites. The most accepted parameters are $\cos \alpha_{av} / \cos(\alpha_{av} - 1)$ and the mean Si–Si distance which has a dependence on both the bond angles and lengths.\textsuperscript{29}

Two problems restrict the quality of the linear correlations obtained in this manner. Firstly the quality of the positional data must be accurate (e.s.d.’s better than 0.004Å and 0.02° if possible). Secondly reliable assignments of the \textsuperscript{29}Si NMR resonances to specific T-sites, with well resolved NMR spectra to provide accurate chemical shifts. The first condition can be realized from refinements of high quality single crystal XRD data, and the second criteria may be met through 2-D NMR correlation experiments such as COSY and INADEQUATE.\textsuperscript{37} To date the main limitation preventing these correlations from being completely quantitative arises from uncertainties in the XRD derived structural parameters, rather than the precision of the \textsuperscript{29}Si chemical shifts.\textsuperscript{29} However, in at least one case,\textsuperscript{38} reliance on these correlations produced incorrect assignments of the \textsuperscript{29}Si NMR resonances. Consequently the published correlations should only be used to draw qualitative conclusions and not as a definitive method for assigning the NMR spectra.

\section*{8.1.3 Previous Investigations of the Low-Loaded $p$-xylene / ZSM-5 Complex}

Fyfe \textit{et al.} first reported changes in the powder XRD patterns and \textsuperscript{29}Si MAS NMR spectra of ZSM-5 with sorbed $p$-xylene, and correctly deduced they where the result of framework lattice distortions.\textsuperscript{16,39} It was also found that the powder XRD pattern of $p$-xylene
sorbed in ZSM-5 at loadings greater than two but less than four molecules/u.c. were indicative of a change to orthorhombic symmetry.\textsuperscript{16,21}

The \textsuperscript{29}Si MAS NMR spectrum of the low-loaded \textit{p}-xylene / ZSM-5 complex can be resolved in terms of twelve resonances of equal intensity in agreement with the proposed \textit{Pnma} space group at temperatures from 173 K to 393 K.\textsuperscript{30-32} \textsuperscript{29}Si 2-D COSY and INADEQUATE experiments at room temperature were used to assign the individual \textsuperscript{29}Si NMR resonances and the connectivities found were consistent with orthorhombic space group \textit{Pnma} symmetry.\textsuperscript{37} Figure 8.1 shows \textsuperscript{1}H-\textsuperscript{29}Si CP MAS spectra for the low-loaded \textit{p}-xylene / ZSM-5 complex acquired at 173 and 193 K with the assignments indicated. Fyfe and co-workers also reported phase diagrams for highly siliceous ZSM-5 containing various amounts of sorbed \textit{p}-xylene at temperatures ranging from 293 to 393 K determined from \textsuperscript{29}Si MAS NMR experiments.\textsuperscript{19,40}

Mentzen and Vigné-Maeder proposed locations for \textit{p}-xylene from powder X-ray diffraction data in an MFI-type zeolite containing some boron at low loadings.\textsuperscript{24} Using the framework coordinates of \textit{TPA}\textsuperscript{+} ZSM-5 reported by Baerlocher\textsuperscript{41} and space group \textit{Pnma}, powder XRD patterns were simulated and compared these to the experimentally determined patterns. The best agreement was found when the centroid of the \textit{p}-xylene ring was positioned on the mirror plane with the methyl groups lying along the straight channels. Several orientations of the \textit{p}-xylenes were considered and they concluded that the organic molecules might be statistically disordered with two simultaneous orientations in the channels.\textsuperscript{24}

Reischman \textit{et al.} proposed equilibrium absorption sites for \textit{p}-xylene in the channels of ZSM-5 based on calculated van der Waals interactions between the hydrocarbon and the zeolite and between the hydrocarbon molecules themselves.\textsuperscript{8} Their calculations used the \textit{Pnma} framework coordinates of Olson \textit{et al.}\textsuperscript{28} and indicated that the most energetically favourable sorption sites for loadings up to 4 molecules/u.c. were the channel intersections with the methyl-methyl axes along the straight channel. This configuration had a calculated energy of -82 kJ/mol,
Figure 8.1 $^1$H-$^{29}$Si CP MAS NMR spectra of the \( p \)-xylene / ZSM-5 complex at a loading of 3 molecules / u.c. recorded at (a) 173 K and (b) 193 K. 32 scans were acquired using a 30 ms contact time and a recycle delay of 3 s. The assignment of the resonances to specific T-sites is indicated where they could unambiguously determined from a 2-D INADEQUATE experiment at 268 K.\(^{27}\)
which was significantly more favorable than those calculated for several other configurations including molecules in the sinusoidal channels or molecules in both channels (> -50 kJ/mol). They noted that when \( p \)-xylene occupies only the channel intersections, the van der Waals interactions between adjacent molecules are small, and the major contribution comes from framework-oxygen / \( p \)-xylene-hydrogen interactions.

Several other groups have reported theoretical calculations to determine the sorption site of \( p \)-xylene in the MFI framework, usually using silicalite.\(^{21,26}\) In all these calculations the framework has been rigid, and the sorbate is also usually defined as a semi-rigid group.\(^{9,22}\) In some cases a wrong framework symmetry was used and the sorbate-induced framework changes can be quite substantial.\(^{2,7}\) The locations determined are dependent on the potential functions and calculation technique used, and there is not always complete agreement between the various calculations.\(^{9}\)

More recently Diaz and Fyfe have investigated the location of \( p \)-xylene in ZSM-5 with several solid-state NMR techniques at low temperatures (down to 173 K) utilizing different isotopically labeled \( p \)-xylene.\(^{27}\) When three molecules/u.c. \( p \)-xylene having a single \(^{13}\)C-labeled methyl group were sorbed in ZSM-5, only a single \(^{13}\)C resonance was observed for the methyl groups.\(^{27}\) Through the use of selectively deuterated \( p \)-xylene the location of the sorbate molecules at a loading of 3 molecules/u.c. was determined from fitting of \(^1\)H-\(^{29}\)Si CP MAS data for \( p \)-xylene (deuterated at the ring or methyl groups) and correlations between \( T_{CP} \) and the calculated \(^{29}\)Si heteronuclear second moments (see Chapter 6).

In these calculations, a rigid framework and \( p \)-xylene molecule were assumed, using the framework coordinates reported for the single crystal XRD determination of the low-loaded form of \( p \)-dichlorobenzene, and an ideal geometry for the sorbate molecule.\(^{4}\) From analysis of the CP behavior it was deduced that the molecule was located near the channel intersections. Starting from a position near the channel center, the \( p \)-xylene location was moved around in the straight channel using small steps and a range of orientations. For each orientation and position the
heteronuclear $^{29}\text{Si}-^1\text{H}$ second moments $M_2$ were calculated (cut-off distance of 8 Å) and a plot of the reciprocal of experimentally determined $T_{CP}$ values vs. $M_2$ made. Three almost identical solutions yielded very similar, highly linear correlations, and the $^1\text{H}-^{29}\text{Si}$ CP MAS NMR spectra simulated (using $T_{CP}$ to determine the peak intensities) showed very similar agreements with the experimentally observed spectrum. The "best" solution was chosen from these and had the molecular centre exactly coincident with the mirror plane and the methyl-methyl axes parallel to [010] in accord with the observation of a single $^{13}\text{C}$ resonance. In the other solutions, the ring centre was displaced by less than 0.3 Å from the mirror plane and the molecules showed small angular deviations from the $b$ and $c$ axes.

8.2 MATERIALS AND METHODS

8.2.1 Crystal Preparation and Sorbate Loading

Large single crystals of ZSM-5 were grown by Dr. W. Schwieger using hydrothermal synthesis (3-5 days at 175 °C) with tetraproplyammonium chloride. The molar composition of the reaction mixture was $\text{SiO}_2$ (12.2) NaAlO$_2$ (0.04), NaOH (44.9), TPABr (43.1), H$_2$O (200). Due to the small quantity of material obtained, bulk elemental analysis was not done. The crystals were thoroughly washed with distilled water then calcined in air at 500 °C to remove the template. An optical microscope was used to select large crystals (dimensions > 0.15 mm) having no visible defects or twinning. These were loaded into 0.3 mm diameter quartz X-ray capillaries (wall thickness 0.01 mm, graded quartz-Pyrex transition piece attached), and connected to a purpose-built apparatus constructed of Pyrex glass (see Figure 2.2). Details of the method used to load the crystal with $p$-xylene are given in Section 2.3.2.

The capillaries were isolated and the loading of the ZSM-5 powder was verified by thermal gravimetric analysis (TGA) and $^{29}\text{Si}$ MAS NMR. TGA (temperature ramp 10 °C / min. to 600 °C under flowing nitrogen gas) indicated a weight loss equal to 3.4 (0.3) molecules/u.c. As a more sensitive check that the low-loading (< 4 molecules/u.c.) had been achieved, $^{29}\text{Si}$ MAS
NMR spectra of the ZSM-5 powder were acquired. These were in agreement with those reported in the literature for sorbate loadings greater than two but less than four molecules $p$-xylene per u.c.\textsuperscript{19,20} Individual capillaries containing the single crystals were isolated, immersed in liquid nitrogen, and sealed. They were stored at room temperature to allow an equilibrium loading to re-establish before the X-ray diffraction data were collected.

### 8.2.2 Data Collection and Refinement of Reflection Data

#### 8.2.2.1 Data Collection

The crystal selected for study had dimensions of $0.2 \times 0.2 \times 0.15$ mm. Data were collected by Dr. S. Rettig at a temperature of 180 K on a Rigaku ACF7 diffractometer equipped with an Area Detector System Corporation charge-coupled device (CCD) detector (size $98 \times 98$ mm) using graphite monochromated Mo $K\alpha$ radiation. 768 CCD images were stored (recording time 96 s/image) in $\omega$ and $\phi$ scan modes with 0.3 degree steps between images up to $\theta_{\text{max}} = 30.05^\circ$. A total time of 21 hours was required for the data collection during which the crystal was cooled by a flow of cold nitrogen gas. Table 8.1 summarizes other data collection parameters.

#### 8.2.2.2 Definitions of $R$-indices Used

As described in the SHELXL-97 literature,\textsuperscript{42} a variety of parameters are available which can be used to monitor the success of a refinement. The diffraction experiment measures intensities and their standard deviations, which after the various corrections give $F_o^2$ and $\sigma(F_o^2)$. Refinement against all $F^2$-values is demonstrably superior to refinement against $F$-values greater than some threshold [say $4\sigma(F)$], because more experimental information is incorporated (suitably weighted) and the chance of getting stuck in a local minimum is reduced.

The progress and quality of the refinement was monitored using $wR_2$, the weighted $R$-factor based on $F^2$.\textsuperscript{42}
Table 8.1 Crystal data and structure refinement for the low-loaded p-xylene / ZSM-5 complex at 180 K.

**CRYSTAL DATA**

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C_{22.8} H_{38.6} Si_{96} O_{192}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula weight</td>
<td>1517.66</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a=19.989(4) \text{ Å}, \ b=19.899(4) \text{ Å}, \ c=13.362(3) \text{ Å} )</td>
</tr>
<tr>
<td>Cell volume</td>
<td>5315(2) \text{ Å}^3</td>
</tr>
<tr>
<td>Reflections used to determine cell parameters Z</td>
<td>1</td>
</tr>
<tr>
<td>Calculated Density</td>
<td>1.935 g/cm(^3)</td>
</tr>
<tr>
<td>Absorption Coefficient</td>
<td>(\mu = 0.685 \text{ mm}^{-1})</td>
</tr>
<tr>
<td>Crystal form</td>
<td>Block</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.20 x 0.15 mm</td>
</tr>
<tr>
<td>Crystal colour</td>
<td>Colourless (clear)</td>
</tr>
<tr>
<td>Crystal mounting</td>
<td>Sealed quartz capillary (0.3 mm diameter)</td>
</tr>
</tbody>
</table>

**DATA COLLECTION**

<table>
<thead>
<tr>
<th>Diffractometer</th>
<th>Rigaku ACF7 with ADSC CCD detector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data Collection Temperature</td>
<td>180(2) K</td>
</tr>
<tr>
<td>Radiation Type</td>
<td>Mo K(\alpha) (graphite monochromated)</td>
</tr>
<tr>
<td>Wavelength</td>
<td>(\lambda = 0.71073 \text{ Å})</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>(2.10 \leq \theta \leq 30.05^\circ)</td>
</tr>
<tr>
<td>Miller index ranges</td>
<td>(-28 \rightarrow h \rightarrow 24, -25 \rightarrow k \rightarrow 23, -15 \rightarrow l \rightarrow 18)</td>
</tr>
<tr>
<td>Number of measured reflections</td>
<td>47400</td>
</tr>
<tr>
<td>Number of observed reflections ([ I &gt; \sigma(I) ] )</td>
<td>45435</td>
</tr>
<tr>
<td>Unique reflections (after averaging)</td>
<td>7420</td>
</tr>
<tr>
<td>(R) index for symmetry equivalent reflections</td>
<td>(R_{\text{int}} = 0.0398)</td>
</tr>
<tr>
<td>(R) index from counting statistics</td>
<td>(R_{\sigma} = 0.0464)</td>
</tr>
<tr>
<td>Completeness to (\theta = 30.05)</td>
<td>93.0%</td>
</tr>
<tr>
<td>Maximum and minimum transmission</td>
<td>0.9043 and 0.8752</td>
</tr>
<tr>
<td>Number of CCD images collected</td>
<td>768</td>
</tr>
<tr>
<td>Exposure time per CCD image</td>
<td>96 seconds</td>
</tr>
<tr>
<td>Scan mode</td>
<td>(\omega ) and (\phi) oscillation, (\chi = -90^\circ)</td>
</tr>
<tr>
<td>Scan range</td>
<td>(-23^\circ \leq \omega \leq 17.8^\circ, 0^\circ \leq \phi \leq 190.2^\circ)</td>
</tr>
<tr>
<td>Background measurements</td>
<td>Determined during image integration</td>
</tr>
</tbody>
</table>

266
Table 8.1 (continued) Crystal data and structure refinement for the low-loaded \( p \)-xylene / ZSM-5 complex at 180 K.

**REFINEMENT**

<table>
<thead>
<tr>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on ( F^2 )</td>
</tr>
<tr>
<td>Final ( R ) indices ([ I &gt; 2\sigma(I) ] )</td>
<td>( R_1(F) = 0.0437, \ wR_2(F^2) = 0.1148 )</td>
</tr>
<tr>
<td>( R ) indices (all data)</td>
<td>( R_1(F) = 0.0711, \ wR_2(F^2) = 0.1238 )</td>
</tr>
<tr>
<td>Goodness-of-fit (all data)</td>
<td>( S(F^2) = 1.1080 )</td>
</tr>
<tr>
<td>Number of reflections used</td>
<td>7420</td>
</tr>
<tr>
<td>Number of restraints</td>
<td>6 (to fix hydrogen positions)</td>
</tr>
<tr>
<td>Number of least squares parameters</td>
<td>374</td>
</tr>
<tr>
<td>H-atom treatment</td>
<td>Fixed ( U ) at calculated positions</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>( w=1/ [ \sigma^2(F_o^2) + (0.0743 P)^2 + 0.3534 P] )</td>
</tr>
<tr>
<td>where ( P = (F_o^2 + 2F_c^2) / 3 )</td>
<td></td>
</tr>
<tr>
<td>Largest and mean least squares shift</td>
<td>0.002 ( \Delta / \sigma ), 0.000 ( \Delta / \sigma )</td>
</tr>
<tr>
<td>Largest ( \epsilon ) Density Peak and Hole</td>
<td>( \Delta \rho_{\text{max}} = 1.038 \text{ e/Å}^3, \ \Delta \rho_{\text{min}} = -0.641 \text{ e/Å}^3 )</td>
</tr>
<tr>
<td>Absorption correction method</td>
<td>Semi-empirical using equivalent reflections</td>
</tr>
<tr>
<td>Structure refinement program</td>
<td>SHELXL-97 (Sheldrick, 1997)</td>
</tr>
</tbody>
</table>
\[ wR_2 = \left\{ \Sigma \left[ w(F_o^2 - F_e^2)^2 \right] / \Sigma \left[ w(F_o^2) \right] \right\}^{1/2} \]

Here \( F_e \) is the calculated intensity and \( w \) is the weighting scheme used:

\[ w = 1 / \left[ \sigma^2(F_o^2) + (aP)^2 + bP \right] \]

where

\[ P = \left[ 2F_e^2 + \text{Max}(F_o^2,0) \right] / 3 \]

The use of this combination of \( F_o^2 \) and \( F_e^2 \) was shown by Wilson\(^{13}\) to reduce statistical bias. For comparison with older refinements based on \( F \), a conventional index \( R_1 \) (Eq. 8.4) based on observed \( F \) values larger than \( 4\sigma(F_o) \) was also calculated.

\[ R_1 = \Sigma |F_o - |F_e| | / \Sigma |F_o| \]

In general, the smaller the values of these \( R \)-factors, the better the agreement between the model and the diffraction data. Another parameter which describes the quality of the final structure is the Goodness of Fit, \( S \), and this is also based on \( F^2 \):

\[ S = \left\{ \Sigma \left[ w(F_o^2 - F_e^2)^2 \right] / (n-p) \right\}^{1/2} \]

Here \( n \) is the number of reflections and \( p \) is the total number of parameters refined. \( S \) should be close to unity when the weights of the observations have been correctly assessed, the errors in the model are negligible in comparison with the errors in the data, and there are no significant systematic errors.\(^{14}\)

Two parameters which describe the quality of the reflection data are \( R_{\text{int}} \) (Eq. 8.6) and \( R_{\text{sigma}} \) (Eq. 8.7).

\[ R_{\text{int}} = \Sigma \left| F_o^2 - F_o^2 \text{(mean)} \right| / \Sigma \left[ F_o^2 \right] \]

\[ R_{\text{sigma}} = \Sigma \left[ \sigma(F_o^2) \right] / \Sigma \left[ F_o^2 \right] \]
In Eq. 8.6 both summations involve all input reflections for which more than one symmetry equivalent is averaged, and the summation in Eq. 8.7 is over all reflections in the merged list.

8.2.2.3 Processing and Refinement of the Reflection Data

Intensities of the reflections were determined by three-dimensional integration of the CCD images. Initially a dynamic profile-fitting function was used to perform the peak integration, however this yielded non-positive definite thermal parameters for the framework atoms during the early stages of the refinement. Subsequently a constant volume integration technique which used fixed volumes for the individual peaks was employed and this gave well-behaved intensity data. Background intensities were measured from the images in the vicinity of the individual peaks and subtracted during the integration procedure. The final intensities were corrected for absorption using a semi-empirical method based on an analysis of equivalent reflections. Lorentz and polarization corrections were also applied. Cell parameters were determined from a least squares fitting of 35854 reflections and are given in Table 8.1.

The final data file contained the Miller indices (indexing done by D*TREK software\textsuperscript{45}), the $F^2$ and $\sigma(F^2)$ values for 47400 reflections (45435 with $I > 1\sigma$). This data set was pre-processed using the \textit{teXsan for Windows} software\textsuperscript{46} and showed systematic extinctions indicating the crystal was orthorhombic with possible space groups \textit{Pnma} (No. 62) or \textit{Pn2}_1\textit{a} (No. 33).\textsuperscript{47} \textit{Pnma} symmetry was confirmed by successful refinement (see below). Before refinement commenced, the data were exported in the format required for the refinement program \textit{SHELXL-97}.\textsuperscript{42}

\textit{SHELXL-97} was run on an IBM-compatible PC with a Pentium 200 processor under the Windows NT operating system. Starting coordinates of framework atoms were taken from those reported in the literature for TPAORT.\textsuperscript{2} All framework atoms were treated as zero valent Si or O with anisotropic temperature factors. The atomic scattering factors used were taken from the International Tables,\textsuperscript{27} and any systematically absent reflections were automatically rejected by
the refinement program. After the equivalent reflections were merged and their indices converted to standard symmetry equivalents, a set of 7420 unique (averaged) reflections was obtained.

Using these data, anisotropic, full matrix least squares refinement on $F^2$ of the framework atoms only (with site occupancies fixed to 1.0) converged to $R_1 = 6.64\%$ ($wR_2 = 23.03\%$, $w = 1 / \sigma(F^2)$). The Fourier difference map calculated at this stage revealed several peaks with significant electron density. The four highest were assigned to C atoms of $p$-xylene (the other four C's are related by mirror plane at $y = 0.25$).

As check for reduced symmetry and/or disorder, attempts were made to refine the whole system (i.e. framework and sorbate) in $Pn2_1a$. To achieve this a complete set of the mirror related 12 Si and 26 O atoms was generated (using $x, y, z \rightarrow x, 0.5-y, z$) and several cycles of refinement in $Pnma$ carried out using these atoms to reorient the thermal ellipsoids. The two sets were combined and refinement proceeded in $Pn2_1a$. However during this refinement the thermal factors for several framework atoms went non-positive definite or the $R$ factors became unstable even when constraints were applied to keep the formerly mirror-related framework atoms equivalent.

To test for the presence of disorder in the $p$-xylenes, several different models were used including two rigid $p$-xylene molecules with separate occupancies. In this case one set moved onto the mirror plane while the other carbons became non-positive definite or the C–C bond lengths and the geometry of the molecule became unreasonable. A similar disordered model was tried in $Pnma$ but was also badly behaved. Consequently the refinement was continued in $Pnma$ with four C atoms having a common (refined) occupancy, the ring centre coincident with the mirror plane at $y = 0.25$ and individual anisotropic thermal parameters for all atoms (Si, O, C). During the final cycles, six constraints were used to fix the five unique hydrogen atoms of the $p$-xylene (isotropic with occupancy equal to that of the carbons) at calculated positions (C–H = 0.98 Å, C–C–H = 120°).
Using this model, the refinement converged to $R_1 = 4.37\%$ ($wR_2 = 11.48\%$, weighting scheme given in Table 8.1) and a goodness-of-fit parameter $S = 1.108$ for 7420 reflections and 374 parameters. The average and maximum shift/e.s.d. values in the last refinement cycle were 0.002 and 0.000 respectively. The final difference synthesis showed small amounts of residual electron density with the highest peak (1.038 e/Å³) located in the centre of the zig-zag channel. A possible explanation for this is residual debris not completely removed during the calcination. A small peak was also detected near the $p$-xylene molecule, but all other peaks were in close vicinity of the framework atoms and attributed to "rest density" of these atoms. The occupancy of the carbon atoms refined to 0.714(7) which corresponds to 2.85(3) $p$-xylene molecules/unit cell, in close accord with the loading determined from TGA analysis of the powder sample.

Heating during the sealing of the capillary may have resulted in a slight loss of sorbate, and it is also possible that the cooling of the crystal and capillary during the data collection may have had a small effect on the precise sorbate loading.

Final atomic fractional coordinates and equivalent isotropic thermal displacement factors for the framework and sorbate atoms (excluding hydrogens) determined from the refinement are listed in Table 8.2. The individual anisotropic thermal parameters are listed in Appendix G.

Figures were generated using ORTEP-3 for Windows® and some geometrical analysis (e.g. of the coordination spheres) was done with the PLATON-98 software.

8.3 RESULTS AND DISCUSSION

This structure represents a major advance since it is the first reported single crystal structure determination where a volatile organic sorbate was loaded to less than 4 molecules/u.c. in a single crystal; with the exception of the high-loaded $p$-xylene / ZSM-5 complex, the single crystal XRD structure determinations of the other sorbate / ZSM-5 systems reported previously contained sorbates which were solids at room temperature. The crystal investigated was of comparable size to those used by other groups in previous ZSM-5 single crystal XRD structure
Table 8.2  Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\AA^2 \times 10^3$) for the low-loaded $p$-xylene / ZSM-5 complex at 180 K. $U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

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<th>$U_{eq}$</th>
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Cell parameters are very accurately determined since they were found from fitting of more than 35000 reflections compared to the usual 25 on conventional single crystal XRD systems.

Data collection at low temperature (180 K for >20 hours) was made possible through the use of a CCD detector. This allowed the simultaneous collection of Bragg reflections from a wide angular region, and thus greatly reduced the collection time needed (in this case from more than 7 days to less than 24 hours). An associated benefit of the CCD detector is the significant reduction in the size of crystal required, which is especially important for the type of system investigated here.

Although, in general, the intensities measured for individual reflections are less accurately determined using a CCD detector compared to a conventional counter in a given time, many reflections are collected several times which allows for averaging, and thus the overall statistics are often significantly improved. Another advantage is that all of the data for a complete hemisphere (representing a complete set of reflections) is collected and stored; thus if the wrong space group or cell is inadvertently chosen, the data can simply be re-indexed rather than having to collect the 'missed' reflections.

The \( p \)-xylene molecules were located in the straight channels at the intersection with the zig-zag channels, in agreement with other single crystal structure determinations reported for host-guest ZSM-5 / sorbate systems. The labeling of the framework atoms is indicated in Figures 8.2 and 8.3. The orientation of the \( p \)-xylene molecule in the straight channel is shown in Figure 8.3, where the presence of the mirror plane through O23, O34, O25 and O26 can be easily seen.

Van Koningsveld and co-workers found \( Pnma \) symmetry for two other single crystal XRD structures of low-loaded / ZSM-5 complexes containing naphthalene\(^7\) or \( p \)-dicholorobenzene\(^7\) but needed to invoke a model having disordered molecules at two orientations (related by the mirror plane imposed by the \( Pnma \) symmetry). This disorder may actually be the result of a lower symmetry which is not resolved due to limitations in the data. When a non-
Figure 8.2  Numbering scheme of the Si and O atoms in the asymmetric unit of the ZSM-5 framework in \textit{Pnma} viewed approximately along (a) [100] and (b) [010].
Figure 8.3 ORTEP drawings of p-xylene in ZSM-5 with numbering scheme used for Si and O atoms. (a) View along [010] showing the orientation of the p-xylene molecules at the intersection of the straight and zig-zag channels. (b) View down [100].
centrosymmetric molecule (p-nitroaniline) was sorbed in ZSM-5 two space groups were found: \( Pn2_1a \) and \( Pnma \). In the former case the framework configuration was virtually identical to that determined previously for the unloaded high temperature (\( Pnma \)) phase of ZSM-5, and a large number of constraints were needed to suppress the effects of strong correlations between the \( (Pnma) \) “mirror-related” framework atoms. Although disorder might model this effectively, it is more chemically reasonable that the overall symmetry is reduced, at least in the case of non-centrosymmetric molecules (e.g. p-nitroaniline and p-chlorotoluene).

This apparent contradiction can be understood if the contributions to the scattering by the sorbate and framework atoms are considered. The scattering by the carbon atoms in a sorbate will be much less than that due to the framework atoms, and may not be large enough to “violate” the \( Pnma \) symmetry. These space groups exhibit the same systematic extinctions and the presence or absence of the mirror plane perpendicular to \( b \) cannot be deduced from analysis of the reflection extinctions alone. Moreover, \( Pn2_1a \) is a subgroup of \( Pnma \) and can be obtained by eliminating the inversion centre which has the effect of removing the mirror plane at \( y = 0.25 \).

8.3.1 Geometry of the Framework

In Table 8.3 the framework geometry (ranges and averages for bond lengths and angles) determined for low-loaded \( p \)-xylene / ZSM-5 in the present work is compared to those reported for previous ZSM-5 structures. Full details of the Si–O bond lengths, as well as O–Si–O, Si–O–Si bond angles for the individual T-sites are given in Appendix G. The present structure represents the most accurate determination of the ZSM-5 framework to date; the thermal displacement parameters for the Si and O atoms in the ZSM-5 framework, as well as the observed variation in the Si-O bond lengths, are considerably smaller than any previously reported for ZSM-5. For example the range of Si–O bond lengths in low-loaded \( p \)-xylene form of ZSM-5 is 0.016 Å compared with \textit{ca.} 0.03 Å or greater for other structures, and the range of the averages for the individual Si–O–Si bond angles is narrower by more than two degrees (Table
8.3). The estimated standard deviations of the bond lengths and bond angles are small, being less than 0.002 Å and 0.1° respectively (see Appendix G).

The more accurate determination stems primarily from the low temperature (180 K) at which the data was acquired and large number of reflections collected (93% completeness), resulting in reduced thermal errors and a high observation / parameter ratio (≈ 20) respectively. The average Si–O bond length is slightly longer (by ca. 0.005 Å) than that seen for the low-loaded sorbate / ZSM-5 complexes, and significantly longer (0.015 Å) than those reported for the high-loaded complexes. Another striking difference is that the minimum Si–O bond length is somewhat longer than that observed in other ZSM-5 systems, although the maximum is very similar to those in other structures. The average Si-O-Si angle is also at least 2° lower than in other ZSM-5 structures. These may be a result of the lower temperature at which the diffraction data was collected (all of the other structures were determined at or above room temperature) as the lattice is quite flexible and can change to accommodate thermal stresses caused by cooling or heating.

The pore sizes mainly determine the molecular sieving and diffusion properties of zeolites, and while they are often referred to in terms of the number of T-atoms in the rings outlining the openings, it is really the oxygens which define the effective or “free” pore size owing to their larger van der Waals radii. One way to describe the dimensions of the channels is through use of the diagonal O⋯O distances across the rings. The free pore dimensions accessible to guests can easily be calculated from these by subtracting twice the van der Waals radii of oxygen (1.35 Å). In Table 8.4 the minimum and maximum diagonal O⋯O distances across the 10-rings defining the channels in ZSM-5 are listed for the low-loaded p-xylene / ZSM-5 complex and those reported for the other ZSM-5 single crystal determinations. In framework structures with \textit{Pnma} symmetry, the two 10-rings defining the straight channel are related by a mirror plane, and those describing the zig-zag channel share an inversion center. In the monoclinic space group \textit{Pn2}_1 and the orthorhombic \textit{P2}_1\textit{2}_1\textit{2}_1 symmetry observed for the high-loaded ZSM-5
Table 8.3 Comparison of the framework geometry in several ZSM-5 structures as determined by single crystal X-ray diffraction.

<table>
<thead>
<tr>
<th>Structure(a)</th>
<th>Ref.</th>
<th>Temp (K)</th>
<th>Si-O Bond Lengths (Å)</th>
<th>O-Si-O Bond Angles (°)</th>
<th>Si-O-Si Bond Angles (°)</th>
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<td></td>
<td></td>
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<td>Range</td>
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<td>Average</td>
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<td>1.595</td>
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(a) See Table 6.1 for description of codes. (b) Range of the averages calculated for each crystallographically inequivalent Si atom.
Table 8.4 Minimum and maximum diagonal O••O distances (Å) across the 10-rings in several ZSM-5 structures. Free pore dimensions may be calculated from these by subtracting twice the oxygen van der Waals radius (i.e. $2 \times 1.35$ Å).

<table>
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<tr>
<th>Structure&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>MONO</th>
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<th>TPAORT&lt;sup&gt;(b)&lt;/sup&gt;</th>
<th>HLPXY</th>
<th>HLPDCB</th>
<th>LLPDCB&lt;sup&gt;(b)&lt;/sup&gt;</th>
<th>LLPNA&lt;sup&gt;(b)&lt;/sup&gt;</th>
<th>LLPXY&lt;sup&gt;(b)&lt;/sup&gt;</th>
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<sup>(a)</sup> See Table 6.1 for description of codes and references. <sup>(b)</sup> In these structures the two 10-rings in the straight channel are equivalent because they are related by mirror plane in space group $Pnma$. <sup>(c)</sup> Ratio of longest over shortest diagonal distance which is related to the eccentricity (deviation from circular) of the 10-rings.
/ sorbate complexes, there are two independent 10-rings defining each of the straight and
sinusoidal channels respectively.

As seen from the values listed in Table 8.4, there is a fair amount of variation between
the three general structure types (empty framework, high- and low-loaded), but there are general
similarities within each group. A useful parameter which describes the deviation of the channels
from circular is the ratio of the longest over the shortest diagonal O--O distances (the
eccentricity \( l/s \)). If \( l/s = 1.0 \) the \( T_{10} \) rings are essentially circular, while larger values of \( l/s \)
indicate increasing elliptical distortion. The \( l/s \) ratios for the ZSM-5 structures are listed in Table
8.4. Comparison of the eccentricities for the three structure types indicates that the elliptical
character of the 10-rings is significantly more pronounced when there is a sorbate molecule
present. This elliptical distortion of the 10-rings closely mirrors the shape of the sorbed molecule
and can be clearly seen in Figure 8.4 which shows the packing of the \( p \)-xylenes in the straight
channels of ZSM-5. Note that the distortion produces a free pore dimension that is quite closely
related to the kinetic diameter of \( p \)-xylene (5.85 Å).^5^0

An exception to the guest-induced eccentricity in the 10-rings is seen for the as-
synthesized ZSM-5 containing TPA^+^ ions, where only relatively minor elliptical distortions are
present. This is probably due to the smaller effective kinetic diameter of the propyl groups
compared with those of aromatic ring compounds such as naphthalene and substituted benzenes,
and the associated reduction in close framework-sorbate contacts.

For the low loaded structures the sorbates are located at the channel intersection but lie
in the straight channels, and it is these 10-rings which have \( l/s \) markedly larger than 1.0 (actually
close to 1.2), while the zig-zag channels remain essentially circular. The effective pore
dimensions for straight channels in ZSM-5 containing less than 4 molecules \( p \)-xylene/u.c. (4.6 \times
6.4 Å) are very close to those of the other ZSM-5 structures having sorbates at the channel
intersections, although in the case of \( p \)-dichlorobenzene, a slightly less pronounced elliptical
character is observed. In the high-loaded sorbate / ZSM-5 complexes, molecules are also present
Figure 8.4  View of the low-loaded \( p \)-xylene / ZSM-5 complex down [010] showing the orientations and packing of the \( p \)-xylene molecules in the straight channels. Molecules in adjacent channels are related by inversion centers and two-fold screw axes. Note the elliptical deformation of the channels to accommodate the sorbates.
in the sinusoidal channels and an elliptical distortion is observed for these 10-rings as well. In the empty ZSM-5 framework, all of the 10-rings are more or less circular. These changes reflect the general flexibility of the zeolite framework, and indicate that slight changes in the geometry about each T-atom (mainly in the O–Si–O bond angles) can occur to accommodate sorbed molecules or temperature variations. In many theoretical calculations used to determine preferred sorption sites of guests in the zeolite channel systems (e.g. energy minimizations) the framework is kept rigid, and this may not accurately reflect the real structure.

8.3.2 Geometry and Packing of the p-xylene Molecules

The C–C bond lengths and C–C–C bond angles determined for the p-xylene molecules sorbed in ZSM-5 at loading of 2.85 molecules/u.c. are given in Table 8.5. The labeling of the atoms in Table 8.5 is different than used in the structure determination (see Table 8.1) and the new labeling scheme is indicated in Figure 8.5. During the refinement of the XRD data, these atoms had an equal occupancy that was freely varied, and individual anisotropic thermal factors for the four independent C atoms. In the previously published single crystal determinations of low-loaded sorbate / ZSM-5 complexes, the sorbate molecules were refined as rigid groups with ideal geometries, and sometimes with fixed occupancies as well (For the two high-loaded forms (p-xylene and p-dichlorobenzene) the sorbate geometries were unconstrained).

The bond lengths and angles are in excellent agreement with those determined for a single crystal of p-xylene at 180 K (Table 8.5) The geometry reported\(^2\) for p-xylene molecules in the straight channels of the high-loaded p-xylene / ZSM-5 complex are also listed in Table 8.5 and a comparison reveals that the present structure determination has significantly lower e.s.d.'s in the bond lengths and a geometry that agrees very well with those found for p-xylene at the same temperature.

The anisotropic thermal displacement parameters for p-xylene (Table G.1, Appendix G) are similar to those seen in the high-loaded form\(^2\) and are quite elongated in the [010] direction.

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Figure 8.5 Labeling of \( p \)-xylene carbon atoms in (a) X-ray determined structure of low-loaded form of ZSM-5 and (b) Table 8.5. Apostrophes indicate symmetry related atoms generated by the mirror plane \( m \) in the space group \( Pnma \).

Figure 8.6 Angles and coordinates used to describe orientations of sorbates in ZSM-5. The coordinates of the ring centre are \( x,y,z \). (a) Angles \( \alpha_1, \beta_1 \) and \( \gamma_1 \) define the orientation of the long molecular axis relative to the crystal axes \( a, b, \) and \( c \) respectively. (b) Angles \( \alpha_2, \beta_2 \) and \( \gamma_2 \) are measured to a vector which is normal to the plane of the ring. See footnotes to Table 6.1 for further information.
Table 8.5 Comparison of bond lengths (Å) and bond angles (°) in p-xylene molecules at the channel intersections of ZSM-5 with those in a single crystal of p-xylene at 180 K. Estimated standard deviations are given in parentheses.

<table>
<thead>
<tr>
<th>Structure $^{(a)}$</th>
<th>LLPXY$^{(b,c)}$</th>
<th>HLPXY$^{(d)}$</th>
<th>p-xylene$^{(c,d)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bond Lengths</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.38(1)</td>
<td>1.37(2)</td>
<td>1.394(2)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.39(1)</td>
<td>1.38(3)</td>
<td>1.389(2)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.38(1)</td>
<td>1.43(2)</td>
<td>1.393(2)</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.38(1)</td>
<td>1.41(2)</td>
<td>1.394(2)</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.45(2)</td>
<td>1.44(2)</td>
<td>1.389(2)</td>
</tr>
<tr>
<td>C6-C1</td>
<td>1.38(1)</td>
<td>1.37(2)</td>
<td>1.393(2)</td>
</tr>
<tr>
<td>mean</td>
<td>1.39</td>
<td>1.40</td>
<td>1.392</td>
</tr>
<tr>
<td>C1-C7</td>
<td>1.50(1)</td>
<td>1.52(3)</td>
<td>1.503(2)</td>
</tr>
<tr>
<td>C4-C8</td>
<td>1.50(1)</td>
<td>1.52(3)</td>
<td>1.503(2)</td>
</tr>
<tr>
<td>mean</td>
<td>1.50</td>
<td>1.52</td>
<td>1.503</td>
</tr>
<tr>
<td><strong>Endocyclic Angles</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>121.6(6)</td>
<td>122(1)</td>
<td>121.0(1)</td>
</tr>
<tr>
<td>C2-C3-C4</td>
<td>121.6(6)</td>
<td>124(1)</td>
<td>121.3(1)</td>
</tr>
<tr>
<td>C4-C5-C6</td>
<td>120.0(6)</td>
<td>122(1)</td>
<td>121.0(1)</td>
</tr>
<tr>
<td>C5-C6-C1</td>
<td>120.0(6)</td>
<td>121(1)</td>
<td>121.3(1)</td>
</tr>
<tr>
<td>mean</td>
<td>120.8</td>
<td>122</td>
<td>121.2</td>
</tr>
<tr>
<td>C2-C1-C6</td>
<td>118(1)</td>
<td>118(2)</td>
<td>117.7(1)</td>
</tr>
<tr>
<td>C3-C4-C5</td>
<td>118(1)</td>
<td>113(2)</td>
<td>117.7(1)</td>
</tr>
<tr>
<td>mean</td>
<td>118</td>
<td>116</td>
<td>117.7</td>
</tr>
<tr>
<td><strong>Exocyclic Angles</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2-C1-C7</td>
<td>121.7(9)</td>
<td>120(1)</td>
<td>121.2(1)</td>
</tr>
<tr>
<td>C6-C1-C7</td>
<td>119.9(8)</td>
<td>121(1)</td>
<td>121.0(1)</td>
</tr>
<tr>
<td>C3-C4-C8</td>
<td>121.7(9)</td>
<td>125(1)</td>
<td>121.2(1)</td>
</tr>
<tr>
<td>C5-C4-C8</td>
<td>119.9(8)</td>
<td>122(1)</td>
<td>121.0(1)</td>
</tr>
<tr>
<td>mean</td>
<td>120.8</td>
<td>122</td>
<td>121.1</td>
</tr>
</tbody>
</table>

$^{(a)}$ LLPXY: 2.85 molecules of p-xylene / u.c.; HLPXY: 8 molecules of p-xylene / u.c.

$^{(b)}$ p-xylene located on mirror plane (see Figure 8.5 for the labelling scheme).

$^{(c)}$ p-xylene molecule has a centre of symmetry.

$^{(d)}$ Data from reference 2.
No noticeable distortions in the [100] or [001] directions are observed, indicating that the deviation of the methyl-methyl vector from the straight channel axis is quite small. A possible interpretation of the ellipsoid shapes is that the energy minimum for the sorbate molecules is somewhat flat and we are seeing some thermal motion of the $p$-xylene molecules.

As seen in Figures 8.3 and 8.4, the $p$-xylene molecule lies at the intersection with the methyl-methyl axis aligned along the straight channel. The plane of the aromatic ring is tilted away from the $a$ and $c$ axes so that it faces the opening to the zig-zag channel (defined by Si-1, Si-2, Si-5, Si-6 and Si-9). The $p$-xylene molecules form loosely connected chains along [010], with neighbouring molecules in each straight channel related by an inversion centre, and alternating ring orientations in adjacent channels along the $c$ direction (Figure 8.4). The C–C contact distance between terminal (methyl) carbons residing in the same channel is 4.05 Å, which is very close to that reported for the high-loaded $p$-xylene / ZSM-5 complex (4.08 Å) and indicates the packing along the channels is similar in these two structures. Methyl carbons of molecules residing in adjacent channels are separated by a distance of 11.75 Å.

The location and rotational orientation of the adsorbed $p$-xylene molecules within the framework can be described by the fractional coordinates of the centre of the aromatic ring ($x$, $y$, $z$), and the angles between the methyl-methyl axis and the $a$, $b$, and $c$ axes ($\alpha l$, $\beta l$, $\gamma l$ respectively), and from a vector normal to the plane of the ring to these axes ($\alpha 2$, $\beta 2$, and $\gamma 2$). These variables are defined in Figure 8.6. The location and orientation of $p$-xylene molecules determined in the present work, together with the corresponding values calculated from the coordinates and cell dimensions of other ZSM-5 / sorbate systems determined by single crystal XRD are presented in Table 8.6.

If the sorbate molecule is centrosymmetric, and the center is coincident with the mirror plane in space group $Pnma$, there will only be two orientations for the molecules as seen for $p$-xylene within the straight channels in Figure 8.4. However if the molecular center is not coincident with the mirror plane, then disorder will be present and there will be four orientations.
Table 8.6  Comparison of the locations and orientations\(^{(a)}\) for different organic molecules adsorbed at the channel intersections in ZSM-5. These were calculated from the unit cell dimensions and fractional atomic coordinates given in the references indicated.

<table>
<thead>
<tr>
<th>Structure(^{(b)})</th>
<th>HLPXY</th>
<th>HLPDCB</th>
<th>LLPDCB</th>
<th>LLPNA</th>
<th>LLPXY</th>
<th>NAPH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method(^{(c)})</td>
<td>crystal</td>
<td>crystal</td>
<td>crystal</td>
<td>crystal</td>
<td>crystal</td>
<td>NMR</td>
</tr>
<tr>
<td>Reference</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>this work</td>
</tr>
<tr>
<td>(x)</td>
<td>0.510</td>
<td>0.512</td>
<td>0.486</td>
<td>0.486</td>
<td>0.486</td>
<td>0.484</td>
</tr>
<tr>
<td>(y)</td>
<td>0.238</td>
<td>0.240</td>
<td>0.240</td>
<td>0.253</td>
<td>0.271</td>
<td>0.250</td>
</tr>
<tr>
<td>(z)</td>
<td>-0.019</td>
<td>-0.025</td>
<td>-0.019</td>
<td>-0.026</td>
<td>-0.030</td>
<td>-0.019</td>
</tr>
<tr>
<td>(\alpha 1(\text{o}))</td>
<td>88</td>
<td>88</td>
<td>84</td>
<td>85</td>
<td>84</td>
<td>90</td>
</tr>
<tr>
<td>(\beta 1(\text{o}))</td>
<td>7</td>
<td>9</td>
<td>5</td>
<td>7</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>(\gamma 1(\text{o}))</td>
<td>97</td>
<td>99</td>
<td>89</td>
<td>84</td>
<td>81</td>
<td>90</td>
</tr>
<tr>
<td>(\alpha 2(\text{o}))</td>
<td>149</td>
<td>152</td>
<td>47</td>
<td>45</td>
<td>46</td>
<td>51</td>
</tr>
<tr>
<td>(\beta 2(\text{o}))</td>
<td>92</td>
<td>92</td>
<td>93</td>
<td>89</td>
<td>87</td>
<td>90</td>
</tr>
<tr>
<td>(\gamma 2(\text{o}))</td>
<td>120</td>
<td>117</td>
<td>137</td>
<td>135</td>
<td>136</td>
<td>140</td>
</tr>
</tbody>
</table>

\(^{(a)}\) \(x\), \(y\), and \(z\) define the fractional atomic coordinates of the aromatic ring center (ignoring substituents) except for napthelene where they describe the molecular center. The angles are defined in Figure 8.6. \(^{(b)}\) See Table 6.1 for definitions of the codes describing the different sorbates and loadings in ZSM-5. \(^{(c)}\) Structures determined from single crystal X-ray diffraction (crystal), powder X-ray diffraction (powder), or \(^1\text{H-}^{29}\text{Si CPMAS NMR experiments (NMR).}\)
For the high-loaded sorbate / ZSM-5 complexes which have $P2_12_12_1$ symmetry, only two orientations will be observed. Only the parameters for one of these orientations is given is Table 8.6 since the others are related by the appropriate symmetry operations in each space group.

The disorder observed in these cases may be a result of the symmetry imposed on the system by the space group selected for refinement. The higher symmetry is observed occurs because the framework atoms contribute most of the scattered X-ray intensity. NMR is more sensitive to the local geometry of the individual T-sites and may provide the key to unraveling this pseudo symmetry versus disorder controversy.

Comparison of the values given in Table 8.6 reveals that the location and orientation of $p$-xylene are similar to that found for other low-loaded ZSM-5 complexes. In the present work the ring centroid lies exactly on the mirror plane for $p$-xylene. This is in agreement with the observation of a single $^{13}$C NMR resonance for the methyl carbon of the sorbed $p$-xylene (in the high-loaded from the methyl groups are no longer equivalent and four resonances are observed; two for the methyl’s in the straight channel and two for those in the zig-zag channels). In all other cases the sorbate molecules are shifted slightly (up to 0.4 Å) from the mirror plane and thus are disordered.

The angular rotation of the $p$-xylene ring relative to the crystallographic axes is, overall, quite similar to those found for the other low-loaded ZSM-5 complexes, but some differences are apparent. For $p$-xylene the methyl-methyl axis is exactly parallel to the [010] axis ($\alpha_1 = \gamma_1 = 90^\circ$, $\beta_1 = 0^\circ$), compared with deviations of up to $11^\circ$ seen for the long molecular axes of the other sorbates; only naphthalene is so closely aligned to the straight channel axes. $\alpha_2$ and $\gamma_2$ are also slightly higher for the low-loaded $p$-xylene / ZSM-5 complex than in any of the other low-loaded structures.

Striking differences are seen for the orientation of the aromatic ring plane in the low- and high-loaded sorbate / ZSM-5 complexes. When the sorbate loading is less than 4 molecules/u.c. $\alpha_2$ is approximately $50^\circ$ and $\gamma_2$ is nearly $140^\circ$. If eight molecules are present then $\alpha_2$ increases to

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ca. 150° and y2 is reduced by about 20°. This change of almost 100° in α2 reflects the rotation of the sorbates in the straight channel to have a more favourable interaction with the terminal ring-substituent atoms of molecules present in the zig-zag channels in the high-loaded forms. The elliptical distortion of the straight channels (see Table 8.4) in the high loaded form also reflects the different molecular orientations and occurs in almost the opposite direction to that seen in the low-loaded complexes.5,4

8.3.3 Comparisons with p-xylene Orientations Determined by Other Methods

The orientations and locations proposed from the two previous investigations of the low-loaded p-xylene / ZSM-5 complex by powder X-ray diffraction27 and NMR27 are given in Table 8.6. In both cases the centre of the aromatic ring lies on the mirror plane, and the methyl-methyl axis is exactly along the straight channel, in agreement with the present XRD structure. There are small differences in the precise position of the ring centroid relative to the channel (by up to 0.2 Å), and the angles between the vector normal to the plane of the aromatic ring vary by about 6°. Overall the locations and rotational orientation within the channels determined from NMR and powder XRD investigations are in close agreement with the present structure.

No coordinates were published for the locations found by energy minimization calculations, so the orientational parameters could not be computed for these; however it was reported that the molecules were located at the channel intersections with the CH₃–CH₃ axis parallel to [010].8,26

8.3.4 Prediction of ²⁹Si Chemical Shifts

In previous correlations between chemical shifts and structural parameters derived from framework atoms from XRD determined structures, the limiting factor was the relatively large e.s.d.'s of XRD derived parameters. In the present work the structural parameters have been determined to a high degree of accuracy, and NMR data acquired in a similar temperature range
was also available, providing a sensitive test of the correlations. Four linear correlations were considered:

\[ \delta = a \text{ [mean Si-Si distance]} + b \] 8.8

\[ \delta = a \text{ [mean } \frac{\cos \alpha}{(\cos \alpha - 1)} \text{ ]} + b \] 8.9

\[ \delta = a [\text{ } \alpha_{av} \text{ } ] + b \] 8.10

\[ \delta = a \text{ [cos } \alpha_{av} \text{ / (cos } \alpha_{av} - 1)\text{ ]} + b \] 8.11

where \( \delta \) is the isotropic \(^{29}\text{Si}\) chemical shift in ppm referenced to TMS, \( \alpha \) is the Si–O–Si angle and \( \alpha_{av} \) is the average angle for each T-site.

The various geometrical parameters calculated from the coordinates in the present work for these four equations are listed in Table 8.7. \(^{29}\text{Si}\) MAS NMR spectra were acquired at 193 K and 173 K (Figure 8.1) and linear interpolation was used to estimate the \(^{29}\text{Si}\) chemical shifts at 180 K. Only those resonances which could be reliably assigned to specific T-sites (using 2-D INADEQUATE experiment obtained at 268 K, and spectra obtained at lower temperatures) were included in the fitting. The uncertainty in \( \delta \) is estimated to be better than 0.1 ppm. Plots of \( \delta \) versus the various structural parameters are presented in Figures 8.7 and 8.8, and the results of linear least-squares fitting of the data are presented in Table 8.8. The regression coefficients are greater than those previously reported and are likely a direct result of the more accurate geometrical parameters determined in the present study. In Figure 8.7(b) the correlation reported in reference 29 for several ZSM-5 structures is added for comparison (dashed line) and is in close agreement.

Some scatter in the data is apparent, particularly for Si-12 and Si-1. The equations derived are in close agreement with those previously reported. However, the correlations are still not reliable enough for complete assignment of all resonances in the spectra, since distinct changes in the chemical shifts are apparent even over relatively small temperature ranges (Figure 8.1) thus it is emphasized that these correlations are not yet good enough to permit unambiguous assignments of resonances in different sorbate / ZSM-5 systems.
Table 8.7 $^{29}$Si chemical shifts and structural parameters for ZSM-5 loaded with 2.85 molecules of $p$-xylene/u.c. at 180 K.

<table>
<thead>
<tr>
<th>T-Site</th>
<th>Chemical Shift $\delta$ (ppm)</th>
<th>Mean Si-O-Si angle $\alpha_{av}$ ($^\circ$)</th>
<th>Mean $\cos \alpha / [\cos \alpha - 1]$</th>
<th>$\cos \alpha_{av} / [\cos \alpha_{av} - 1]$</th>
<th>Mean Si-Si Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si1</td>
<td>-112.3</td>
<td>150.80</td>
<td>0.4661</td>
<td>0.4661</td>
<td>3.094</td>
</tr>
<tr>
<td>Si2</td>
<td>-117.0</td>
<td>156.90</td>
<td>0.4791</td>
<td>0.4911</td>
<td>3.128</td>
</tr>
<tr>
<td>Si3</td>
<td>-113.6</td>
<td>151.89</td>
<td>0.4687</td>
<td>0.4709</td>
<td>3.103</td>
</tr>
<tr>
<td>Si4</td>
<td>-115.0</td>
<td>154.13</td>
<td>0.4736</td>
<td>0.4804</td>
<td>3.118</td>
</tr>
<tr>
<td>Si5</td>
<td>148.35</td>
<td></td>
<td>0.4598</td>
<td>0.4545</td>
<td>3.079</td>
</tr>
<tr>
<td>Si6</td>
<td>150.32</td>
<td></td>
<td>0.4649</td>
<td>0.4638</td>
<td>3.085</td>
</tr>
<tr>
<td>Si7</td>
<td>148.97</td>
<td></td>
<td>0.4615</td>
<td>0.4575</td>
<td>3.083</td>
</tr>
<tr>
<td>Si8</td>
<td>-117.4</td>
<td>157.47</td>
<td>0.4801</td>
<td>0.4931</td>
<td>3.135</td>
</tr>
<tr>
<td>Si9</td>
<td>149.38</td>
<td></td>
<td>0.4625</td>
<td>0.4595</td>
<td>3.086</td>
</tr>
<tr>
<td>Si10</td>
<td>-109.3</td>
<td>146.80</td>
<td>0.4556</td>
<td>0.4468</td>
<td>3.073</td>
</tr>
<tr>
<td>Si11</td>
<td>149.38</td>
<td></td>
<td>0.4625</td>
<td>0.4595</td>
<td>3.089</td>
</tr>
<tr>
<td>Si12</td>
<td>-113.3</td>
<td>150.21</td>
<td>0.4646</td>
<td>0.4634</td>
<td>3.092</td>
</tr>
</tbody>
</table>

† Chemical shifts are referenced to TMS and were estimated from interpolation of spectra acquired at 173 K and 193 K. Only those resonances which could be unambiguously assigned to specific T-sites are listed.

Table 8.8 Linear regression analysis of $^{29}$Si chemical shifts $\delta$ against the various geometric parameters indicated for ZSM-5 loaded with 2.85 molecules of $p$-xylene/u.c. at 180 K.

<table>
<thead>
<tr>
<th>$X$</th>
<th>Linear Regression</th>
<th>Correlation Coefficient $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Si-O-Si angle $\alpha_{av}$ ($^\circ$)</td>
<td>$\delta = -0.72X - 4.12$</td>
<td>0.967</td>
</tr>
<tr>
<td>Mean $\cos \alpha / [\cos \alpha - 1]$</td>
<td>$\delta = -317.52X - 35.14$</td>
<td>0.973</td>
</tr>
<tr>
<td>$\cos \alpha_{av} / [\cos \alpha_{av} - 1]$</td>
<td>$\delta = -167.76X - 34.62$</td>
<td>0.973</td>
</tr>
<tr>
<td>Mean Si-Si Distance (Å)</td>
<td>$\delta = -123.65X - 270.09$</td>
<td>0.961</td>
</tr>
</tbody>
</table>
Figure 8.7 NMR and XRD correlation diagrams for zeolite ZSM-5 containing 2.85 molecules of p-xylene/u.c. at 180 K. Only those NMR resonances which could be unambiguously assigned to specific T-sites are included. (a) Plot of chemical shift $\delta$ versus the mean Si-O-Si angle $\alpha_{av}$. (b) Plot of $\delta$ vs. the average of $\cos \alpha / [\cos \alpha - 1]$. Equations for the linear regressions (solid lines) are given in Table 8.8. The dashed line in (b) is the correlation reported in reference 29 for several ZSM-5 structures.
Figure 8.8 NMR and XRD correlation diagrams for zeolite ZSM-5 containing 2.85 molecules of \( p \)-xylene / u.c. at 180 K. Only those NMR resonances which could be unambiguously assigned to specific T-sites are included. (a) Plot of chemical shift \( \delta \) versus \( \cos \alpha / [\cos \alpha - 1] \) for the average Si–O–Si angle \( \alpha_{av} \). (b) Plot of \( \delta \) vs. the mean Si–Si distance. Equations for the linear regressions (solid lines) are given in Table 8.8.
8.4 SUMMARY AND CONCLUSIONS

The structure of ZSM-5 loaded with 2.85 molecules per unit cell of \( p \)-xylene was determined from refinement of single crystal X-ray diffraction data. This is the first structure determined for a volatile organic sorbed in ZSM-5 at a controlled loading and was achieved using a specially-designed, purpose-built apparatus. The diffraction data were collected at 180 K using a diffractometer with a CCD detector, and a virtually complete hemisphere of independent Bragg reflections were accumulated, allowing the most accurate determination of the structural parameters for the ZSM-5 framework reported to date.

The sorbed \( p \)-xylene molecules were located in the straight channels at the intersection with the sinusoidal channels, and have their methyl-methyl axes exactly parallel to [010]. The orientation is in good accord with those previously observed for the other low-loaded ZSM-5 / sorbate complexes, and agrees closely with those proposed determined from energy minimization calculations,\(^{8,26}\) and powder XRD.\(^{27}\)

Recent NMR investigations of the low-loaded \( p \)-xylene / ZSM-5 complex have been utilized to predict the sorbate location and orientation, and the resulting solution corresponds very closely to that determined in the present XRD structure determination.\(^{27}\) These results prove that the NMR techniques described in this thesis can be used to determine the locations(s) and orientation(s) of guests species within the channels of microporous materials such as zeolites. With appropriate precautions and suitable data analysis strategies (for example based on the methods outlined in Chapters 3 and 6), cross polarization, REDOR, and TEDOR NMR experiments should permit the three-dimensional structure of host-guest structures of sorbates in microporous materials to be determined. In cases when single crystal X-ray diffraction methods are not practical, the techniques developed in this thesis provide powerful and effective tools which have the potential to greatly expand the understanding of these important materials.
SUPPLEMENTARY DATA FOR CHAPTER 8

The following supplementary data are listed in Appendix G:

**Table G.1** Anisotropic displacement factors for Si, O and C.

**Table G.2** Bond lengths in the ZSM-5 framework.

**Table G.3** Bond angles in the ZSM-5 framework.

REFERENCES FOR CHAPTER 8

1 Dia, A.C.; Fyfe, C.A. Personal communication.


27 Diaz, A.C., Fyfe, C.A. Unpublished work, Chemistry Dept., University of British Columbia, Canada.


45 D*TREK software for SGI Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, Texas, TX 77381, U.S.A. http://www.msc.com/

46 teXsan for Windows 1.01 Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, Texas, TX 77381, U.S.A. http://www.msc.com/


CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

9.1 SUMMARY AND CONCLUSIONS

The purpose of the research reported in this thesis was to develop solid-state NMR techniques which could be used to determine the three-dimensional structures of guest-host complexes. In particular, these investigations were directed to developing an experimental protocol and the necessary data analysis techniques to locate guest species within the channels and cages of microporous materials such as zeolites. Although the results reported here are for fluorine-containing guest species in purely siliceous materials, these techniques can be readily extended to other investigate other systems containing spin-1/2 nuclei.

The general strategy developed was as follows: First, the resonances in the $^{29}$Si MAS NMR spectrum need to be assigned to specific T-sites within the zeolite framework. This can be accomplished using, for example, 2-D INADEQUATE experiments. The next step is to determine specific internuclear distances between nuclei in the guest species and the framework (Si) atoms. Knowledge of three or more such distances may be sufficient to locate the guest within the channels and cages of the host lattice. The approach adopted in the present work was to use the MAS NMR techniques of cross polarization (CP), REDOR and TEDOR. In principle, these techniques allow the magnitude of the $I$-$S$ heteronuclear dipolar coupling to be measured, and since this is inversely proportional to the cube of the $I$-$S$ distance, they provide direct methods to measure the necessary distances.
Octadecasil, a clathrasil which contains encapsulated fluoride ions, was selected as the model compound for optimizing the experimental techniques, spectrometer configurations, and data analysis methods. $^{19}$F-$^{29}$Si CP, REDOR and TEDOR NMR experiments were performed. The Si-F distances between the T-1 Si and the fluoride ion in the D4R unit determined directly from these three techniques were in excellent agreement with that known from the single crystal XRD structure. Because of the low natural isotopic abundance of $^{29}$Si, and because the closest fluoride-fluoride distance in octadecasil is > 9.3 Å, the T-1 silicon / fluoride ion closely approximates an isolated $^{19}$F-$^{29}$Si spin pair. Nonlinear least squares fitting of the CP data was made possible by expressing the equations derived by Hediger et al. in terms of Bessel functions.

From these experiments it was concluded that when the spin system can be described as an isolated $I/S$ spin pair, the distances determined from CP, REDOR, and TEDOR should be, in principle, of comparable accuracy. However, the three techniques have quite different dependencies on the various relaxation properties of the nuclei in the system being investigated, and this provides some degree of flexibility for selecting the method(s) best suited to a particular sample. In any case, it is highly recommended that at least two of the techniques be used to validate the results. Because the REDOR experiment provides normalized data, it can sometimes provide additional information about the number of $S$ spins which are not dipolar coupled to an $I$ spin, which may be useful to determine site occupancies for example.

For the T-2 site in octadecasil, the analysis of the experimental data was complicated by the fact that up to four $^{19}$F nuclei were dipolar coupled to the $^{29}$Si nucleus. However, when the tetrahedral arrangement and partial occupancies (known from the crystal structure) of the D4R units by the fluoride ions was included in the theoretical calculations, good agreement was obtained between the calculated and observed REDOR and TEDOR dephasing. It was necessary to extend the approach reported for multi-spin REDOR calculations to permit fitting of the
TEDOR data. These results represent the first $^{19}$F-$^{29}$Si REDOR and TEDOR experiments reported in the literature, as well as the first multi-spin TEDOR analyses.

A series of calculations on a selection of 3-spin, $I_S$ systems was performed to gain insight into the likelihood of being able to obtain reliable distance information from analysis of REDOR and TEDOR data acquired on systems where little or no information regarding the number of spins, or the geometrical arrangement of these, is available. It was apparent that even for the simple systems studied, it is highly unlikely that direct and unambiguous distance determinations can be obtained. The problem will be compounded when the noise present in experimental data is considered, and more spins and/or relative motions are present. Furthermore, it is possible to obtain erroneous distances if an isolated spin pair is assumed and multiple spins are in fact present.

Thus the best approach will be to try and ensure that the spin system approximates an isolated spin pair as closely as possible, (e.g. by isotopic substitution and dilution in the unlabeled compound), or several isolated spin pairs. If this is not possible, the only alternative is to acquire several REDOR and TEDOR data sets (with different parameters), then propose a model of the spin system which fully describes the relative geometric arrangement (i.e. with all angles and distances implicitly defined). Using this model, the theoretical dephasing can be calculated and compared to the experimental data. The model is modified and the calculations re-run until optimal agreement between the calculated and experimental dephasing is obtained for all of the experimental data sets. With this approach, there will be no direct determinations of distances, but structural information can still be (indirectly) obtained. This method will be most efficient if constraints can be placed upon the model which limit the possible number of spins and internuclear distances. This may be the case for sorbate molecules in zeolites since the guests must lie within the channel system.

The low-loaded form of the $p$-difluorobenzene / ZSM-5 complex was chosen as a test case for applying these NMR techniques to a system where no prior information about the
location of the sorbate molecules within the channel systems was available. Loading ZSM-5 with 4 molecules of p-difluorobenzene per unit cell caused the framework to change from monoclinic (P21/n.1.1 symmetry, 24 T-sites) to a phase having 12 T-sites at temperatures above ca. 293 K. From the appearance of the 29Si MAS NMR spectra, orthorhombic Pnma symmetry is proposed for this phase, as has been reported previously for three other low-loaded, para-disubstituted aromatic / ZSM-5 complexes.5-7 Loadings higher than 4 molecules/u.c. could not be obtained for samples prepared at ambient pressure and temperature, even when excess p-difluorobenzene was added.

Cooling the sample below 290 K resulted in a transformation back to a phase having 24 T-sites, which was maintained to the lowest temperatures accessible (215 K). The 29Si NMR chemical shifts observed for this phase indicated that it was almost identical to the monoclinic phase adopted by the empty ZSM-5 framework. Equipment and an experimental protocol were developed which allowed experiments with stable MAS rates to be performed at low temperatures for periods of 2 days or longer. It was found that dry air (rather than nitrogen) should be used as the drive gas for the low temperature experiments, in order to prevent the loss of the oxygen gas from within the sample. The nuclear relaxation times of both the sorbates and framework nuclei are dependent on the concentration of paramagnetic oxygen, becoming significantly longer as the concentration decreases.

The success of 1H-29Si and 19F-29S polarization transfer observed during CP experiments proves that the sorbate molecules remain within the ZSM-5 channel system during, and after, this phase transition. The orthorhombic, Pnma and monoclinic, P21/n.1.1 symmetries proposed for these two phases were subsequently verified and the lattice constants determined from analysis of powder XRD data. A partial assignment of the 29Si resonances to specific T-sites was obtained from analysis of 2-D CP-INADEQUATE experiments.

The relatively high temperature (290 K) at which the framework changed to adopt the same (monoclinic) symmetry observed for the empty ZSM-5 indicates that the sorbate-
framework interactions are much weaker than in the case of the low-loaded p-xylene / ZSM-5 complex, which maintains \textit{Pnma} symmetry to temperatures at least as low as 173 K.\textsuperscript{8} It is anticipated that the transformation to monoclinic symmetry for the ZSM-5 framework observed in the present case may also occur in other sorbate / ZSM-5 systems at low temperatures.

Two programs were written as part of the effort to locate p-difluorobenzene within the ZSM-5 framework. These utilize the $T_{CP}$ values determined from fitting variable contact time CP experimental data, and calculate the heteronuclear second moments as the sorbate molecule is translated (and rotated) through the channels. The program searches for positions and orientations which have linear correlations for the $1/T_{CP}$ and calculated $M_2$ values for a set of silicons. This approach had been successfully used previously to locate the p-xylene molecules in ZSM-5\textsuperscript{8,9} Using these programs, $^1$H-$^{29}$Si and $^{19}$F-$^{29}$Si CP data acquired at 230 K and 235 K respectively were analyzed. It was discovered the sorbate molecules were undergoing slow diffusion that affected the CP, REDOR and TEDOR data, and thus lower temperatures need to be used. Although the precise position and orientation of the p-difluorobenzene molecule were not obtained, a location in the straight channel very close to the intersection with the zig-zag channels is consistent with the experimental data.

A single crystal of ZSM-5 was loaded with a precisely controlled amount of p-xylene using a purpose-built piece of apparatus developed as part of the present work. The low-loaded form of the p-xylene / ZSM-5 complex prepared contained 2.85 molecule/u.c., and single crystal XRD data collected at 180 K was successfully refined in the orthorhombic space group \textit{Pnma}. The p-xylene molecules were located in the straight channels at the channel intersections, with the methyl-methyl axes aligned parallel to the $b$ axis, in general agreement with the locations and orientations proposed previously from other techniques.\textsuperscript{8,10,11} This structure represents the most accurate determination of the ZSM-5 framework distances and angles reported to date.

In summary, using the NMR techniques (and analysis methods) developed in the present work, in conjunction with the general strategy proposed, determination of the complete 3-
dimensional structures of sorbate-zeolite complexes is possible. At the present time however, it is
not routine, and care must be taken to ensure that: (i) the spin system approximates isolated spin
pairs if at all possible, (ii) the guest molecules are not moving on the time scale of the dipolar-
based NMR experiments.

$^{29}$Si MAS NMR experiments can provide direct information about the number of T-sites
for sorbate / zeolite complexes. When used in conjunction with powder X-ray diffraction data,
the space group symmetry, cell parameters, and temperatures at which phase transitions (if any)
occur can be determined. This information is invaluable for determining the best loadings and
temperatures for collecting single crystal XRD data.

9.2 SUGGESTIONS FOR FUTURE WORK

For the $p$-difluorobenzene / ZSM-5 complex, additional INADEQUATE experiments are
needed at several temperatures to confirm the preliminary assignment. Further experiments at
temperatures lower than 230 K could slow the sorbate diffusion enough that the molecules could
be reliably located using CP, REDOR and TEDOR experiments. Static $^2D$ NMR investigations of
$p$-difluorobenzene-$d_4$ in ZSM-5 could provide information about the nature of the sorbate
motions, and be used to probe the temperatures at which these are minimized. Several single
crystals of ZSM-5 loaded with ca. 4 molecules/u.c. of $p$-difluorobenzene have been prepared, and
X-ray diffraction data acquired at 180 K and room temperature. A structure determination will be
attempted in the near future.

The techniques developed in this thesis could be applied to locate sorbates in other
zeolite frameworks where highly crystalline, purely siliceous samples are available (e.g.
mordenite, ZSM-11, and ZSM-12). These techniques may also allow the fluoride ions to be
located in other microporous materials synthesized from fluoride-containing media (e.g. the as-
synthesized AlPO$_4$s and GaPO$_4$s) using $^{19}$F-$^{31}$P CP, REDOR, and TEPOR. It is important that
methods are developed which can be used to determine if the spin system can be treated as
consisting of isolated spin pairs. Although selective isotopic enrichment combined with dilution in the corresponding unlabeled compound sometimes provides a possible solution, it is not always an option.

The algorithm used to perform the powder averaging needed to calculate the theoretical dephasing in the present work is very computationally intensive, which significantly hinders fitting experimental multi-spin data within a reasonable time period. Methods which could be implemented to increase the efficiency of the powder averaging include the approaches proposed by Aldermann et al.,2 Wang and Hanson,13 and the recently reported REPULSE algorithm.14

The measurement of heteronuclear dipolar couplings for isolated IS spin pairs using CP, REDOR and TEDOR is relatively straightforward. However, once the observed nuclei are coupled simultaneously to two or more spins (i.e. IS spin systems) the determination of unambiguous distance information is virtually impossible without some prior knowledge of (fairly explicit) information regarding both the number of spins, and the relative geometrical arrangement of these. A new technique, θ-REDOR, has recently been presented15 which seeks to reduce these problems, and this should be investigated.

The NMR techniques developed in this thesis to determine internuclear distances from measurements of the heteronuclear dipolar interactions may be applied to other systems containing spin-1/2 nuclei. Related techniques have been developed for non-spin 1/2 systems,16,17 which may allow cations such as 23Na to be located, or framework-sorbate distances to be obtained in aluminium-containing materials. There are also several techniques for measuring homonuclear dipolar couplings,16,18 and these may provide a means to determine sorbate-sorbate distances, and investigate the problem of disordered sorbate molecules, which will be very difficult or impossible to solve by diffraction techniques.16,18

One of the most important areas which offers the potential for advancing the current knowledge is to enlarge the database of reliable sorbate / zeolite structures. At present time, single crystal XRD structures still represent the most unambiguous method for determining the
positions and orientations of guest species within microporous materials. However, the experimental protocol developed in this thesis are at the stage where it is viable to determine the three-dimensional structures of sorbate / zeolite complexes from solid-state NMR investigations. Using the special apparatus developed in the present work (Chapter 2), it is now possible to load single crystals of these materials with precisely controlled amounts of volatile organic sorbates (or even mixtures). High-quality XRD data can be collected at low temperatures using a diffractometer equipped with CCD or image plate detectors, and the structures determined. At the present time high quality single crystals of ZSM-5 and zeolite A are available which are large enough for single crystal X-ray diffraction studies. Furthermore the synthesis of single crystals of AlPO₄-5 and mordenite having dimensions suitable for single-crystal XRD studies have been reported.¹⁹ These single crystal structure determinations should be carried out.
REFERENCES FOR CHAPTER 9


7 Single crystal XRD structure of low-loaded p-xylene / ZSM-5 complex. (Chapter 8).

8 Díaz, A.C., Fyfe, C.A. Unpublished Results, University of British Columbia, Canada.


APPENDIX A

SCHEMATICS OF NMR SPECTROMETER CONFIGURATIONS

Three different configurations of the Bruker MSL 400 NMR Spectrometer were used to perform the experiments reported in this thesis. Schematics showing the connections, amplifiers, synthesizers, filters, and attenuators are presented in this appendix.
Schematics for the three spectrometer configurations are given in Figures A1, A2 and A.3. Abbreviations used in these figures are listed in Table A.1. Many of the experiments performed in the current investigations required non-standard configurations because F3 could not be directly observed, which meant either the F1 (range 10 - 400.13 MHz) or the F2 (400.13 MHz only) receivers had to be utilized.

**Figure A.1** Schematic of set-up used for $^{29}\text{Si}$ spectroscopy with high power $^1\text{H}$ decoupling, and for $^1\text{H}-^{29}\text{Si}$ cross polarization experiments.

**Figure A.2** Schematic of set-up used for $^{19}\text{F}-^{29}\text{Si}$ CP, REDOR, and TEDOR NMR experiments with mixing of F2 and F3 to generate the $^{29}\text{Si}$ frequency. The phase control of the $^{29}\text{Si}$ signal was achieved using a single (constant) r.f. phase for F3 and varying the F2 phase. $^{19}\text{F}$ could be observed directly using the F1 receiver (with F1 frequency set to 376.434 MHz) if the appropriate connections to the F2 preamplifier insert ($^1\text{H} / ^{19}\text{F}$) were made.

**Figure A.3** Schematic of set-up used for $^{19}\text{F}-^{29}\text{Si}$ CP, REDOR, and TEDOR NMR experiments without the need for frequency mixing. The $^{19}\text{F}$ frequency was generated by tripling F3 and this means that the r.f. phases were also tripled (see Table A.2). The phase cycling used in the pulse programs needed to take this into consideration. $^{19}\text{F}$ could be observed using the F1 receiver if the appropriate connections to the F2 preamplifier insert ($^1\text{H} / ^{19}\text{F}$) were made, and the F3 carrier frequency (SFF3) and offset (O3) were set to one-third of those for F1 (SF and O1 respectively). In this case, these frequencies had to be multiples of 100 Hz, as required by the specifications of the F3 synthesizer (Programmed Test Sources PTS-250).
Table A.1 Abbreviations used in the Spectrometer Configuration Schematics.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>Band Pass</td>
</tr>
<tr>
<td>EXT STD</td>
<td>External Standard</td>
</tr>
<tr>
<td>HP</td>
<td>High Power</td>
</tr>
<tr>
<td>INT STD</td>
<td>Internal Standard</td>
</tr>
<tr>
<td>LP</td>
<td>Low Pass</td>
</tr>
<tr>
<td>REJ</td>
<td>Reject</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
</tbody>
</table>

Table A.2 Phases of the F3 signal before and after tripling.

<table>
<thead>
<tr>
<th>BEFORE Tripling</th>
<th>AFTER Tripling</th>
</tr>
</thead>
<tbody>
<tr>
<td>+X (0°)</td>
<td>+X (0°)</td>
</tr>
<tr>
<td>+Y (90°)</td>
<td>−Y (270°)</td>
</tr>
<tr>
<td>−X (180°)</td>
<td>−X (540° = 180°)</td>
</tr>
<tr>
<td>−Y (270°)</td>
<td>+Y (810° = 90°)</td>
</tr>
</tbody>
</table>
Figure A.1 Schematic of MSL 400 spectrometer configuration used to perform $^1$H / $^{29}$Si experiments. The $^1$H channel connections shown are those for high power decoupling or cross polarization.
Figure A.2 Schematic of MSL 400 spectrometer configuration used to perform $^{19}$F / $^{29}$Si experiments with mixing. The $^{29}$Si frequency (79.495 MHz) was generated by mixing F2 (400.13 MHz) with a frequency-doubled F3 signal (160.3125 MHz). The $^{29}$Si signal was then unmixed and observed at 400.13 MHz. The $^{19}$F frequency (376.434 MHz) was generated directly.
Figure A.3 Schematic of MSL 400 spectrometer configuration used to perform $^{19}$F/$^{29}$Si experiments without mixing. The $^{19}$F frequency (376.434 MHz) is obtained by tripling the F3 frequency (125.478 MHz) and amplifying it enough to drive the high power amplifier (tuned to 376.434 MHz). The reflected power could be monitored during the experiment with the oscilloscope.
APPENDIX B

PULSE AND AUTOMATION PROGRAMS

This appendix contains a compilation of the pulse and automation programs written to perform the NMR experiments reported in this thesis. They are written for a Bruker MSL-400 running DISMSL91. Details of the command and programming structure may be found in the DISMSL Manual (version 911101):

Bruker Analytische Messtechnik GMBH
Silberstrifen D-7512 Rheinstetten 4
Germany

Bruker Instruments, Inc.
Fortune Drive
Manning Park
Billerica, MA 01821
U.S.A.

Pulse programs are included for the three spectrometer configurations shown in Appendix A: (i) $^1$H on F2 (400.13 MHz) and $^{29}$Si (79.495 MHz) on F1, (ii) $^{29}$F on F1 (376.434 MHz) and $^{29}$Si obtained by mixing F2 with (frequency-doubled) F3, and (iii) $^{29}$Si on F1 with $^{19}$F obtained by tripling and amplifying F3. The programs include examples of scripts compiled to measure pulse lengths, relaxation times, and to acquire CP, REDOR, TEDOR, and INADEQUATE spectra. Several automation programs used to acquire or process the spectral files, and to calculate delays for REDOR and TEDOR experiments are also given. Standard pulse programs available with the DISMSL software have not been included. A complete listing of the filenames and a brief description of the specific function of the each program script is given below.
B.1 INDEX OF PROGRAMS

B.1.1 Single Nucleus Experiments

HSOLIDC.PC  One-pulse experiment for F1.
HQUADF2F.PC  One-pulse experiment for F2/F3 with mixing of F2 and F3.
LQUADF3.PC  One-pulse experiment for F3 with frequency tripling on F3.

B.1.2 Pulse Length Determination

LVD1.AUM  Automation to vary pulse length D1.
L90FSI.PC  Measurement of F2/F3\pi/2-pulse using CP from tripled F3.
L180FSI.PC  Measurement of F2/F3 \pi-pulse using CP from tripled F3.

B.1.3 Relaxation Time Measurements

CPTONE.PC  Measurement of F1 T1 using CP from F2.
HCPT1RHO.PC  Measurement of F1 T1\rho using CP from F2.

B.1.4 Cross Polarisation Experiments

HCPCYCL.PC  CP from F2 to F1 with different F2 power during CP and decoupling.
LVD.AUM  Automation to vary contact time (VD) using a variable delay list.
LFSICPD.PC  CP from F3 (tripled) to F1 with decoupling of F3 during acquisition.

B.1.5 INADEQUATE Experiments

HINADMAS.PC  Program to acquire 2-D INADEQUATE using CP from F2 to F1.
LINAD2D.PC  Program to acquire 2-D INADEQUATE on F1 without CP.
H2DAQ.AUM  Automation to acquire 2-D INADEQUATE serial file.
HCOMBINE.AUM  Automation to add two .SER files (e.g. two INADEQUATE FID's).
LADDSMX.AUM  Automation to add two .SMX files (e.g. two INADEQUATE plots).
B.1.6 REDOR Experiments

LREDSIF.PC
REDOR experiment with all dephasing pulses on F1 (unobserved) and simple90-τ-180-τ spin-echo sequence on F2/F3 (observed). All dephasing pulses are positioned at 1/2 of the rotor cycle.

LREDCAL.AUM
Automation to calculate delays for LREDSIF.PC from pulse lengths and spinning speed.

LREDOR.AUM
Automation to acquire series of REDOR experiments using LREDF3F1.PC or LREDSIF.PC by reading in offsets for F1 from offset list.

LREDF3F1.PC
REDOR experiment with dephasing pulses on F2/F3 (observed) and single 180 pulse on unobserved F1 with initial presaturation on F2/F3. All dephasing pulses are positioned at 1/2 of the rotor cycle.

LREDCAL2.AUM
Automation to calculate delays for LREDF3F1.PC from pulse lengths and spinning speed.

LRED1.PC
$S_6$ REDOR experiment dephasing pulses on F3 (tripled) with CP from F3. All dephasing pulses are positioned at 1/2 of the rotor cycle.

LRED2.PC
$S_7$ REDOR experiment dephasing pulses on F3 (tripled) with CP from F3. All dephasing pulses are positioned at 1/2 of the rotor cycle.

LREDCAL5.AUM
Automation to calculate delays for LRED1.PC and LRED2.PC from pulse lengths and spinning speed.

LREDFID.AUM
Automation to acquire series of REDOR experiments using LRED1.PC and LRED2.PC.

B.1.7 TEDOR Experiments

LTEDF1F2.PC
TEDOR experiment from F1 to F2/F3 with dephasing pulses on F2/F3 BEFORE transfer and on F1 AFTER transfer. All dephasing pulses positioned at 1/4 and 3/4 of the rotor cycle.

TEDORCAL.AUM
Automation to calculate delays for LTEDF1F2.PC from pulse lengths and spinning speed.

LIC4.AUM
Automation to vary m (increment C4), the number of rotor cycles AFTER coherence transfer with a fixed number of rotor cycles BEFORE transfer.

LIC1.AUM
Automation to vary n (increment C1), the number of rotor cycles BEFORE coherence transfer with a fixed number of rotor cycles AFTER transfer.
LTEDMOVB.PC  TEDOR experiment from F1 to F2/F3 with dephasing pulses on F2/F3 BEFORE coherence transfer and on F1 AFTER transfer. Pulses BEFORE transfer can be MOVED (e.g. to 1/3, 2/3 of each rotor cycle using TEDCAL13.AUM). Pulses AFTER transfer are at 1/4 and 3/4 of each rotor cycle.

TEDCAL13.AUM  Automation to calculate delays for LTEDMOVB.PC with pulses BEFORE transfer at 1/3, 2/3 and 1/4, 3/4 of each rotor cycle AFTER.

LTEDMOVA.PC  TEDOR experiment from F1 to F2/F3 with dephasing-pulses on F2/F3 BEFORE transfer and on F1 AFTER transfer. Pulses AFTER transfer can be MOVED (e.g. to 1/5, 4/5 of each rotor cycle using TEDCAL15.AUM). Pulses BEFORE transfer are at 1/4 and 3/4 of each rotor cycle.

TEDCAL15.AUM  Automation to calculate delays for LTEDMOVA.PC with pulses BEFORE coherence transfer at 1/4, 3/4 and 1/5, 4/5 of each rotor cycle AFTER.

LREFTED.PC  1-D refocussed TEDOR using transfer from F3 to F1 and tripling of F3. All dephasing pulses positioned at 1/4 and 3/4 of the rotor cycle.

LRTCAL.AUM  Automation to calculate delays for LREFTED.PC from pulse lengths and spinning speed.
B.2 PROGRAM LISTINGS

B.2.1 Single Nucleus Experiments

; HSOLIDC.PC
; ONEPULSE ACQUISITION WITH PHASE CYCLING
; (RING DOWN DELAY INDEPENDANT OF DW)

PROT F2
START, D1 [F1 @PLS1 RGATE] ; PULSE WITH PHASE LIST 1
   D3 [STA RGATE] ; RING DOWN DELAY AND TRIGGER
   AQ
LOOP C4 TIMES
   D0 ; ACQUISITION
END LOOP
++PLS1
GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
RLS, +X -Y -X +Y
END LISTS

; RECEIVER MODE : RPN OR QPN
; TRIGGER MODE : NT

; HQUADF2F.PC
; CREATION OF FREQUENCY BY MIXING OF F2 AND F3
; ONEPULSE ACQUISITION WITH QUADRATURE PHASE CYCLE

PROT F2
START, D1 [F3 +X F2 PLS1^ RGATE]
   D3 [STA RGATE] ; RING DOWN DELAY AND TRIGGER
   AQ ; ACQUISITION
   D0 ; RECYLE DELAY
GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
RLS, +X -Y -X +Y
END LISTS

; RECEIVER MODE : RPN OR QPN
; TRIGGER MODE : NT
; REC:F2, DECOUPLER MODE DO
; LQUADF3.PC
; ONEPULSE ACQUISITION ON F3 USING TRIPLET
; TRIPLING MEANS +Y AND -Y SWAPPED
; WITH QUADRATURE PHASE CYCLE

PROT F3
START, D1 [F3 PLS1^ RGATE]
   D3 [STA RGATE] ; RING DOWN DELAY AND TRIGGER
   AQ
   D0 ; ACQUISITION
   ; RECYCLE DELAY
GOTO START

BEGIN LISTS
PLS1, +X+Y-X-Y
RLS, +X-Y-X+Y
END LISTS

; RECEIVER MODE : RPN OR QPN
; TRIGGER MODE : NT
; MUST SET REC:F1, O3 = O1 / 3, SFF3 = SF /3 IN 100 HZ STEPS
B.2.2 Pulse Length Determination

; LVD1.AUM
; TO INCREMENT D1 TO MEASURE PULSE LENGTHS
; USE WITH E.G. HSOLIDC.PC
; A LEWIS JUNE 5 1996

D1=2U ; INITIAL D1
D16=1U ; INCREMENT
RF #1.001

1 ZE
  VDEL = D1
  GO
  WR #1
  IF #1
  D1=D1 + D16 ; INCREMENT D1 BY ADDING D16
  IN=1 ; LOOP TO 1 NE TIMES

EXIT

; L90FS1.PC
; CROSS POLARIZATION PULSE SEQUENCE WITH PHASE ALTERNATION
; CP FROM F3 TO F1, OBSERVE F1
; TRIPLET MEANS F-19 BY F3 HAS +Y AND -Y INTERCHANGED
; DETERMINATION OF 90 DEG F1 PULSE
; A. LEWIS FEB 6 1997

PROT XT

START, 30U
  D11 [F3 PLS1^] ; SOURCE 90 DEGREE
  D5 [F3 -Y F1 PLS2^ RGATE] ; CONTACT PULSE
  2U [RGATE] ; 2 US SWITCHING DELAY
  D1 [F1 @PLS3 RGATE] ; F1 90 DEG PULSE
; NOTATION IMPORTANT FOR SMALL PULSES (> 0.7 US)
  D3 [RGATE STA] ; DEAD TIME DELAY
  AQ ; USE NT FOR ACQUISITION
  D0 ++ PLS3 ; INCREMENT PULSE LIST 3,
  GOTO START ; AND RECYCLE DELAY

BEGIN LISTS
PLS1, +X -X
PLS2, +X +X +Y +Y -X -X -Y -Y
PLS3, -Y -Y +X +X +Y +Y -X -X
RLS, +X -X +Y -Y -X +X -Y +Y

END LISTS

; RECEIVER MODE : RPN, TRIGGER MODE : NT
; DECOUPLER MODE : DO, NS=8*N
; L180FSI.PC
; CROSS POLARIZATION PULSE SEQUENCE WITH PHASE ALTERNATION
; DETERMINATION OF 180 DEG F1 PULSE WITH CP FROM F3
; FOR F-19 ON F3 SO TRIPLER -Y AND +Y INTERCHANGED
; A. LEWIS FEB 6 1997

PROT XT

START, D11 [F3 PLS1*] ; SOURCE 90 DEGREE
D5 [F3 -Y F1 PLS2* RGATE] ; CONTACT PULSE
2U ; 2 US SWITCHING DELAY
D1 [F1 @PLS3 RGATE] ; OBSERVED 90 DEG PULSE

; NOTATION IMPORTANT FOR SMALL PULSES (> 0.7 US)
2U
D2 [F1 @PLS3 RGATE] ; OBSERVED 180 PULSE
D3 [RGATE STA] ; DEAD TIME DELAY
AQ ; USE NT FOR ACQUISITION
D0 ++ PLS3 ; INCREMENT PULSE LIST 3,

GOTO START

BEGIN LISTS
PLS1, +X-X
PLS2, +X +X +Y +Y -X -X -Y -Y
PLS3, -Y -Y +X +X +Y +Y -X -X
RLS, +X -X +Y -Y -X +X -Y +Y

END LISTS

; RECEIVER MODE : RPN
; TRIGGER MODE : NT
; DECOUPLER MODE: DO
; NS=8*N
B.2.3 Relaxation Time Measurements

; CPTONE.PC
; T1 RELAXATION USING CP FROM F2 TO F1
; SEE TORCHIA D.A., J.M.R., 30, (1978), 613-616

PROT XT

START,
D0 [RGATE] ; RELAXATION
D11 [F2 PLS1^] ; 90 DEG. PROTON PULSE
D5 [F1 +X F2 -Y RGATE] ; CONTACT PULSE
D1 [F1 +Y] ; 90 DEG. F1 PULSE
LOOP 1000 TIMES ; FOR LONG T1
VD ; VAR DELAY SET IN MILLISECS IN VD LIST
END LOOP ; THUS GET VD IN SECONDS
D1 [F1 PLS2^ RGATE] ; RECOVERY PULSE
D3 [F2 -Y RGATE STA] ; DEAD TIME
D7 [F2 -Y] ; OBSERVATION
GOTO START

BEGIN LISTS
PLS1, +X -X
PLS2, +X +X +Y +Y -X -X -Y -Y
RLS, +X -X +Y +Y -X -X +Y +Y
END LISTS

; SET RPN, NT, USE NS = 8*N

; HCPT1RHO.PC
; TO MEASURE F1 T1-RHO USING CP FROM F2 TO F1
; WITH INVERSION OF SPIN TEMPERATURE

PROT XT

START,
D11 [F2 @PLS1] ; F2 90 DEGREE
VD [F2 -Y RGATE]
D5 [F2 -Y F1 @PLS2 RGATE] ; CONTACT TIME
D3 [F2 -Y STA RGATE]
D7 [F2 -Y] ; USE NT FOR ACQUISITION
D0 ++PLS1 ++PLS2 ; RECYCLE DELAY
GOTO START

BEGIN LISTS
PLS1, 4(+X) 4(-X)
PLS2, +X -Y -X +Y +X -Y +X -Y
RLS, +X -Y -X +Y
END LISTS
; RECEIVER MODE: RPN, TRIGGER MODE NT
; DECOUPLER MODE DO, NS=8*N
B.2.4 Cross Polarization Experiments

; HCPCYCL.PC
; CROSS POLARIZATION PULSE SEQUENCE
; POLARIZATION TRANSFER FROM F2 TO F1
; WITH SPIN TEMPERATURE INVERSION
; DECOUPLER POWER LEVEL CAN BE CHANGED

PROT XT
START, 10U [DECPL=S1]
D11 [F2 @PLS1] ; PROTON 90 DEGREE
D5 [F2 -Y F1 @PLS2 RGATE] ; CONTACT TIME
D3 [F2 -Y STA RGATE DECPL=S2]
D7 [F2 -Y] ; USE NT FOR ACQUISITION
D0 ++PLS1 ++PLS2 ; RECYCLE DELAY
GOTO START
BEGIN LISTS
PLS1, 4(+X)4(-X)
PLS2, +X -Y -X +Y -X +Y -X -Y
RLS, +X -Y -X +Y
END LISTS
; RECEIVER MODE: RPN, TRIGGER MODE: NT
; DECOUPLER MODE: DO, NS=8*N

; LVD.AUM
; READ IN VDEL VALUE FROM VD LIST
; AND CHECK VDEL IS LESS THAN D16 SO DON'T FRY ANYTHING
; FOR USE WITH LFSICPD.PC OR ANY CP PROG WITH D17 DELAY INCLUDED

; RF #1.026 ; SET FILE EXTENSION
1 ZE
2 VD ; READ IN NEXT VDEL VALUE FROM VD LIST
D17 = VDEL ; NOW CHECK VDEL IS OK
D16 = 101M ; MAXIMUM ALLOWABLE CONTACT TIME
D17 = D16 - D17 ; IF D17 < 0 SHOULD STOP
; MUST HAVE A DELAY D17 IN THE PULSE PROG !!!!
3 GO
4 WR #1 ; WRITE FILE
5 IF #1 ; INCREMENT EXTENSION
6 IN=1 ; LOOP TO START NE TIMES
EXIT

321
LFSICPD.PC
CROSS POLARIZATION FROM F3 TO F1 FOR F19 TRIPLER AMP
WITH DECOUPLING OF F3 DURING ACQUISITION
TRIPLING OF F3 MEANS -Y = +Y; +Y = -Y
PULSE SEQUENCE WITH QPN AND INVERSION OF SPIN TEMPERATURE
A. LEWIS AUG 8 1997
USE WITH LVD.AUM TO RECORD VARIABLE CONTACT TIME

PROT XT
START, D17
D1 D1 [F3 @PLS1]
VD [F3 +Y F1 @PLS2 RGATE]
D3 [F3 +Y STA RGATE]
D7 [F3 -Y]
D0 ++PLS1 ++PLS2

GOTO START
BEGIN LISTS
PLS1, 4(+X) 4(-X)
PLS2, +X -Y -X +Y +X -Y +X -Y
RLS,  +X -Y -X +Y
END LISTS
; RECEIVER MODE: RPN ; REC=F1
; TRIGGER MODE NT
; NS=8*N

; DELAY TO TRAP LONG VD VALUES
; SOURCE 90 DEGREE
; CONTACT TIME
; TRIGER RECEIVER
; DECOUPLE DURING ACQUISITION
; RECYCLE DELAY
B.1.4 INADEQUATE Experiments

; HINADMAS.PC
; CP INADEQUATE PULSE PROGRAM FOR CPMAS SPECTROSCOPY
; H.GRONDEY AND R.BENN
; MPI FUER KOHLENFORSCHUNG, MUELHEIM A.D.RUHR

PROT NONE
START, 10U [DECPL=S1]
   D11 [F2 PLS1^ RGATE]
   D5  [F1 PLS3^ F2 @PLS2 RGATE]
   D6  [DECPL=S2 F2 @PLS2 RGATE] ; (2N+1)/4J DELAY
   D2  [F1 PLS5^ RGATE] ; 180 DEGREE PULSE
   D6  [F2 @PLS2 RGATE]
   D1  [F1 PLS4^ RGATE]
   D4  [F2 @PLS2 RGATE] ; 3U DELAY
   D10 [F1 PLS6^ RGATE]
   D3  [F2 @PLS2 STA RGATE]
   D7  [F2 PLS2^]
   D0  [RGATE]
GOTO START

BEGIN LISTS
PLS1,  32 (+X -X)
PLS2,  -Y
PLS3,  8 (-Y) 8 (+X) 8 (+Y) 8 (-X)
      8 (+Y) 8 (-X) 8 (-Y) 8 (+X)
PLS4,  +X +X +X +X +X +X +X +X
      +Y +Y +Y +Y +Y +Y +Y +Y
PLS5,  +X +X +X +X -X -X -X -X
      +Y +Y +Y +Y -Y -Y -Y -Y
PLS6,  +X +Y -X -Y +X +Y -X -Y
      -X -Y +X +Y -X -Y +X +Y
RLS,   +X -Y -X +Y
END LISTS

; RECEIVER PHASE: RPN, NS=64*N
; LINAD2D.PC
; INADEQUATE PULSE PROGRAM FOR F1
; DECOUPLING F3
; A. LEWIS MAY 6 1998 AFTER H.GRONDEY AND R.BENN
; MPI FUER KOHLENFORSCHUNG, MUELHEIM A.D.RUHR
; SEE BAX ET AL J.A.C.S. (1980) 102, 4829

PROT F1
START, D1 [F1 PLS1^ RGATE] ; INITIAL 90
  D6 [F3 +X RGATE] ; (2N+1)/4J DELAY
  D2 [F1 PLS3^ RGATE] ; 180 DEGREE PULSE
  D6 [F3 +X RGATE]
  D1 [F1 PLS2^ RGATE]
  D4 [F3 +X RGATE] ; 3U DELAY
  D10 [F1 PLS4^ RGATE] ; 135 DEGREE PULSE
  D3 [F3 +X STA RGATE]
  AQ [F3 +X]
  D0 [RGATE]
GOTO START

BEGIN LISTS
PLS1, 8 (+X) 8 (+Y) 8 (-X) 8 (-Y)
PLS2, 8 (+X) 8 (+Y) 8 (-X) 8 (-Y)
PLS3, +X +X +X -X -X -X +X +X
  +Y +Y +Y -Y -Y -Y +Y +Y
PLS4, +X +Y -X -Y +X +Y -X -Y
  -X -Y +X +Y -X -Y +X +Y
RLS, +X -Y -X +Y
END LISTS
; RECEIVER PHASE: RPN, USE NT, NS = 32 * N
; SET SW1=SW2, SI=TD, USE H2DAQ.AUM TO INCREMENT D4
; SET ND4=1 SO D4 INCREMENTED BY IN FROM 3U ONCE EACH EXPT
; H2DAQ.AUM
; STANDARD 2D ACQUISITION PROGRAM

D4 = 3U ;RESET TO 3U!
1  ZE
2  GO
3  WR #1
4  IF #1
5  I4
6  IN=1
7  EXIT

; HCOMBINE.AUM
; TO ADD TWO SERIAL FILES
; FILES #1 + #3 = #4 ARE SERIAL FILES
; SET DC=1 SO FILES ARE ADDED

1  RE #1 ; FIRST SERIAL FILE
WR #2 ; TEMPORARY 1D FILE
RE #3 ; SECOND SERIAL FILE
AT #2
WR #4 ; OUTPUT FILE
IF #1
IF #3
IF #4
2  IN=1
EXIT

LADDSMX.AUM
; TO ADD TWO .SMX 2D FILES
; FILES #1,3 AND 4 ARE .SMX FILES!!!
; FILE # 2 (TEMPORARY FILE) MUST BE NORMAL FILE E.G. JUNK
; SO ADD .SMX TO THE FILENAMES WHEN ENTERING THEM
; SET DC = 1 SO ADD FILES!
; SET NE EQUAL TO S11 SO CORRECT NUMBER OF ROWS

1  RSR #1 ; READ SUB ROW
WR #2 ; WRITE TEMPORARY SUB ROW FILE
RSR #3 ; READ SECOND SMX FILE
AT #2 ; ADD TWO SUB ROWS
WSR #4 ; OUTPUT SMX FILE
IF #1 ; INCREMENT FILE EXTENSIONS
IF #3
IF #4
2  IN=1 ; LOOP TO 1 NE TIMES
EXIT
B.2.6 REDOR Experiments

; LRREDIF.PC
; A LEWIS OCT 24 1995
; 1-D REDOR PULSE SEQUENCE
; FOR F1 - F2/F3 FREQUENCIES, E.G. F-19 AND SI-29
; ALLOWS DIFFERENT PULSE LENGTHS ON F1 & F2
; 180 PULSES ON UNOBSERVED NUCLEI
; AT 1/2 AND FULL ROTOR PERIODS
; WITHOUT PRESATURATION
; USE LRREDCAL.AUM TO CALC DELAYS D3, D22, D23 AND D24

PROT ALL
START, 10U
D1 [F3 +X F2 @PLS1 RGATE]
D22
D12 [F1 @PLS2 RGATE]
LOOP C1 TIMES ; N = 2*C1 + 2
D23
D12 [F1 @PLS3 RGATE]
D23
D12 [F1 @PLS2 RGATE]
END LOOP
D24
D2 [F3 +X F2 @PLS4 RGATE]
D24
LOOP C1 TIMES
D12 [F1 @PLS2 RGATE]
D23
D12 [F1 @PLS3 RGATE]
D23
END LOOP
D12 [F1 @PLS2 RGATE]
D22
D3 [STA RGATE] ; MAKE D3=D1/2 AND USE NT
D7
LOOP C2 TIMES
D0
END LOOP
++PLS1
++PLS2
++PLS3
++PLS4
GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
PLS2, +X
PLS3, +Y
PLS4, +Y +X -Y -X
RLS, +X -Y -X +Y
END LISTS
; TRIGGER MODE NT, REC = F2, USE RPN
; TO CALCULATE DELAYS USE LREDCAL.AUM
; D23 = [T(ROT)-2*D12]/2
; D22 = [T(ROT)-D1-D12]/2
; D24 = [T(ROT)-D2-D12]/2

; LREDCAL.AUM
; A LEWIS OCT 12 1995
; MICROPROGRAM TO CALCULATE DELAYS FOR REDOR EXPERIMENT
; TO BE USED IN CONNECTION WITH LREDFF1F2.PC AND LREDSIF.PC
; 180 PULSES ON F1 AT 1/2 AND FULL ROTOR PERIODS
; ENTER D1 (F2 90), D2 (F2 180)
; AND D12 (F1 180) AND K3 SPINNING FREQ BEFORE RUNNING THIS!!!

C2 = 2
C3 = 50 ; FOR PRESATURATION
D13 = 1M
D14 = D13 / K3 ; TIME FOR ONE ROTOR PERIOD
; K3 IS THE SPINNING FREQUENCY IN KHZ
D15 = D1 + D12
D16 = D15 / C2 ; D1/2 + D12/2
D17 = D12 / C2 ; D12/2
D19 = D2 / C2 ; D2/2
D20 = D17 + D19 ; D12/2 + D2/2
D18 = D14/C2 ; 1/2 OF ROTATIONAL PERIOD ; NOW CALC DELAYS USED IN
PULSE PROG
D3 = D1 / C2 ; D1/2
D22 = D18 - D16 ; T/2 - D1/2 - D12/2
D23 = D18 - D12 ; T/2 - D12
D24 = D18 - D20 ; T/2 - D12/2 - D2/2

EXIT
; LREDOR.AUM
; A LEWIS JAN 14 1996
; TO RECORD SERIES OF REDOR FID'S
; RECORDS TWO SPECTRA OFF AND ON RES
; READS IN OFFSET VALUES FROM OFFSET LIST
; INCREMENTS C1 (N=2C1 +2)
; OFFSET LIST MUST HAVE 2 OF EACH OFFSET !!!!

C1=6 ; SET INITIAL C1 VALUE

RF #1.010
RF #2.010
2 ZE
O1 ; READ IN OFF RES O1 VALUE
O1 ; READ IT IN AGAIN
II ; INITIALISE INTERFACE
GO
WR #1
IF #1
ZE
O1 ; READ IN ON RES O1 VALUE
O1 ; READ IT IN AGAIN
II ; INITIALISE INTERFACE
GO
WR #2
IF #2
3 IC1 ; INCREMENT C1 BY IC1
4 IN=2 ; LOOP NE TIMES
EXIT
; LREDF3F1_PC
; A LEWIS JAN 12 1996
; 1-D REDOR SEQUENCE
; FOR F1 - F2/F3 FREQUENCIES, E.G. F-19 AND SI-29
; ALL PULSES ON OBSERVED NUCLEI (F2/F3) EXCEPT ONE
; 180 PULSES AT 1/2 AND FULL ROTOR PERIODS
; ALLOWS DIFFERENT PULSE LENGTHS ON F1 & F2/F3
; USES PRESATURATION
; USE LREDCAL2.AUM TO CALC DELAYS D3, D22, D23 AND D24

PROT ALL

START, 10U
LOOP C3 TIMES ; SET C3 = 50
   D1 [F3 +X F2 +X RGATE]  
   1M ; 1 MS DELAY
END LOOP ; PRESATURATION
   D0 ; RELAXATION DELAY SET TO 1 * T1
   D1 [F3 +X F2 @PLS1 RGATE]  
   D22 
   D2 [F3 +X F2 @PLS2 RGATE]  
   LOOP C1 TIMES ; N = 2*C1 + 2
      D23
   D2 [F3 +X F2 @PLS3 RGATE]  
      D23
   D2 [F3 +X F2 @PLS2 RGATE]  
   END LOOP
   D24
   D12 [F1 @PLS4 RGATE] ; SINGLE 180 ON UNOBSERVED
      D24
   LOOP C1 TIMES
   D2 [F3 +X F2 @PLS2 RGATE]  
      D23
   D2 [F3 +X F2 @PLS3 RGATE]  
      D23
   END LOOP
   D2 [F3 +X F2 @PLS2 RGATE]  
      D22
   D3 [STA RGATE] ; MAKE D3=D1/2 AND USE NT
       D7
       10M ; DELAY
       ++PLS1
       ++PLS2
       ++PLS3
       ++PLS4
GOTO START

BEGIN LISTS
PLS1, +X -Y -X +Y
PLS2, +X
PLS3, +Y
PLS4, +Y +X -Y -X
RLS, +X -Y -X +Y
END LISTS
; TRIGGER MODE : NT, REC = F2, USE RPN
; TO CALCULATE DELAYS USE LREDCAL2.AUM
; D23 = [T(ROT)-2*D2]/2
; D22 = [T(ROT)-D1-D2]/2
; D24 = [T(ROT)-D2-D12]/2

; LREDCAL2.AUM
; A LEWIS  JAN 12 1996
; MICROPROGRAM TO CALCULATE DELAYS FOR REDOR EXPERIMENT
; TO BE USED IN CONNECTION WITH LSIFRED.PC OR LREDF3F1.PC
; ENTER D1 (F2 90), D2 (F2 180)
; AND D12 (F1 180) AND K3 SPINNING FREQ BEFORE RUNNING THIS!!!

C2 = 2
C3 = 50 ; FOR PRESATURATION
D13 = 1M
D14 = D13/K3 ; =T, TIME FOR ONE ROTOR PERIOD
; K3 IS THE SPINNING FREQUENCY IN KHZ!
D15 = D1 + D2
D16 = D15 / C2
D17 = D12 / C2
D20 = D2 / C2
D21 = D17 + D20
D18 = D14 / C2 ; =T/2, 1/2 OF ROTATIONAL PERIOD
; NOW CALC DELAYS USED IN PULSE PROGRAM
D3 = D1 / C2 ; D1/2
D22 = D18 - D16 ; T/2 - D1/2 - D2/2
D23 = D18 - D2 ; T/2 - D2
D24 = D18 - D21 ; T/2 - D12/2 - D2/2
EXIT
; LRED1.PC
; S(0) EXPERIMENT WITHOUT DEPHASING, USE WITH LRED2.PC
; A LEWIS AUG 15 1997
; REDOR PULSE SEQ WITH CP FROM F3 TO F1 (OBSERVED)
; CP-180-ACQ ON F1 (SPIN TEMP INVERSION)
; WITHOUT DEPHASING 180'S ON F3 (TRIPLED)
; ALLOWS DIFFERENT PULSE LENGTHS ON F1 & F3
; USE LREDCAL5.AUM TO CALC THE DELAYS

PROT XT
START, 5U
  D11 [F3 @PLS1 RGATE] ; INITIAL 90 ON SOURCE
  D5 [F3 +Y F1 @PLS2 RGATE] ; CONTACT TIME
  D22
  D12 [RGATE]
  LOOP C1 TIMES ; N = 2*C1 + 2
    D23
    D12 [RGATE]
    D23
    D12 [RGATE]
  END LOOP
  D24
  D2 [F1 @PLS3 RGATE]
  D24
  LOOP C1 TIMES
    D12 [RGATE]
    D23
    D12 [RGATE]
    D23
  END LOOP
  D12 [RGATE]
  D22
  D3 [STA RGATE] ; MAKE D3=D1/2 AND USE NT
  D7
  D0
  ++PLS1
  ++PLS2
  ++PLS3
GOTO START

BEGIN LISTS
PLS1, 4(+X) 4(-X)
PLS2, +X -Y -X +Y +X +Y
RLS, +X -Y -X +Y
END LISTS
; USE NS = 16 * N AND NT, RPN
; TO CALCULATE DELAYS USE LREDCAL5.AUM
; D22 = T(ROT)/2 -D1/2 - D12/2
; D23 = T(ROT)/2 - D12
; D24 = T(ROT)/2 -D12/2 - D2/2

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; LRED2.PC
; S(F) EXPERIMENT WITH DEPHASING, USE WITH LRED1.PC
; A LEWIS AUG 15 1997
; REDOR PULSE SEQ WITH CP FROM F3 TO F1 (OBSERVED)
; CP-180-ACQ ON F1 (SPIN TEMP INVERSION)
; DEPHASING 180'S ON F3 (TRIPLED)
; ALLOWS DIFFERENT PULSE LENGTHS ON F1 & F3
; USE LREDCAL5.AUM TO CALC THE DELAYS

PROT XT
START, 5U
  D11 [F3 @PLS1 RGATE] ; INITIAL 90 ON SOURCE
  D5 [F3 +Y F1 @PLS2 RGATE] ; CONTACT TIME
  D22
  D12 [F3 +X RGATE]
  LOOP C1 TIMES ; N = 2*C1 + 2
    D23
    D12 [F3 +Y RGATE]
    D23
    D12 [F3 +X RGATE]
  END LOOP
  D24
  D2 [F1 @PLS3 RGATE]
  D24
  LOOP C1 TIMES
    D12 [F3 +Y RGATE]
    D23
    D12 [F3 +X RGATE]
    D23
  END LOOP
  D12 [F3 +Y RGATE]
  D22
  D3 [STA RGATE] ; MAKE D3=D1/2 AND USE NT
  D7
  D0
  ++PLS1
  ++PLS2
  ++PLS3
  GOTO START

BEGIN LISTS
PLS1, 4(+X) 4(-X)
PLS2, +X -Y -X +Y +X +Y
PLS3, +X +Y +X +Y +X -Y -X -Y -X
RLS, +X -Y +X -Y
END LISTS
; USE NS = 16 * N AND NT, RPN
; TO CALCULATE DELAYS USE LREDCAL5.AUM
; D22 = T(ROT)/2 -D1/2 -D12/2
; D23 = T(ROT)/2 - D12
; D24 = T(ROT)/2 -D12/2 - D2/2
; LREDCAL5.AUM
; A LEWIS  AUG 15 1997
; MICROPROGRAM TO CALCULATE DELAYS FOR REDOR EXPERIMENT
; TO BE USED IN CONNECTION WITH LRED1.PC AND LRED2.PC
; 180 PULSES ON F3 AT 1/2 AND FULL ROTOR PERIODS
; ENTER D1 (F1 90), D2 (F1 180), D11 (F3 90), D12 (F3 180)
; AND K3 SPINNING FREQ BEFORE RUNNING THIS!!!

C2 = 2
C3 = 50 ; FOR PRESATURATION
D13 = 1m
D14 = D13 / K3 ; TIME FOR ONE ROTOR PERIOD
                ; K3 IS THE SPINNING FREQ IN KHZ!
D15 = D1 + D12
D16 = D15 / C2 ; D1/2 + D12/2
D17 = D2 + D12
D18 = D17 / C2 ; D2/2 + D12/2
D19 = D14 / C2 ; 1/2 OF ROTATIONAL PERIOD

; NOW CALC DELAYS USED IN PULSE PROG
D3 = D1 / C2 ; D1/2
D22 = D19 - D16 ; T/2-D1/2 - D12/2
D23 = D19 - D12 ; T/2 - D12
D24 = D19 - D18 ; T/2 - D2/2 - D12/2
EXIT
; LREDFID.AUM
; RECORDS CP REDOR S(0) AND S(F) SPECTRA
; READING IN THE PULSE PROGS LRED1.PC AND LRED2.PC
; A LEWIS AUG 15 1997
; FOR CP FROM F3 TO F1, OBSERVE F1, DEPHASING ON F3
; INCREMENTS C1 (N=2*C1), C1 MUST BE >= 1 !!!

C1=0 ; SET INITIAL C1 VALUE, C1>=1 !!
; SET IC1 THE INCREMENT FOR C1 OUTSIDE !!

;RF #1.008 ; RESET FILE EXTENSIONS FOR OFF RES. FID
;RF #2.008 ; RESET FILE EXTENSION FOR ON RES. FID

1 RP LRED1 ; READ IN THE S(0) PULSE PROG
 II ; INITIALISE INTERFACE
 ZE ; ZERO MEMORY
 GO ; ACQUIRE OFF RES FID
 WR #1 ; WRITE OFF RES FID
 IF #1 ; INCREMENT EXTENSION

2 RP LRED2 ; READ IN S(F) PULSE PROG
 II ; INITIALISE INTERFACE
 ZE ; ZERO MEMORY
 GO ; ACQUIRE ON RES FID
 WR #2 ; WRITE ON RES FID
 IF #2 ; INCREMENT EXTENSION

; NOW INCREMENT THE N LOOP COUNTER C1
IC1 ; INCREMENT LOOP COUNTER
IN=1 ; LOOP TO START NE TIMES

EXIT
B.2.7 TEDOR Experiments

; LTEDF1F2.PC
; 1-D TEDOR PULSE PROGRAM
; TRANSFER FROM F1 TO F2/F3 (F-SI)
; PULSES AFTER TRANSFER ARE ON F1 (F)
; 90 DEGREE TIMES SHOULD BE ALMOST EQUAL
; SET D1 = TRUE F1 90 TIME
; AND D2 = TRUE F2/F3 180 TIME
; THEN SET K3 = ROTOR SPEED (KHZ)
; AND RUN TEDORCAL.AUM TO CALCULATE
; DELAYS D3, D23, D24 AND D25

PROT ALL
START, D1 [F1 @PLS1 RGATE]
   D23
   D2 [F3 +X F2 @PLS2 RGATE]
   LOOP C1 TIMES ; N = 2C1+2
       D24
       D2 [F3 +X F2 @PLS6 RGATE]
       D24
       D2 [F3 +X F2 @PLS2 RGATE]
   END LOOP
   D24
   D2 [F3 +X F2 @PLS6 RGATE]
   D25
D2 [F1 @PLS3 F3 +X F2 @PLS2 RGATE]
   D25
   D2 [F3 +X F2 @PLS2 RGATE]
   LOOP C1 TIMES
       D24
       D2 [F3 +X F2 @PLS6 RGATE]
       D24
       D2 [F3 +X F2 @PLS2 RGATE]
   END LOOP
   D24
   D2 [F3 +X F2 @PLS6 RGATE]
   D23
D1 [F1 @PLS5 F3 +X F2 @PLS4 RGATE] ; TRANSFER PULSE
   D23
   D2 [F1 @PLS8 RGATE]
   D24
LOOP C4 TIMES ; M = C4+1
   D2 [F1 @PLS7 RGATE]
   D24
   D2 [F1 @PLS8 RGATE]
   D24
END LOOP
   D2 [F1 @PLS7 RGATE]
   D23
D3 [STA RGATE] ; SET D3=D1/2
   D0 ; AND USE NT
   ++PLS1 ++PLS2 ++PLS3 ++PLS4
BEGIN LISTS
PLS1, +X +X -Y -X -X +Y +Y
PLS2, +X
PLS3, +Y +Y +X +X -Y -Y -X -X
PLS4, +X +X -Y -Y -X -X +Y +Y
PLS5, -Y +Y -X +X +Y -Y +X -X
PLS6, -Y
PLS7, -Y
PLS8, +X
RLS, +X -X -Y +X +Y -Y
END LISTS

; RECEIVER MODE RPN, TRIGGER MODE NT, NS = 8*N
; D3 = D1/2
; D23 = T(ROT)/4 - D2/2 - D1/2
; D24 = T(ROT)/2 - D2
; D25 = T(ROT)/4 - D2

; TEDORCAL.AUM
; MICROPROGRAM TO CALCULATE DELAYS FOR TEDOR EXPERIMENT
; WILL POSITION 180 PULSES AT 1/4 & 3/4 OF THE ROTOR PERIOD
; BEFORE AND AFTER THE COHERENCE TRANSFER
; TO BE USED IN CONNECTION WITH KTEDORS2.PC, HTEDNMV.PC
; LTEDF1F2.PC, TEDF1F2.PC, LTEDF1.PC AND HTEDF1.PC,
; ENTER D1, D2, AND K3 = SPINNING FREQUENCY BEFORE RUNNING THIS

C5 = 2
C2 = 4
C3 = 3
D13 = 1M
D14 = D13/K3 ; T = ROTOR PERIOD
; K3 IS THE SPINNING FREQUENCY IN KHZ
D15 = D1+D2
D16 = D15/C5 ; D1/2 + D2/2
D17 = D14/C2 ; 1/4 OF ROTATIONAL PERIOD
D18 = D14/C5 ; 1/2 OF ROTATIONAL PERIOD

; NOW CALC DELAYS USED IN PULSE PROG
D3 = D1/C5 ; D1/2
D23 = D17 - D16 ; T/4 - D1/2 - D2/2
D24 = D18 - D2 ; T/2 - D2
D25 = D17 - D2 ; T/4 - D2
EXIT
; LIC4.AUM
; TO INCREMENT C4
; FOR VARYING M IN TEDOR EXPERIMENT
; SET C1 AND IC4=1

C4=0 ; SET INITIAL C4 VALUE
RF #1.001 ; RESET FILE EXTENSION
1 ZE
  GO
  WR #1
  IF #1
  IC4 ; INCR. C4 BY IC4
2 IN=1 ; LOOP TO 1 NE TIMES
EXIT

; LIC1.AUM
; INCREMENTS C1 BY IC1
; USE FOR VARYING N IN TEDOR EXPERIMENTS
; SET C4 AND IC1=1

RF #1.001 ; RESET FILE EXTENSION
C1=0 ; SET INITIAL C1 VALUE
1 ZE
  GO
  WR #1
  IF #1
  IC1 ; INCREMENT C1 BY IC1
2 IN=1 ; LOOP TO 1 NE TIMES
EXIT
PROT ALL
START, D1 [F1 @PLS1 RGATE]
   D26
   D2 [F3 +X F2 @PLS2 RGATE]
   LOOP C1 TIMES ; N = 2C1+2
      D27
      D2 [F3 +X F2 @PLS6 RGATE]
      D28
      D2 [F3 +X F2 @PLS2 RGATE]
   END LOOP
   D27
   D26
   D2 [F3 +X F2 @PLS6 RGATE]
   D29
   D2 [F1 @PLS3 F3 +X F2 @PLS2 RGATE]
   D29
   D2 [F3 +X F2 @PLS2 RGATE]
   LOOP C1 TIMES
      D27
      D2 [F3 +X F2 @PLS6 RGATE]
      D28
      D2 [F3 +X F2 @PLS2 RGATE]
   END LOOP
   D27
   D26
   D1 [F1 @PLS5 F3 +X F2 @PLS4 RGATE] ; TRANSFER PULSE
   D23
   D2 [F1 @PLS8 RGATE]
   D24
   LOOP C4 TIMES ; M = C4+1
      D2 [F1 @PLS7 RGATE]
      D24
      D2 [F1 @PLS8 RGATE]
      D24
   END LOOP
   D22
   D2 [F1 @PLS7 RGATE]
   D23
   D3 [STA RGATE] ; SET D3=D1/2
   D0 ; AND USE NT
++PLS1
++PLS2
++PLS3
++PLS4
BEGIN LISTS
PLS1, +X +X -Y -Y -X -X +Y +Y
PLS2, +X
PLS3, +Y +Y +X +X -Y -Y -X -X
PLS4, +X +X -Y -Y -X -X +Y +Y
PLS5, -Y +Y -X +X +Y -Y +X -X
PLS6, -Y
PLS7, -Y
PLS8, +X
RLS, +X -X -Y +Y -X +X +Y -Y
END LISTS

; RECEIVER MODE: RPN, TRIGGER: NT, NS = 8*N
; D3 = D1 / 2
; D23 = T(ROT)/4 - D2/2 - D1/2
; D24 = T(ROT)/2 - D2
; D25 = T(ROT)/4 - D2

; TEDCAL13.AUM
; A. LEWIS AUG 12 1995
; MICROPROGRAM TO CALCULATE DELAYS FOR TEDOR EXPERIMENT
; PULSES AT 1/3, 2/3 BEFORE TRANSFER AND 1/4, 3/4 AFTER TRANSFER
; TO BE USED IN CONNECTION WITH LTEDMOV.BPC
; ENTER D1, D2, AND K3 = SPINNING FREQUENCY BEFORE RUNNING THIS

C5 = 2
C2 = 4
C3 = 3
C6 = 8
C7 = 6
D13 = 1M
D14 = D13/K3 ; = R (K3 IS THE SPINNING FREQ IN KHZ)
D15 = D1 +D2
D16 = D15/C5 ; D16 IS 3/2 OF D1
D17 = D14/C2 ; 1/4 OF ROTATIONAL PERIOD = R/4
D18 = D14/C5 ; 1/2 OF ROTATIONAL PERIOD = R/2
D19 = D14 / C3 ; R/3
D20 = D19 * C5 ; 2R/3
D3 = D1/C5 ; D1/2
D23 = D17 - D16 ; R/4 -D1/2 - D2/2
D24 = D18 - D2 ; R/2 - D2
D25 = D17 - D2 ; R/4 - D2
D26 = D19 - D16 ; R/3 - D1/2 - D2/2
D27 = D20 - D2 ; 2R/3 - D2
D28 = D19 - D2 ; R/3 - D2
D29 = D19 - D2 ; R/3 - D2
EXIT
; LTEDMOVA.PC
; 1-D TEDOR
; TRANSFER FROM F1 TO F2/F3 (F-SI)
; ALLOWS POSITION OF PULSES AFTER TRANSFER TO BE MOVED
; PULSES BEFORE ARE AT 1/4 AND 3/4
; PULSES AFTER TRANSFER ARE ON F1 (F)
; 90 DEGREE TIMES SHOULD BE ALMOST EQUAL
; SET D1 = TRUE F1 90 TIME AND D2 = TRUE F2/F3 180 TIME
; THEN SET K3 = ROTOR SPEED (KHZ)
; AND RUN E.G.TEDCAL15.AUM (PULSES AT 1/5, 4/5)
; TO CALC DELAYS D3, D23, D24 AND D25, D26, D27 AND D28

PROT ALL
START, D1 [F1 @PLS1 RGATE]
D23
D2 [F3 +X F2 @PLS2 RGATE]
  LOOP C1 TIMES ; N = 2C1 + 2
  D24
  D2 [F3 +X F2 @PLS6 RGATE]
  D24
  D2 [F3 +X F2 @PLS2 RGATE]
END LOOP
D24
D2 [F3 +X F2 @PLS6 RGATE]
D25
D2 [F1 @PLS3 F3 +X F2 @PLS2 RGATE]
D25
D2 [F3 +X F2 @PLS2 RGATE]
  LOOP C1 TIMES
  D24
  D2 [F3 +X F2 @PLS6 RGATE]
  D24
  D2 [F3 +X F2 @PLS2 RGATE]
END LOOP
D24
D2 [F3 +X F2 @PLS6 RGATE]
D23
D1 [F1 @PLS5 F3 +X F2 @PLS4 RGATE] ; TRANSFER PULSE
  D26
  D2 [F1 @PLS8 RGATE]
  D27
  LOOP C4 TIMES ; M = C4 + 1
  D2 [F1 @PLS7 RGATE]
  D28
  D2 [F1 @PLS8 RGATE]
  D27
END LOOP
D2 [F1 @PLS7 RGATE]
D26
D3 [STA RGATE] ; SET D3 = D1/2
D0 ; AND USE NT
++PLS1
++PLS2
++PLS3
++PLS4

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BEGIN LISTS
PLS1, +X +X -Y -X +Y +Y
PLS2, +X
PLS3, +Y +Y +X +X -Y -Y -X -X
PLS4, +X +X -Y -Y -X -X +Y +Y
PLS5, -Y +Y -X +X +Y -Y +X -X
PLS6, -Y
PLS7, -Y
PLS8, +X
RLS, +X -X -Y +Y -X +X +Y -Y
END LISTS

; RECEIVER MODE: RPN, TRIGGER: NT, NS = 8 * N

; TEDCAL15.AUM  A. LEWIS AUG 13 1995
; MICROPROGRAM TO CALCULATE DELAYS FOR TEDOR EXPERIMENT
; PULSES AT 1/4, 3/4 BEFORE TRANSFER AND 1/5, 4/5 AFTER TRANSFER
; TO BE USED IN CONNECTION WITH LTEDMOVA.PC
; ENTER D1, D2, AND K3 = SPINNING FREQUENCY BEFORE RUNNING THIS

C5 = 2
C2 = 4
C3 = 3
C8 = 5
C6 = 8
C7 = 6
D13 = 1M
D14 = D13/K3 ; = R (K3 IS THE SPINNING FREQ IN KHZ)
D15 = D1 + D2
D16 = D15/C5 ; D16 IS 3/2 OF D1
D17 = D14/C2 ; 1/4 OF ROTATIONAL PERIOD = R/4
D18 = D14/C5 ; 1/2 OF ROTATIONAL PERIOD = R/2
D19 = D14/C8 ; R/5
D20 = D19 * C3 ; 3R/5
D21 = D19 * C5 ; 2R/5
D3 = D1/C5 ; D1/2
D23 = D17 - D16 ; R/4 - D1/2 - D2/2
D24 = D18 - D2 ; R/2 - D2
D25 = D17 - D2 ; R/4 - D2
D26 = D19 - D16 ; R/5 - D1/2 - D2/2
D27 = D20 - D2 ; 3R/5 - D2
D28 = D21 - D2 ; 2R/5 - D2

EXIT
; LREFTED.PC
; 1-D REFOCUSED TEDOR
; TRANSFER FROM F3 TO F1 USING TRIPLER ON F3
; SO F3 +Y AND -Y PHASES ARE INTERCHANGED
; A. LEWIS JAN 12 1998
; PHASE CYCLING AS FOR REFOCUSED INEPT
; DEPHASING BEFORE TRANSFER ON F1 AT 1/4 3/4, N=2C1+2
; DEPHASING AFTER TRANSFER ON F3 AT 1/4, 3/4, M=2C4+2
; ALLOWS DIFFERENT PULSE LENGTHS ON F1 AND F3
; D1 = F1 90, D2 = F1 180, D11 = F3 90, D12 = F3 180
; SET K3 = ROTOR SPEED (KHZ), USE LRTCAL.AUM TO CALC
; DELAYS D22, D23, D24, D25, D26, D27, D28, AND D29

PROT ALL
START, D11 [F3 @PLS1 RGATE] ; INITIAL 90 PULSE
   D22 [F1 +X] ; T/4
   LOOP C1 TIMES ; N = 2C1+2
      D23
      D2 [F1 +Y RGATE]
      D23
      D2 [F1 +X RGATE]
   END LOOP
   D23
   D2 [F1 +Y RGATE]
   D24
D2 [F3 @PLS2 F1 @PLS3 RGATE] ; SIMULTANEOUS 180 TO REFOCUS
   D24
   D2 [F1 +X RGATE]
   LOOP C1 TIMES
      D23
      D2 [F1 +Y RGATE]
      D23
      D2 [F1 +X RGATE]
   END LOOP
   D23
   D2 [F1 +Y RGATE]
   D25
D1 [F3 @PLS4 F1 @PLS5 RGATE] ; COHERENCE TRANSFER
   D26
   D12 [F3 +X RGATE] ; NOW DEPHASING ON F3
   LOOP C4 TIMES ; M = 2C4+2
      D27
      D12 [F3 +Y RGATE]
      D27
      D12 [F3 +X RGATE]
   END LOOP
   D27
   D12 [F3 +Y RGATE]
   D28
D2 [F3 @PLS2 F1 @PLS6 RGATE] ; SIMULTANEOUS 180 TO REFOCUS
   D28
   D12 [F3 +X RGATE]
   LOOP C4 TIMES
      D27

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D12 [F3 +Y RGATE]
D27
D12 [F3 +X RGATE]
END LOOP
D27
D12 [F3 +Y RGATE]
D29
D3 [STA RGATE] ; SET D3=D1/2 AND USE NT
AQ ; ACQUIRE ECHO
D0 ; RELAXATION DELAY RECYCLE ON 5*T1 (F3)
++PLS1
++PLS2
++PLS3
++PLS4
++PLS5
++PLS6
GOTO START

BEGIN LISTS
PLS1, 8(+X) 8(-X)
PLS2, +X -X
PLS3, +X -X
PLS4, -Y -Y +Y +Y
PLS5, 4(+X) 4(+Y) 4(-X) 4(-Y)
PLS6, +X -X +X -X +Y -Y +Y -Y
RLS, +X +X -X -X +Y +Y -Y -Y
END LISTS

; RECEIVER MODE: RPN, REC:F1
; TRIGGER MODE: NT
; NS = 16*N
MICROPROGRAM TO CALCULATE DELAYS FOR REFOC. TEDOR EXPERIMENT
TO BE USED WITH LRDFTED.PC
F1 AND F3 PULSES ARE SIMULTANEOUS!!
ENTER D1 (F1 90), D2 (F1 180), D11 (F3 90), D12 (F3 180)
AND K3 = SPINNING SPEED IN KHZ, BEFORE RUNNING THIS

C5 = 2
C2 = 4
D13 = 1M
D14 = D13 / K3 ; ONE ROTOR PERIOD
D3 = D1 / C5 ; D1/2
D17 = D2 / C5 ; D2/2
D16 = D14 / C2 ; 1/4 ROTOR CYCLE
D15 = D14 / C5 ; 1/2 ROTOR CYCLE
D21 = D11 / C5 ; D11/2
D29 = D12 / C5 ; D12/2

; NOW CALC DELAYS USED IN PULSE PROG
D22 = D16 - D21 ; T(ROT)/4 - D11/2 - D2/2
D23 = D15 - D2 ; T(ROT)/2 - D2
D24 = D16 - D2 ; T(ROT)/4 - D2
D25 = D16 - D17 ; T(ROT)/4 - D2/2 - D1/2
D26 = D16 - D3
D27 = D15 - D12 ; T(ROT)/2 - D12
D28 = D16 - D29
D29 = D29 - D17 ; T(ROT)/4 - D12/2 - D2/2
D29 = D29 - D21 ; T(ROT)/4 - D12/2 - D11/2

EXIT
FUNCTIONS AND *MATHEMATICA* CODE FOR FITTING DATA FROM CROSS POLARIZATION, REDOR AND TEDOR NMR EXPERIMENTS

Functions used to fit data from Hartmann-Hahn CP, REDOR and TEDOR experiments are presented in this appendix. Details of the fitting and the code used to perform this in the *Mathematica* programming environment are also given where appropriate.
C.1 HARTMANN-HAHN CROSS POLARIZATION

C.1.1 Cross Polarization Behavior for Isolated IS Spin Pairs

C.1.1.1 Functions Used To Describe HHCP Behavior

The Hartmann-Hahn cross polarization (HHCP) behavior for isolated IS spin pairs in a polycrystalline (powder) sample is described in Chapter 3. The signal intensity of the S spins, $M(t)$, following HHCP for a contact time $\tau$ is defined by Eq. C.1 where $M_0$ is the net magnetization of the I spins following the initial $\pi/2$ pulse.

$$M(t) = M_0 \left( \frac{1}{2} - \frac{g_f(\tau)}{2} \right)$$  \hspace{1cm} \text{(C.1)}

For a powder sample

$$g_f(\tau) = \frac{1}{2} \int_0^\pi \cos \left( |b_f| \tau \right) \sin \theta \ d\theta$$  \hspace{1cm} \text{(C.2)}

where $f$ indicates the precise Hartmann-Hahn matching condition ($\omega_{1l} - \omega_{1s} = f\omega_0$), and the functions $b_f$ are defined in Eqs. 3.4, 3.12 and 3.13. For a stationary (non-spinning) sample there is only a single matching condition; $f = 0$. Under MAS there are four sideband matching conditions ($f = \pm 1, f = \pm 2$) separated by the spinning speed $\omega_0$. Note that it is only necessary to perform the integration over a single angle $\theta$ to produce the powder average since it is not possible to detect the phase of the dipolar coupling.

The functions $g_f(\tau)$ for the five possible matching conditions are given in Table C.1 and can be evaluated using numerical integration but this does not permit efficient nonlinear fitting of the function. However, using the methodology reported by Mueller, it is possible to express $g_f(\tau)$ in terms of Bessel functions of the first kind. These functions were derived for the five possible matching conditions and are given in Table C.1. The Mathematica code used to determine the theoretical HHCP behavior for isolated IS spin pair in terms of both numerical...
Table C.1 Functions $g_r(\tau)$ which describes the Hartmann–Hahn cross polarization behaviour for isolated $IS$ spin pairs in a powder sample at various matching conditions, $f$. The functions are expressed as exact integrals and in terms of Bessel functions of the first kind. $D$ is the heteronuclear dipolar coupling in Hz, and $\tau$ is the contact time in seconds.

<table>
<thead>
<tr>
<th>Matching Condition</th>
<th>Exact Integral</th>
<th>$g_r(\tau)$</th>
<th>Bessel Functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 \hspace{1em} (STATIC)</td>
<td>[ \frac{1}{2} \int_0^{\pi} \cos \left( \frac{\pi D \tau}{2} \left( 3 \cos^2 \theta - 1 \right) \right) \sin \theta , d\theta ]</td>
<td>[ \cos \left( \frac{\pi D \tau}{2} \right) J_0 \left( \frac{3\pi D \tau}{2} \right) - 2 \sum_{k=1}^{\infty} \frac{1}{(4k^2 - 1)} J_k \left( \frac{3\pi D \tau}{2} \right) \cos \left( \frac{\pi D \tau}{2} + \frac{k\pi}{2} \right) ]</td>
<td></td>
</tr>
<tr>
<td>$\pm 1 \hspace{1em} (MAS)$</td>
<td>[ \frac{1}{2} \int_0^{\pi} \cos \left( \frac{\pi D \tau}{\sqrt{2}} \sin 2\theta \right) \sin \theta , d\theta ]</td>
<td>[ J_0 \left( \frac{\pi D \tau}{\sqrt{2}} \right) + 2 \sum_{k=1}^{\infty} \frac{1}{(1 - 4(2k)^2)} J_{2k} \left( \frac{\pi D \tau}{\sqrt{2}} \right) ]</td>
<td></td>
</tr>
<tr>
<td>$\pm 2 \hspace{1em} (MAS)$</td>
<td>[ \frac{1}{2} \int_0^{\pi} \cos \left( \frac{\pi D \tau}{2} \sin^2 \theta \right) \sin \theta , d\theta ]</td>
<td>[ \cos \left( \frac{\pi D \tau}{2} \right) J_0 \left( \frac{\pi D \tau}{2} \right) - 2 \sum_{k=1}^{\infty} \frac{(-1)^k}{(1 - 4k^2)} J_k \left( \frac{\pi D \tau}{2} \right) \cos \left( \frac{\pi D \tau}{2} + \frac{k\pi}{2} \right) ]</td>
<td></td>
</tr>
</tbody>
</table>
integration and Bessel functions of the first kind is outlined below using the static ($f = 0$)
matching condition in the absence of relaxation as an example.

Define the function $\text{StatPowder}$ which corresponds to numerical integration of Eq. C.1.

$\text{StatPowder}$ utilizes the numerical integration routine $\text{NIntegrate}$ provided with $\text{Mathematica}$,
and because $\text{Mathematica}$ requires arguments for trigonometric functions to be in radians, the $D t$
/ 2 term in Eq. C.2 has been multiplied by $2\pi$.

$$\text{StatPowder}[d_, t_] := N[0.5 - 0.25 \times \text{NIntegrate[}
                          \cos[d \times t \times \pi \times (3 \times \cos[e] \times \cos[e] - 1)] \times \sin[e],
                          \{e, 0, \pi\}]);$$

A list of data points (list3) is generated using $\text{StatPowder}$ and a plot of these versus the
dimensionless parameter $D \tau$ is generated (plot3).

$$\text{maxtime} = \frac{10}{1000}; \text{numpoints} = 30; \text{incr} = N\left[\frac{\text{maxtime}}{\text{numpoints}}\right];$$
$$\text{dip} = 1000; \text{list3} = \{(0, 0)\}; \text{time} = \text{incr}; i = 2;$$

$$\text{Do[AppendTo[list3, \{(dip \times \text{time}, \text{StatPowder}[dip, \text{time}])\}];}
        \text{time} = \text{time} + \text{incr}; i = i + 1, \{\text{numpoints}\};$$

$$\text{plot3} = \text{ListPlot[list3, \text{PlotJoined} \to \text{False},}
                        \text{Prolog} \to \text{AbsolutePointSize[5]},
                        \text{PlotRange} \to \{(0, \text{maxtime} \times \text{dip}), (0, 1)\},
                        \text{PlotLabel} \to \text{"Static Powder - no relaxation"},
                        \text{AxesLabel} \to \{\text{"D t"}, \text{"\text{"}}\}$$

Define a function $\text{StatPowBess}$ describing Eq. C.1 in terms of Bessel functions as given in Table
C.1:

$$\text{StatPowBess}[d_, t_] :=
N[0.5 - 0.5 \left(\cos[\pi \times \frac{d}{2} \times t] \times \text{BesselJ}[0, 3 \times \pi \times \frac{d}{2} \times t]\right) +
\text{Sum}[\frac{1}{(4k^2 - 1)} \times \cos[\pi \times \frac{d}{2} \times t + \frac{k \times \pi}{2}] \times \text{BesselJ}[k, 3 \times \pi \times \frac{d}{2} \times t],
(k, 1, 5)]]$$
Here \( d \) is the \( I_S \) heteronuclear dipolar coupling in Hz, \( t \) is the contact time in seconds, and the variable \( k \) determines the number of Bessel functions to include in the sums. Mueller\(^5\) had suggested that including five terms provides sufficient accuracy and thus \( k = 5 \) was used in this case. Note that the cosine argument in the Bessel functions must be converted to radians by introducing an additional factor of \( 2\pi \).

A list is generated using StatPowBess and the results plotted as described above for the numerical integration. The resulting two plots are overlaid and show exact agreement as seen in Figure C.1. Similar analysis was carried out to check the validity of all expressions derived in terms of Bessel functions, and to confirm that the functions used to analyze the experimental CP, REDOR and TEDOR data were in agreement with those reported in the literature.

![Figure C.1 Theoretical Hartmann-Hahn cross polarization behavior calculated for an isolated \( I_S \) spin pair in a static powder sample \((f = 0)\) using numerical integration of Eq. C.1 (filled circles) and in terms of Bessel functions (curve). No relaxation effects have been included.](image-url)
C.1.1.2 Nonlinear Least Squares Fitting of Experimental HHCP Data

In this section the steps required for performing visual and nonlinear least squares fitting of the experimental HHCP data in the Mathematica programming environment are outlined in detail using the function for a non-spinning powder sample \((f = 0)\) as an example. The code given is for Mathematica version 3.0, and the effects of relaxation have been included as described in Section 3.3. The equations describing the other matching conditions given in Table C.1 may also be used once the appropriate functions have been defined.

First set the text style for plots and load the package required for nonlinear regression analysis:

```mathematica
TextStyle = {FontFamily -> "Times"};
<< Statistics'NonlinearFit`
```

Next define a list `StatData1` containing the experimental data points and plot the data as an object called `plotStat1`. In this case the data are in the form \{(contact time (ms), peak area)\}.

```mathematica
StatData1 = {{0, 0}, {1.2, 97.8}, {6.0, 103.6}, {0.2, 34.5}, {2.2, 103.5}, {3.2, 97.3}, {4.25, 102.9}, {5.25, 104.4}, {0.4, 84.4}, {1.4, 88.8}, {2.4, 103.5}, {3.4, 97.8}, {1.9, 90.9}, {2.0, 98.4}};

plotStat1 = ListPlot[StatData1, PlotJoined -> False, Prolog -> AbsolutePointSize[5], PlotRange -> All, PlotLabel -> "Static CP", AxesLabel -> {"Time/ms", ""}]
```

Now define the equation `StatBessRelax` which describes the HHCP behavior for a static powder \((f = 0)\) with full relaxation (Eq. 3.14) in terms of Bessel functions. Here \(d\) is the \(I-S\) heteronuclear dipolar coupling, \(t\) is the contact time, \(m\) is a scaling factor to match the experimental and theoretical intensities, \(S\) \((0.5 \leq S \leq 1)\) is the parameter defining the degree of isolation of the \(I\) spins, \(r_1\) and \(r_2\) are the parameters describing the relaxation, \(t_1r\) is the spin-
lattice relaxation of the $I$ nuclei in the rotating frame, and the variable $k$ determines the number of Bessel functions to include in the sums (five in this case).

\[
\text{StatBessRelax}[d_, t_, m_, S_, r1_, r2_, tlr_] := N[m \cdot \exp\left[ -\frac{t}{tlr} \right] \cdot \\
\left( 0.5 - 0.5 \cdot \exp\left[ -\frac{t}{r1} \right] \cdot \left( \cos\left[ \frac{\pi dt}{2} \right] \cdot \text{BesselJ}\left[0, \frac{3\pi dt}{2}\right] \right) - \\
2 \cdot \sum_{k=1}^{5} \left( \cos\left[ \frac{\pi dt}{2} + \frac{k\pi}{2} \right] \cdot \text{BesselJ}\left[k, \frac{3\pi dt}{2}\right] \cdot \frac{1}{4k^2 - 1} \right) + \\
\left( (S - 0.5) \cdot \left( 1 - \exp\left[ -\frac{t}{r2} \right] \right) \right) \right];
\]

Visual fitting of the experimental data is then carried out to determine appropriate values for the various parameters. First the parameters are assigned values and a list $\text{stat1}$ is created. Note that several parameter values are divided by a factor of 1000 to convert them from milliseconds to seconds. A graph of the theoretical curve is produced ($\text{plotfit1}$) and the plot of the experimental data ($\text{plotStat1}$) overlaid for comparison. The parameters are adjusted until an acceptable match between the experimental and theoretical plots is obtained.

\[
\text{maxtau} = 10000; \text{numpoints} = 100; \text{incr} = \frac{\text{maxtau}}{\text{numpoints}}; \\
\text{dip} = 1442; \text{mag} = 182.5; \text{Seq} = 0.9; \\
\text{ratel} = \frac{2.2}{1000}; \text{rate2} = \frac{26.7}{1000}; \text{tlr} = \frac{2000}{1000}; \\
\text{stat1} = \{\{0, 0\}\}; \text{tau} = \text{incr}; i = 2; \\
\text{Do}[\text{AppendTo}[\text{stat1}, \{\text{tau}*1000, \text{StatBessRelax}[\text{dip}, \text{tau}, \text{mag}, \text{Seq}, \text{ratel}, \text{rate2}, \text{tlr}]\}]; \text{tau} = \text{tau} + \text{incr}; i = i + 1, \{\text{numpoints}\};
\]

\text{plotfit1} = \text{ListPlot}[\text{stat1}, \text{PlotJoined} \to \text{True}, \\
\text{PlotRange} \to \text{All}, \text{AxesLabel} \to \{\"Time/ms\", \"\"\}] \\
\text{Show}[\text{plotStat1}, \text{plotfit1}, \\
\text{Prolog} \to \text{AbsolutePointSize}[5], \text{PlotRange} \to \text{All}]
\]
Using these parameter values as initial starting values, nonlinear least squares fitting of the experimental cross polarization data to determine the $I$-$S$ heteronuclear dipolar coupling $D$ is then performed utilizing the Mathematica procedure `NonlinearRegress` which minimizes the $\chi^2$ merit function.

```mathematica
NonlinearRegress[StatData1,
    StatBessRelax[dc, ct 1000, m, 0.9, r1, r2, 2000],
    ct, {ct, 1446}, {m, 182}, {r1, 2.26 1000}, {r2, 25 1000},
    Method -> LevenbergMarquardt,
    ShowProgress -> True]
```

The Levenberg-Marquardt algorithm was found to be the most efficient method for the minimum search. In this case not all of the parameters are allowed to vary freely during the fitting; $S$ and $t1r$ were fixed to values of 0.9 and 2 respectively. The output from this procedure are used as input to plot the theoretical curve and compare it to the experimental data as above. The procedure `NonlinearRegress` also generates a regression report containing the best fit parameters, the asymptotic standard errors and confidence interval of the fitted parameters.

### C.1.2 Cross Polarization Behavior in a Network of Strongly Coupled $I$ Spins

The HHCP behavior for spins in a strongly dipolar-coupled network is different from that observed for isolated $IS$ spin pairs. The underlying assumptions and equations describing the intensity of the $S$ spin signal as a function of the contact time are given in Section 3.3.3. If $T_{1p}$ of the $S$ spins is much longer than that of the $I$ spins then $T_{1p}(I)$ dominates the decay and a function of the form given in Eq. 3.15 can be used to fit the experimental HHCP data. Below is the `Mathematica` function `epfunc` which was used for nonlinear least squares fitting of HHCP data when the there was a network of strongly coupled $I$ spins.
\[
\text{cpfunc}[a_, tcp_, tlrho_, time_] = \\
a * \left( \frac{1}{tcp} \right) \times (\text{Exp}[-time / tlrho] - \text{Exp}[-time / tcp]) ;
\]

Here \(a\) is a scaling factor to match experimental and theoretical intensities, \(tcp\) defines the time constant describing the build-up of magnetization due to polarization transfer, \(tlrho\) defines (exponential) decay in rotating frame, and \(time\) is the contact time.

**C.2 ROTATIONAL ECHO DOUBLE RESONANCE**

**C.2.1 REDOR Behavior for Isolated IS Spin Pairs**

The REDOR experiment is described in detail in Section 3.4. The equations and Mathematica scripts used during fitting of the experimental data, and to investigate the theoretical behavior REDOR for different pulse positions and numbers of spins are presented below.

**C.2.1.1 REDOR Functions and Nonlinear Fitting**

The REDOR behavior for an isolated IS spin pair is defined\(^5,6\) by Eq. C.2 where \(\lambda = nD\tau_r\) is a dimensionless parameter which is the product of the number of rotor cycles \(n\), the IS heteronuclear dipolar coupling \(D\), and the rotor period \(\tau_r\).

\[
\frac{\Delta S}{S_0} = 1 - \frac{1}{2\pi} \int_0^\pi \int_0^\pi \cos[\Delta \Phi_R(\alpha, \beta, \lambda)] \sin\beta \ d\beta \ d\alpha 
\]

For a mirror symmetric REDOR pulse sequence with the dephasing pulses positioned at \(t_1\) the dipolar phase accumulated over each rotor period, \(\Delta \Phi_R\), is:\(^5\)
\[ \Delta \Phi_R = \oint_0^{\tau_i} \omega_{\beta}(\alpha, \beta, t) \, dt - \oint_0^{\tau_e} \omega_{\beta}(\alpha, \beta, t) \, dt \]  

where \( \omega_{\beta} \) is defined in Eq. 1.14 and the minus sign reflects the action of the I spin pulse. The complete expression is:

\[ \Delta \Phi_R = \frac{\lambda}{2} \left[ \sin^2 \beta \left( \frac{\sin 2 \left( \alpha + \frac{2\pi t_i}{\tau_i} \right) - \sin 2 \alpha}{2\sqrt{2}} \sin 2 \beta \left( \frac{\sin \left( \frac{2\pi t_i}{\tau_i} \right)}{\sqrt{2}} - \sin \frac{\alpha}{\tau_i} \right) \right] - 2 \sqrt{2} \sin^2 \beta \left( \frac{\sin \left( \frac{2\pi t_i}{\tau_i} \right)}{\sqrt{2}} - \sin \frac{\alpha}{\tau_i} \right) \right] \]  

Figure C.2 shows the theoretical REDOR curves calculated for a selection of possible positions of the dephasing pulses. The Mathematica code used to generate the REDOR curves for dephasing pulses applied at position \( \text{fract} (0 < \text{fract} \leq \tau_r/2) \) is given below. In this example 30 points are calculated as a function of the dimensionless parameter \( nD\tau_r \) with the dephasing pulses at \( \tau_r/5 \).

```mathematica
numpoints = 30; max = 6.0; incr = max/numpoints; nDTr = incr;
intlist5 = {{0, 0}};
fract = 1/5;
Do[sf = 1 - (\[Pi]/2) * NIntegrate[ Sin[\[Beta]] *
            Cos[\[Pi]/4] (\[Pi] \[Beta] Sin[\[Beta]] Sin[2 (\[Alpha] + 2 \pi * fract)] - Sin[2 \[Alpha]] -
            2 \[Sqrt]2 Sin[\[Beta]] Sin[\[Alpha] - 2 \pi * fract] - Sin[\[Alpha]])
            + (\[Pi] \[Beta] Sin[\[Beta]] Sin[2 (\[Alpha] - 2 \pi * fract)] - Sin[2 \[Alpha]] -
            2 \[Sqrt]2 Sin[\[Beta]] Sin[\[Alpha] + 2 \pi * fract] - Sin[\[Alpha]])
            )]
            , \[Beta], 0, \[Pi]]], \[Alpha], 0, \[Pi]], AccuracyGoal -> 3];
Print[nDTr, ", ", sf]; AppendTo[intlist5, {nDTr, sf}];
nDTr = nDTr + incr, {numpoints}]
```

When the dephasing pulse are at \( t_i = \tau_r/2 \), Eq. C.4 is simplified considerably and becomes:
Figure C.2 Theoretical REDOR dephasing calculated for an isolated IS spin pair with different placements of the dephasing $\pi$-pulses in a mirror symmetric REDOR sequence. The dephasing pulses occur at $t_1$ (indicated) during the period before the echo-forming $\pi$-pulse and at $\tau_r - t_1$ after. The curves are plotted as a function of the dimensionless parameter $nD\tau_r$. 
\[ \Delta \Phi_R = \lambda \sin \beta \cos \beta \sin \alpha \]  

Mueller reported that Eq. C.5 can be re-expressed in terms of Bessel functions of the first kind as:

\[
\Delta S / S_0 = 1 - \left[ J_0(\sqrt{2} nD\tau_r) \right]^2 + 2 \sum_{k=1}^{\infty} \left\{ \frac{[J_k(\sqrt{2} nD\tau_r)]^2}{(16k^2 - 1)} \right\} \tag{C.6}
\]

The *Mathematica* code defining a function for the theoretical REDOR behavior for an isolated IS spin pair with dephasing pulses applied at \( \tau_r / 2 \) in terms of Bessel functions of the first kind is:

\[
sred[dip_, nTr_] := 1 - \text{BesselJ}[0, \sqrt{2} \dip \cdot nTr]^2 + \text{Sum}[2. \text{BesselJ}[i, \sqrt{2} \dip \cdot nTr]^2 / (16 i^2 - 1.0), \{i, 1, 5\}] ;
\]

where \( \dip \) is the dipolar coupling and \( nTr \) is the product of the number of rotor cycles and the rotor period \( \tau_r \).

Recently Mueller *et al.*\(^5\) reported a further simplification which allows the calculation of \( \Delta S / S_0 \) in terms of Bessel functions of order 1/4 (Eq. C.7).

\[
\Delta S / S_0 = 1 - J_{1/4}(\sqrt{2} nD\tau_r) \cdot J_{1/4}(\sqrt{2} nD\tau_r) \tag{C.7}
\]

The *Mathematica* code defining a function for the theoretical REDOR behavior for an isolated IS spin pair with dephasing pulses applied at \( \tau_r / 2 \) in terms of Bessel functions of order 1/4 is:

\[
\text{newRed}[n_, d_, tr_] := 1 - (\text{BesselJ}[1/4, \text{Sqrt}[2] n d \text{tr}] \times \
\text{BesselJ}[-1/4, \text{Sqrt}[2] n d \text{tr}]) ;
\]

where \( n \) is the number of rotor cycles, \( d \) is the dipolar coupling, and \( \text{tr} \) is the rotor period.
Either of these forms in terms of Bessel functions can be used for efficient nonlinear fitting of the experimental REDOR data in a manner analogous to that described in Section C.1.1.2.

During the fitting procedure two parameters were varied and optimized; one corresponding to the dipolar coupling, and an additional parameter (a scaling factor) to account for incomplete or statistical site occupancies.

**C.2.1.2 The REDOR Transform**

Mueller et al.\(^8\) have reported a new analytical transform which allows the dipolar coupling to be determined directly from REDOR data for isolated IS spin pairs, as described in Section 3.4. The Mathematica code used to perform this is given below. The original code was kindly supplied by Dr. K. Mueller.

First define a list which contains the experimental data in the form \(\{n, S_f/S_0\}\). Note the use \(S_f/S_0\) rather than \(\Delta S/S_0\) so the data decays to zero.

```plaintext
datalist = 
{\{2, 0.101\}, \{4, 0.106\}, \{6, 0.002\}, \{8, 0.072\}, \{10, -0.008\}, \\
{12, 0.053\}, \{14, -0.007\}, \{16, 0.037\}, \{18, -0.001\}, \{20, 0.0242\}
```

Next define apodization function (three-point Blackman-Harris) used to smooth the experimental data and ensure it decays completely to zero:

```plaintext
smooth[dat_, bj_] := Table[{dat[[j, 1]], N[0.424 + 0.497 Cos[Pi j / b] + 
0.079 Cos[2 Pi j / b] dat[[j, 2]]]}, 
{j, 1, Length[dat]}];
```

Apodize the experimental data and zerofill it to 128 rotor periods:

```plaintext
smdata = smooth[datalist, Length[datalist]]; 
zerolist = Table[\{i, 0\}, \{i, 22, 128, 2\}]; 
zf128 = Join[smdata, zerolist];
```
Define the REDOR transform "kernal" function and create a look-up table:

\[
\text{kernreal}[d_, t_] := -((\sqrt{2} \, d \, t) \, A^2 \, \text{BesseU}[-5/4, (\sqrt{2} \, d \, t)] \, \text{BesseU}[-l/4, (\sqrt{2} \, d \, t)] - (\sqrt{2} \, d \, t) \, A^2 \, \text{BesselJ}[-3/4, (\sqrt{2} \, d \, t)] \, \text{BesselJ}[l/4, (\sqrt{2} \, d \, t)] + (\sqrt{2} \, d \, t) \, A^2 \, \text{BesselJ}[1/4, (\sqrt{2} \, d \, t)] ^2 - \text{BesselJ}[1/4, (\sqrt{2} \, d \, t)] \, (\sqrt{2} \, d \, t) \, A^2 \, \text{BesselJ}[3/4, (\sqrt{2} \, d \, t)] \, \text{BesselJ}[5/4, (\sqrt{2} \, d \, t)];
\]

\[
\text{kreal}[d_, tr_, ii_, if_, ifinc_] :=
\text{Table}[\{i, \text{kernreal}[d, i \, tr]\}, \{i, ii, if, ifinc\}];
\]

\[
\text{makekem}[d_{init}, d_{final}, d_{inc}, tr, ii, if, ifinc_] :=
\text{Table}[\text{kreal}[d, tr, ii, if, ifinc], \{d, d_{init}, d_{final}, d_{inc}\}];
\]

Define the routine to calculate the REDOR Transform spectrum. This uses a simple summation for the integration.

\[
\text{calcspec}[\text{data}_2, \text{ktable}_2, \text{ntot}_2, \text{dint}_2, \text{dinc}_2, \text{npts}_2] :=
\text{Do}[\text{dat2} = \text{data}_2; \text{ktab} = \text{ktable}_2; \text{kern} = \text{ktab}\{\text{k}\};
\text{integr} = \text{N}[\text{Sum}[\text{dat2}\{\text{j}, 2\} \, \text{kern}\{\text{j}, 2\}], \{\text{j}, 1, \text{npts}_2, 1\}];
\text{spec} = \text{Append}[\text{spec}, \{\text{dint} + \text{dinc}(\text{k} - 1), \text{integr}\}],
\{\text{k}, 1, \text{ntot}_2, 1\}]
\]

Calculate the REDOR transform kernal as a look-up table \text{kerntab}. This can take several minutes. Note that we must avoid \text{freq}1 = 0 since the function is not defined at this point. \text{speed}

\[
\text{speed} = 4000;
\]

\[
\text{npnts} = 64; \text{minn} = 2; \text{incr} = 2; \text{speed} = 4000;
\]

\[
\text{freq1} = 0.0005; \text{freq2} = (\text{speed}/2) + \text{freq1};
\]

\[
\text{deltafreq} = \text{N}[(\text{freq2} - \text{freq1}) / \text{npnts}];
\]

\[
\text{kerntab} =
\text{makekern}[\text{freq1}, \text{freq2}, \text{deltafreq}, \text{trot}, \text{minn}, \text{incr} * \text{npnts}, \text{incr}];
\]
Now perform actual calculation (REDOR transform) to produce the dipolar spectrum from the
apodized experimental data and plot it. The list `spec128` contains the transform intensities as a
function of the dipolar frequency.

```
spec = {spec = {};
calcspec[zfl28, kerntab, Length[kerntab],
  freq1, deltafreq, Length[zfl28]];  
spec128 = spec;
trans128 = ListPlot[spec128, PlotJoined->True,
  PlotRange->All,
  PlotLabel->"REDOR Transform"]
```

This analysis assumes the REDOR data was acquired with dephasing pulses positioned
at τ/2. The “wiggle” at small values of dipolar coupling in the REDOR transform “spectrum”
arises from the initial decay of the S/S₀ data. A restriction determining the applicability of the
REDOR transform is that the maximum dipolar coupling observable is half of the spinning speed
used. This means that the spinning speed used must exceed the dipolar coupling by at least three
times if good REDOR transform spectra are to be obtained with the maximum corresponding to
the I-S dipolar coupling clearly defined.

C.2.2 REDOR Behavior For a Single S Spin Dephased by Several I Spins

C.2.2.1 Exact Geometrical Analysis

The background theory and approach to calculating the REDOR dephasing for a single S
spin coupled to several I spins when the explicit geometrical arrangement of the spins is known
is discussed in Section 3.4.2. The Mathematica code used to implement the formalism proposed
by Goetz and Schaefer in terms of a product of cosine functions containing vectorial dot
products as arguments is given below. It is also possible to calculate this in terms of a sum (i.e.
Eq. 3.31) as presented for the multi-spin TEDOR dephasing in Section C.3.2.
First define the REDOR function $\Delta\Phi_R$ (Eq. 3.28) in terms of a dot product between the (rotated) internuclear vector $\mathbf{v} = \{v_1, v_2, v_3\}$ having unit length, and unit vectors along the $y$ and $z$-axes. A compiled function is used to reduce the computation time. The Mathematica package \texttt{Geometry-Rotations} is also loaded since this contains the function \texttt{Rotate3D} used to perform rotations of the vectors through the three Euler angles.

\begin{verbatim}
<< Geometry~Rotations
reddot = Compile[{{vect, _Real, 1}, dipcoup, nT},
             Cos[4 Sqrt[2] * dipcoup * nT * vect[[2]] * vect[[3]]]];
\end{verbatim}

Now define the experimental parameters such as the initial $I-S$ vectors, the angle $\zeta$ between them, and individual $I-S$ dipolar couplings, and evaluate Eq. 3.33 using a simple summation procedure to perform the integration. In this example the dephasing is calculated for an $I_S$ with $\zeta = 20^\circ$, and dipolar couplings $D_1 = D_2 = 100$ Hz. The function \texttt{Rotate3D}[\psi, \theta, \phi] performs successive rotations about the three Euler angles $\psi$, $\theta$, and $\phi$; the first by $\psi$ about the $z$ axis, the second by angle $\theta$ about the $x$ axis, and the third around the $z$ axis by angle $\phi$.

A series of calculations was undertaken to determine the angular step size for the integration and the computation time required to achieve suitable precision. The results are presented in Table C.2 and reveal that a step size of $\pi/40$ radians provides $\Delta S/S_0$ correct to three decimal places, and thus represents a very efficient trade-off in terms of computation time versus precision. Table C.3 lists the theoretical REDOR dephasing $\Delta S/S_0$ calculated for a 3-spin $I_S$ system having $D_1 = D_2 = 100$ Hz for different $I-S-I$ angles $\zeta$. The theoretical behavior for several $I_S$ spin systems is explored further in Chapter 5.
Table C.2 REDOR $\Delta S/S_0$ dephasings calculated using Eq. 3.33 for an exact tetrahedral geometry of four $I$ spins dipolar coupled ($D = 120$ Hz) to a single observed $S$ spin using various step sizes for the numerical integration.

<table>
<thead>
<tr>
<th>Dephasing Time $n\tau_r$ (ms)</th>
<th>$\pi / 20$</th>
<th>$\pi / 40$</th>
<th>$\pi / 60$</th>
<th>$\pi / 90$</th>
<th>$\pi / 180$</th>
<th>Exact$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>0.8</td>
<td>0.04069</td>
<td>0.03918</td>
<td>0.03890</td>
<td>0.03878</td>
<td></td>
<td>0.03867</td>
</tr>
<tr>
<td>1.6</td>
<td>0.14921</td>
<td>0.14779</td>
<td>0.14753</td>
<td>0.14742</td>
<td>0.14375</td>
<td>0.14728</td>
</tr>
<tr>
<td>2.4</td>
<td>0.30726</td>
<td>0.30599</td>
<td>0.30576</td>
<td>0.30566</td>
<td></td>
<td>0.30548</td>
</tr>
<tr>
<td>3.2</td>
<td>0.48658</td>
<td>0.48551</td>
<td>0.48531</td>
<td>0.48523</td>
<td>0.48517</td>
<td>0.48502</td>
</tr>
<tr>
<td>4.0</td>
<td>0.65772</td>
<td>0.65687</td>
<td>0.65672</td>
<td>0.65665</td>
<td></td>
<td>0.65645</td>
</tr>
<tr>
<td>Calculation time per point</td>
<td>1 min</td>
<td>8 min</td>
<td>27 min</td>
<td>1.5 h</td>
<td>12 h</td>
<td></td>
</tr>
</tbody>
</table>

$^\dagger$ Data from Dr. J. Schaefer; personal communication, December 5, 1996.
Table C.3 Theoretical REDOR $\Delta S/S_0$ dephasings calculated using Eq. 3.33 for different geometries of two $I$ spins dipolar coupled ($D_I = D_S = 100$ Hz) to a single (observed) $S$ spin. $\zeta$ is the angle between the two heteronuclear vectors. A step size of $\pi/20$ radians was used for the numerical integrations.

<table>
<thead>
<tr>
<th>$n\tau_r$ (ms)</th>
<th>$\zeta=20^\circ$</th>
<th>$\zeta=45^\circ$</th>
<th>$\zeta=90^\circ$</th>
<th>$\zeta=109^\circ$</th>
<th>$\zeta=120^\circ$</th>
<th>$\zeta=180^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>0.083</td>
<td>0.084</td>
<td>0.084</td>
<td>0.084</td>
<td>0.084</td>
<td>0.082</td>
</tr>
<tr>
<td>4</td>
<td>0.280</td>
<td>0.302</td>
<td>0.295</td>
<td>0.300</td>
<td>0.303</td>
<td>0.269</td>
</tr>
<tr>
<td>6</td>
<td>0.490</td>
<td>0.577</td>
<td>0.553</td>
<td>0.572</td>
<td>0.585</td>
<td>0.445</td>
</tr>
<tr>
<td>8</td>
<td>0.627</td>
<td>0.825</td>
<td>0.776</td>
<td>0.815</td>
<td>0.844</td>
<td>0.521</td>
</tr>
<tr>
<td>10</td>
<td>0.672</td>
<td>0.984</td>
<td>0.920</td>
<td>0.980</td>
<td>1.019</td>
<td>0.497</td>
</tr>
<tr>
<td>12</td>
<td>0.679</td>
<td>1.045</td>
<td>0.992</td>
<td>1.059</td>
<td>1.093</td>
<td>0.442</td>
</tr>
<tr>
<td>14</td>
<td>0.709</td>
<td>1.036</td>
<td>1.022</td>
<td>1.079</td>
<td>1.090</td>
<td>0.426</td>
</tr>
<tr>
<td>16</td>
<td>0.786</td>
<td>1.004</td>
<td>1.032</td>
<td>1.072</td>
<td>1.052</td>
<td>0.459</td>
</tr>
<tr>
<td>18</td>
<td>0.882</td>
<td>0.985</td>
<td>1.027</td>
<td>1.058</td>
<td>1.016</td>
<td>0.500</td>
</tr>
<tr>
<td>20</td>
<td>0.955</td>
<td>0.992</td>
<td>1.003</td>
<td>1.041</td>
<td>0.998</td>
<td>0.510</td>
</tr>
<tr>
<td>22</td>
<td>0.985</td>
<td>1.013</td>
<td>0.964</td>
<td>1.022</td>
<td>0.997</td>
<td>0.486</td>
</tr>
<tr>
<td>24</td>
<td>0.989</td>
<td>1.028</td>
<td>0.926</td>
<td>1.003</td>
<td>1.001</td>
<td>0.462</td>
</tr>
<tr>
<td>26</td>
<td>0.997</td>
<td>1.027</td>
<td>0.907</td>
<td>0.991</td>
<td>1.002</td>
<td>0.464</td>
</tr>
<tr>
<td>28</td>
<td>1.023</td>
<td>1.012</td>
<td>0.913</td>
<td>0.990</td>
<td>0.998</td>
<td>0.488</td>
</tr>
<tr>
<td>30</td>
<td>1.052</td>
<td>0.993</td>
<td>0.937</td>
<td>0.997</td>
<td>0.996</td>
<td>0.505</td>
</tr>
<tr>
<td>32</td>
<td>1.063</td>
<td>0.981</td>
<td>0.965</td>
<td>1.003</td>
<td>0.998</td>
<td>0.498</td>
</tr>
<tr>
<td>34</td>
<td>1.046</td>
<td>0.980</td>
<td>0.986</td>
<td>1.001</td>
<td>1.005</td>
<td>0.475</td>
</tr>
<tr>
<td>36</td>
<td>1.018</td>
<td>0.988</td>
<td>0.998</td>
<td>0.991</td>
<td>1.013</td>
<td>0.459</td>
</tr>
<tr>
<td>38</td>
<td>0.999</td>
<td>0.998</td>
<td>1.002</td>
<td>0.981</td>
<td>1.019</td>
<td>0.462</td>
</tr>
<tr>
<td>40</td>
<td>0.996</td>
<td>1.005</td>
<td>1.000</td>
<td>0.976</td>
<td>1.019</td>
<td>0.473</td>
</tr>
</tbody>
</table>

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C.2.2.2 Single S Spin Dephased by a Gaussian Distribution of I Spins

Blumenfeld et al. have described a method to calculate the REDOR dephasing for a single S spin dipolar coupled to many I spins. This was briefly discussed in Section 3.4.3 and the full details are presented in this section. Blumenfeld and co-workers ignored the geometrical arrangement of the heteronuclear I-S vectors, and made the assumption that there will exist a distribution of dipolar couplings between the individual IS spin pairs. They proposed that a
Gaussian distribution could be used to weight the contribution of the individual IS spin pairs.

The result is a function having a direct dependence on the heteronuclear second moment $M_2(I-S)$:

$$\frac{\Delta S[M_2(I-S)]}{S_0} = \int_0^\infty w(D_i) \frac{\Delta S[D_i]}{S_0} dD$$

where $w(D_i)$ is the Gaussian weighting function:

$$w(D_i) = \frac{1}{\sqrt{2\pi} M_2(I-S)} \exp \left[ -\frac{D_i^2}{2 \left[ M_2(I-S) \right]^2} \right]$$

Eq. C.8 can be evaluated numerically, but requires long computation times. Substitution of $\Delta S/S_0$ by the appropriate expression in terms of Bessel functions of order 1/4 (Eq. C.7) makes it possible to obtain an analytical solution (Eq. C.10).

$$\frac{\Delta S[M_2(I-S)]}{S_0} = 1 - 2F_2 \left[ \left\{ \frac{1}{2}, \frac{1}{2} \left\{ \frac{3}{4}, \frac{1}{4} \right\} \right\}, -4 n^2 M_2(I-S) \tau_i^2 \right]$$

$2F_2$ is a hypergeometric function defined by:\'

$$2F_2 \left[ \{a,b\}, \{c,d\}, z \right] = \sum_{k=0}^\infty \frac{(a_1)_k (a_2)_k \ldots (a_p)_k (b_1)_k (b_2)_k \ldots (b_p)_k z^k}{(c_1)_k (c_2)_k \ldots (c_q)_k (d_1)_k (d_2)_k \ldots (d_q)_k k!}$$

where

$$(a_1)_0 = 1, \text{ and } (a_1)_k = (a_1) (a_1 + 1) (a_1 + 2) \ldots (a_1 + k - 1) \text{ etc.}$$

Unfortunately the hypergeometric function becomes unstable (due to the magnitude of the individual terms and the number of terms) when $n^2 M_2(I-S) \tau_i^2 > 3$ and no longer converges.

However Eq. C.8 can be re-expressed as:

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Eq. C.11 can be evaluated numerically using the Gaussian-Hermite quadrature method since it is of the form:

\[ \int_{0}^{\infty} e^{-x^2} f(x) \, dx = \sum_{i=1}^{n} w_i f(x_i) + R_n \]  

where \( x_i \) is the \( i \)-th root of \( H_n(x) \), the Hermite polynomial of order \( n \), \( w_i \) is defined by Eq. C.13, and \( R_n \) is a (small) remainder term which was not included in the calculation.

The following Mathematica code finds the nodes of the \( n \)-th order Hermite polynomials, calculates the Gaussian weights, and defines the actual GaussREDOR function. Note that \( H_n \) must be large enough (typically \( >150 \)) so that the approximation is acceptable and oscillations are not present in the resulting function. This function was derived by D. Brouwer.

\[ \begin{align*}
H_n &= 150; \\
Hroots &= \text{NSolve}[\text{HermiteH}[H_n, x] == 0, x]; \\
node &= \text{Re}[x] /. Hroots; \\
weight &= \text{Re}[2^{n+1} n! \sqrt{\pi} \frac{H_n! \sqrt{\pi}}{n^2 (H_n'(x_i))^2}] /. Hroots; \\
\text{GaussREDOR}[nT_{\text{r}}, M] &= \\
&= 1 - \sqrt{\frac{\pi}{2}} \sum_{i=1}^{Hn} \text{weight}[[i]] \times \text{BesselJ}[1/4, 2 \sqrt{M} \frac{nT_{\text{r}}}{1000} \times \text{node}[[i]]] \\
&\quad \times \text{BesselJ}[-1/4, 2 \sqrt{M} \frac{nT_{\text{r}}}{1000} \times \text{node}[[i]]];
\end{align*} \]

Here \( nT_{\text{r}} \) is the dephasing time in milliseconds, and \( M \) is the heteronuclear second moment in \( \text{Hz}^2 \). A series of curves calculated for different values of the second moment are given in
Chapter 5. Nonlinear fitting of experimental REDOR data can be achieved using this function as described in Section C.1.1.2 and uses only a single parameter corresponding to $M_2(I-S)$.

C.3 TRANSFERRED ECHO DOUBLE RESONANCE

C.3.1 TEDOR Behavior for Isolated IS Spin Pairs

The theory of the TEDOR experiment is discussed in Section 3.5. In this section the equations and Mathematica code used to determine functions for different positions of the dephasing pulses, and perform nonlinear least squares fitting of the experimental data are presented.

The theoretical TEDOR behavior for an isolated IS spin pair is:

$$S_T = \frac{1}{2\pi} \int_0^{\tau} \int_0^{\tau} \sin[\Delta \Phi_{T,n}(\alpha, \beta, \lambda_n)] \sin[\Delta \Phi_{T,m}(\alpha, \beta, \lambda_m)] \sin\beta \, d\beta \, d\alpha$$  \quad \text{(C.14)}$$

where $n$ is the number of rotor periods before coherence transfer, $m$ is the number of rotor cycles after transfer, $\lambda_n = nD\tau$, and $\lambda_m = mD\tau$. In a TEDOR experiment there are two dephasing $\pi$-pulses applied per rotor period, and these are applied at times $t_1$ and $t_2$ ($0 < t_1 < t_2 < \tau$). The dipolar phase accumulated over each rotor period ($\Delta \Phi_{T,i}$ where $i = n$ or $m$) is:

$$\Delta \Phi_{T,i} = \int_0^{t_1} \omega_D(\alpha, \beta, t) \, dt - \int_{t_1}^{t_2} \omega_D(\alpha, \beta, t) \, dt + \int_{t_2}^{\tau} \omega_D(\alpha, \beta, t) \, dt$$  \quad \text{(C.15)}$$

Eq C.15 can be evaluated in Mathematica for various choices of $t_1$ and $t_2$ as follows:

First define function describing the dipolar coupling under MAS conditions (Eq. 1.14).

\[
\text{omega}[\alpha_, \beta_, \ t_] := \\
\frac{d}{2} \cdot \{ \sin[\beta] \cdot \sin[\beta] \cdot \cos[2(\alpha + \omega_2 \, t)] - \sqrt{2} \cdot \sin[2\beta] \cdot \cos[\alpha + \omega_2 \, t] \} 
\]

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Now this function is integrated using appropriate limits. In this example position the pulses are at one quarter and three quarters of each rotor cycle so \( t_1 = \tau_r / 4 \) and \( t_2 = 3\tau_r / 4 \).

\[
delta_{\phi 4} = \text{Integrate}[\omega[a, b, c], \{c, 0, \tau_r / 4\}] - \text{Integrate}[\omega[a, b, c], \{c, \tau_r / 4, 3\tau_r / 4\}] + \text{Integrate}[\omega[a, b, c], \{c, 3\tau_r / 4, \tau_r\}];
\]

\[
\text{ExpandAll[TrigReduce[delta_{\phi 4} /. \omega_x \tau_x \rightarrow 2 \pi]]}
\]

Table C.4 contains the functions \( \Delta \Phi_{T, i} (i = n \text{ or } m) \) determined for a selection of possible pulse positions using this code. Numerical integration of Eq. C.14 (using the appropriate functions from Table C.4) was used to determine the theoretical TEDOR dephasing for selected pulse positions and several of these are plotted in Figure C.3.

The maximum dephasing occurs when \( t_2 - t_1 = \tau_r / 2 \) and it is apparent that the oscillations are not periodic. There is no restriction that the pulse positions before and after the coherence transfer be the same. Furthermore, it is possible to achieve the same dephasing using different pulse positions. For example, identical behavior is observed with pulses at \( (\tau_r / 3, 2\tau_r / 3) \) and \( (\tau_r / 6, 5\tau_r / 6) \) since the net time during which the dephasing accumulates equals \( \tau_r / 3 \) in both cases (see Figure C.3 (a)).

Inspection of the equations in Table C.4 reveals that the expression for \( \Delta \Phi_{T, i} \) is particularly simple when the dephasing pulses are applied at \( (\tau_r / 4, 3\tau_r / 4) \). Mueller derived an expression for this case in terms of Bessel functions of the first kind:

\[
S_T = \frac{1}{2} \left\{ [J_0(\sqrt{2} \{\lambda_n - \lambda_m\})]^2 - [J_0(\sqrt{2} \{\lambda_n + \lambda_m\})]^2 \right\} - \sum_{k=1}^{\infty} \frac{1}{16k^2 - 1} \left\{ [J_k(\sqrt{2} \{\lambda_n - \lambda_m\})]^2 - [J_k(\sqrt{2} \{\lambda_n + \lambda_m\})]^2 \right\}
\]

C.16

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Table C.4 TEDOR functions $\Delta \phi_{r,i}$ ($i = n$ or $m$) defining the dephasing for the indicated positions of the two dephasing $\pi$-pulses per rotor period as a function of the dimensionless parameter $\lambda_i = iD_{r i}$.

<table>
<thead>
<tr>
<th>Pulse Position</th>
<th>$\Delta \phi_{r,i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\tau_r}{3}, \frac{2\tau_r}{3}$</td>
<td>$\sqrt{2} \lambda_i \sin 2\beta \left[ \sin \left( \alpha + \frac{4\pi}{3} \right) - \sin \left( \alpha + \frac{2\pi}{3} \right) \right] + \frac{\lambda_i}{2} \sin^2 \beta \left[ \sin \left( 2\alpha + \frac{4\pi}{3} \right) - \sin \left( 2\alpha + \frac{8\pi}{3} \right) \right]$</td>
</tr>
<tr>
<td>$\frac{\tau_r}{4}, \frac{3\tau_r}{4}$</td>
<td>$-4\sqrt{2} \lambda_i \cos \alpha \cos \beta \sin \beta$</td>
</tr>
<tr>
<td>$\frac{\tau_r}{5}, \frac{4\tau_r}{5}$</td>
<td>$\sqrt{2} \lambda_i \sin 2\beta \left[ \sin \left( \alpha + \frac{8\pi}{5} \right) - \sin \left( \alpha + \frac{2\pi}{5} \right) \right] + \frac{\lambda_i}{2} \sin^2 \beta \left[ \sin \left( 2\alpha + \frac{4\pi}{5} \right) - \sin \left( 2\alpha + \frac{16\pi}{5} \right) \right]$</td>
</tr>
<tr>
<td>$\frac{\tau_r}{6}, \frac{5\tau_r}{6}$</td>
<td>$\sqrt{2} \lambda_i \sin 2\beta \left[ \sin \left( \alpha + \frac{5\pi}{3} \right) - \sin \left( \alpha + \frac{\pi}{3} \right) \right] + \frac{\lambda_i}{2} \sin^2 \beta \left[ \sin \left( 2\alpha + \frac{2\pi}{3} \right) - \sin \left( 2\alpha + \frac{10\pi}{3} \right) \right]$</td>
</tr>
<tr>
<td>$\frac{\tau_r}{7}, \frac{6\tau_r}{7}$</td>
<td>$\sqrt{2} \lambda_i \sin 2\beta \left[ \sin \left( \alpha + \frac{7\pi}{12} \right) - \sin \left( \alpha + \frac{2\pi}{7} \right) \right] + \frac{\lambda_i}{2} \sin^2 \beta \left[ \sin \left( 2\alpha + \frac{4\pi}{7} \right) - \sin \left( 2\alpha + \frac{24\pi}{7} \right) \right]$</td>
</tr>
<tr>
<td>$\frac{\tau_r}{8}, \frac{7\tau_r}{8}$</td>
<td>$\sqrt{2} \lambda_i \sin 2\beta \left[ \sin \left( \alpha + \frac{7\pi}{4} \right) - \sin \left( \alpha + \frac{\pi}{4} \right) \right] + \lambda_i \sin^2 \beta \cos (2\alpha)$</td>
</tr>
<tr>
<td>$\frac{\tau_r}{9}, \frac{8\tau_r}{9}$</td>
<td>$\sqrt{2} \lambda_i \sin 2\beta \left[ \sin \left( \alpha + \frac{16\pi}{9} \right) - \sin \left( \alpha + \frac{2\pi}{9} \right) \right] + \frac{\lambda_i}{2} \sin^2 \beta \left[ \sin \left( 2\alpha + \frac{4\pi}{9} \right) - \sin \left( 2\alpha + \frac{32\pi}{9} \right) \right]$</td>
</tr>
<tr>
<td>$\frac{\tau_r}{10}, \frac{9\tau_r}{10}$</td>
<td>$\sqrt{2} \lambda_i \sin 2\beta \left[ \sin \left( \alpha + \frac{9\pi}{5} \right) - \sin \left( \alpha + \frac{\pi}{5} \right) \right] + \frac{\lambda_i}{2} \sin^2 \beta \left[ \sin \left( 2\alpha + \frac{2\pi}{5} \right) - \sin \left( 2\alpha + \frac{18\pi}{5} \right) \right]$</td>
</tr>
</tbody>
</table>
Figure C.3  Theoretical TEDOR dephasing for an isolated IS spin pair for the indicated placements of the two dephasing π-pulses in the period following coherence transfer. The curves are plotted as a function of the dimensionless parameter $mD\tau_r$ and were calculated assuming $nD\tau_r = 0.84$ and that the dephasing pulses before coherence transfer were at $\tau_r/4$ and $3\tau_r/4$. The curves are identical for $\tau_r/3$, $2\tau_r/3$ and $\tau_r/6, 5\tau_r/6$ since the net dephasing time is the same ($\tau_r/3$).
Using Eq. C.16, nonlinear least squares fitting of the experimental TEDOR data acquired with all dephasing pulses applied at \((τ/4, 3τ/4)\) was possible. In addition to a parameter for the dipolar coupling, a scaling factor was required to match experimental and theoretical intensities since TEDOR intensities are not normalized. It was found that the use of a weighting function greatly improved the fitting procedure. The best weighting scheme was one determined by the inverse of the number of rotor cycles, since the TEDOR data decay to zero and better signal to noise (and thus more reliable peak intensities) are available at small numbers of rotor periods. A damping function was also applied to account for \(T_2\) decay during the experiment. The Mathematica code used to performing nonlinear fitting of TEDOR data is given below.

First define a list \texttt{teddata} containing the experimental data in form \{(number rotor cycles, peak area), \}, and set the other experimental parameters used to acquire the data. In this case the spinning speed was 4.77 kHz, \(n = 2\), and \(m\) was varied from 1 to 16 (\texttt{maxm}) in increments of one rotor cycle. The package for the nonlinear regression analysis is also loaded.

\begin{verbatim}
<< Statistics'NonlinearFit'
mmax = 16; n = 2; speed = 4770; trot = N[1/speed];

	teddata = {{0, 0}, {1, 12.02}, {2, 19.20}, {3, 24.25}, {4, 22.47}, {5, 15.75},
		{6, 8.47}, {7, 1.81}, {8, -2.52}, {9, -3.65}, {10, -2.78}, {11, -1.15},
		{12, 1.24}, {13, 2.80}, {14, 2.72}, {15, 2.125}, {16, 0.54}};

Calcualte a list containing the weights to be used during the nonlinear fitting:

	weightlist = {};
	incr = 1; maxloop = mmax / incr;
	AppendTo[weightlist, 1.0]; i = 2;
	Do[ w = N[1 / tteddata[[i, 1]]]; AppendTo[weightlist, w];
		i = i + 1, {maxloop}];
\end{verbatim}
Define the function `tedfunc` describing the TEDOR behavior for isolated IS spin pair in terms of Bessel functions (Eq. C.16). Here dampening is dependent on $m$ (since the number of rotor cycles after the coherence transfer was varied), and $sf$ is a scale factor to match the theoretical and experimental intensities.

$$\text{tedfunc}[sfac_, \text{nb}_-, \text{ma}_-, \text{d}_-, \text{tr}_-, \text{lb}_-] := sfac \times \exp[-\text{ma} \times \text{tr} \times \text{lb}] \ast$$

$$\frac{1}{2} \ast \left(\text{N}[\text{BesselJ}[0, \sqrt{2} (\text{ma} - \text{nb}) \times \text{d} \times \text{tr}]] \ast ^2 - \text{N}[\text{BesselJ}[0, \sqrt{2} (\text{ma} + \text{nb}) \times \text{d} \times \text{tr}]] \ast ^2 \right. +$$

$$\left. \sum \left[ \frac{1}{(1 - 16 i^2)} \right.$$

$$\left(\text{N}[\text{BesselJ}[i, \sqrt{2} (\text{ma} - \text{nb}) \times \text{d} \times \text{tr}]] \ast ^2 - \text{N}[\text{BesselJ}[i, \sqrt{2} (\text{ma} + \text{nb}) \times \text{d} \times \text{tr}]] \ast ^2 \right),$$

$$(i, 1, 5) \right].$$

Now do the least squares fitting of the data to obtain the best parameters:

```math
\text{NonlinearRegress}[\text{teddata}, \text{tedfunc}[sf, n, m, \text{dipcoup}, \text{trot}, \text{damp}],
\text{m}, \{(\text{sf}, 65), (\text{dipcoup}, 1200), (\text{damp}, 60)\},
\text{Method} \rightarrow \text{LevenbergMarquardt},
\text{Weights} \rightarrow \text{weightlist},
\text{ShowProgress} \rightarrow \text{True},
\text{RegressionReport} \rightarrow \text{BestFitParameters}];
```

Numerical integration of Eq. C.14 (using the appropriate functions from Table C.4) was used to visually fit experimental TESOR data acquired when the dephasing pulses were not applied at ($t, \pi/4, 3\pi/4$).

**C.3.2 TEDOR Behavior For a Single S Spin Dephased by Several I Spins**

The theoretical TESOR behavior for a single $S$ spin dephased by several $I$ spins can be derived by extending the methodology presented by Naito et al. and Schaefer and co-workers. The basis for the general approach and the underlying assumptions are described in Sections 3.4.2, 3.5.3 and C.2.2. Essentially the $\Delta \Phi_{Ti}$ arguments within the sine functions in Eq. C.14 are replaced by a sum of terms expressed as the appropriate vector dot products (Eqs. 3.38-
3.41). All unique combinations of the individual $\pm D_i$’s must be considered. Eq. C.17 gives the expression which must be evaluated for a 3-spin $I_2S$ system. In this case there are only two combinations of the dipolar couplings which need be considered: $D_1 + D_2$ and $D_1 - D_2$. These combinations are represented as $\pm \lambda_{ij}$ ($i = n$ or $m$, and $j = 1, 2, 3... c$) where $c$ is the number of combinations of the individual $D_i$’s. The expression is integrated over the three Euler angles to reproduce all possible crystallite orientations and achieve a powder average.

$$S_T = \frac{1}{c} \left[ \frac{1}{4\pi^2} \int_0^\pi \int_0^\pi \int_0^\pi \{\sin[\Delta \Phi_{T,m}(\phi, \theta, \psi, +\lambda_{1,n}) + \Delta \Phi_{T,m}(\phi, \theta, \psi, +\lambda_{2,n})] \times \right. $$

$$\{\sin[\Delta \Phi_{T,m}(\phi, \theta, \psi, +\lambda_{1,m}) + \Delta \Phi_{T,m}(\phi, \theta, \psi, +\lambda_{2,m})] \} \sin \theta \sin \theta \ d\theta \ d\phi $$

$$+ \frac{1}{4\pi^2} \int_0^\pi \int_0^\pi \int_0^\pi \{\sin[\Delta \Phi_{T,m}(\phi, \theta, \psi, +\lambda_{1,n}) + \Delta \Phi_{T,m}(\phi, \theta, \psi, -\lambda_{2,n})] \} \times \right. $$

$$\{\sin[\Delta \Phi_{T,m}(\phi, \theta, \psi, +\lambda_{1,m}) + \Delta \Phi_{T,m}(\phi, \theta, \psi, -\lambda_{2,m})] \} \sin \theta \sin \theta \ d\theta \ d\phi \ d\psi \left. \right]$$

C.17

The package Geometry 'Rotations' required to perform rotations of the vectors through the three Euler angles and is loaded using:

```c
<< Geometry 'Rotations'
```

Define compiled functions `tedsum4`, `tedsum3`, and `tedsum2` for four, three, and two $I$ spins coupled to a single $S$ spin respectively. The calculation can be done for the chosen values of the experimental parameters using a simple summation to perform the integration. In this example the spinning speed was 4.540 kHz, $m = 2$, $n$ was varied, and there are four $I$ spins in an exact tetrahedral arrangement about a central $S$ spin. For this 5-spin systems there are eight unique combinations of the $\pm D_i$’s (out of a possible sixteen since, for example, $|D_1 + D_2 + D_3 + D_4| = |D_1 - D_2 - D_3 - D_4|$) which must be included.
tedsum4 = Compile[{nT, mT, {g, _Real, 1}, dipl, {h, _Real, 1}, dip2, {i, _Real, 1}, dip3, {j, _Real, 1}, dip4},
Sin[4*Sqrt[2]*nT*((dipl[[1]]*g[[1]]*g[[3]]) + (dip2[[1]]*h[[1]]*h[[3]]) + (dip3[[1]]*i[[1]]*i[[3]]) + (dip4[[1]]*j[[1]]*j[[3]])] +
Sin[4*Sqrt[2]*mT*((dipl[[1]]*g[[1]]*g[[3]]) + (dip2[[1]]*h[[1]]*h[[3]]) + (dip3[[1]]*i[[1]]*i[[3]]) + (dip4[[1]]*j[[1]]*j[[3]])]]]

tedsum3 = Compile[{nT, mT, {g, _Real, 1}, dipl, {h, _Real, 1}, dip3},
Sin[4*Sqrt[2]*nT*((dipl[[1]]*g[[1]]*g[[3]]) + (dip2[[1]]*h[[1]]*h[[3]]) + (dip3[[1]]*i[[1]]*i[[3]])] +
Sin[4*Sqrt[2]*mT*((dipl[[1]]*g[[1]]*g[[3]]) + (dip2[[1]]*h[[1]]*h[[3]]) + (dip3[[1]]*i[[1]]*i[[3]])]]]

tedsum2 = Compile[{nT, mT, {g, _Real, 1}, dipl, {h, _Real, 1}, dip2},
Sin[4*Sqrt[2]*nT*((dipl[[1]]*g[[1]]*g[[3]]) + (dip2[[1]]*h[[1]]*h[[3]])]] +
Sin[4*Sqrt[2]*mT*((dipl[[1]]*g[[1]]*g[[3]]) + (dip2[[1]]*h[[1]]*h[[3]])]]]

Table C.5 lists the theoretical TEDOR dephasing $S_T$ calculated for a 3-spin $I_S$ system having $D_1 = D_2 = 100$ Hz for different $I-S-I$ angles $\zeta$. The theoretical behavior for several $I_S$ spin systems is explored further in Chapter 5. If required, the statistical occupancy of the individual $I$ spin positions can be accounted for using an appropriate function (e.g., a binomial distribution) to weight the contributions from 5-, 4-, 3-, and 2-spin systems to produce the final curve (see Section 4.3.4.2).
Table C.5 Theoretical TEDOR $S_1$ dephasings calculated using Eq. C.17 for different geometries of two $l$ spins dipolar coupled ($D_l = D_z = 100$ Hz) to a single (observed) $S$ spin. $\zeta$ is the angle between the two heteronuclear vectors. A step size of $\pi/20$ radians was used for the numerical integrations assuming a spinning speed of 2.5 kHz, and that the number of rotor periods after the coherence transfer, $m$, was fixed at 20 ($mD_{\tau_r} \approx 0.84$).

<table>
<thead>
<tr>
<th>$n\tau_r$ (ms)</th>
<th>$\zeta=20^\circ$</th>
<th>$\zeta=45^\circ$</th>
<th>$\zeta=90^\circ$</th>
<th>$\zeta=109^\circ$</th>
<th>$\zeta=120^\circ$</th>
<th>$\zeta=180^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>2</td>
<td>0.091</td>
<td>0.203</td>
<td>0.183</td>
<td>0.204</td>
<td>0.216</td>
<td>0.025</td>
</tr>
<tr>
<td>4</td>
<td>0.199</td>
<td>0.371</td>
<td>0.348</td>
<td>0.379</td>
<td>0.395</td>
<td>0.086</td>
</tr>
<tr>
<td>6</td>
<td>0.312</td>
<td>0.475</td>
<td>0.469</td>
<td>0.497</td>
<td>0.503</td>
<td>0.172</td>
</tr>
<tr>
<td>8</td>
<td>0.391</td>
<td>0.501</td>
<td>0.515</td>
<td>0.535</td>
<td>0.525</td>
<td>0.228</td>
</tr>
<tr>
<td>10</td>
<td>0.399</td>
<td>0.450</td>
<td>0.471</td>
<td>0.486</td>
<td>0.465</td>
<td>0.209</td>
</tr>
<tr>
<td>12</td>
<td>0.337</td>
<td>0.345</td>
<td>0.353</td>
<td>0.370</td>
<td>0.347</td>
<td>0.120</td>
</tr>
<tr>
<td>14</td>
<td>0.247</td>
<td>0.217</td>
<td>0.205</td>
<td>0.225</td>
<td>0.206</td>
<td>0.020</td>
</tr>
<tr>
<td>16</td>
<td>0.181</td>
<td>0.101</td>
<td>0.075</td>
<td>0.093</td>
<td>0.078</td>
<td>-0.029</td>
</tr>
<tr>
<td>18</td>
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</table>
\[ \begin{align*}
&d_1 = 120; m = 2; \text{speed} = 4540; mTrot = N[m / \text{speed}]; \\
&v_1 = N[(0, 0, 1)]; v_2 = N[{0, 2\sqrt{2}/3, -1/3}]; \\
&v_3 = N[{\sqrt{2}/3, -\sqrt{2}/3, -1/3}]; v_4 = N[{\sqrt{2}/3, -\sqrt{2}/3, -1/3}]; \\
nTrot = N[0.25/1000]; \text{numpoints} = 14; \text{numIncr} = 15; \\
&\text{maxbeta} = \pi; \text{maxalpha} = \pi; \text{maxgamma} = \pi; \\
&\text{inc} = N[0.5/1000]; s_4 = 0; \text{numComb} = 8; \\
&\text{dy} = \frac{\text{maxgamma}}{\text{numIncr}}; \text{db} = \frac{-\text{maxbeta}}{\text{numIncr}}; \text{da} = \frac{\text{maxalpha}}{\text{numIncr}}; \\
&\text{intlist4} = \{(0, 0)\}; \\
&\text{Do}[a = 0.0; s_3 = 0.0; \\
&\text{\quad Do}[\gamma = 0.0; s_2 = 0.0; \\
&\text{\quad \quad Do}[\nu = 0.0; s_1 = 0.0; \\
&\text{\quad \quad \quad newV1 = Rotate3D[v_1, a, \gamma, \nu]; \\
&\text{\quad \quad \quad newV2 = Rotate3D[v_2, a, \gamma, \nu]; \\
&\text{\quad \quad \quad newV3 = Rotate3D[v_3, a, \gamma, \nu]; \\
&\text{\quad \quad \quad newV4 = Rotate3D[v_4, a, \gamma, \nu]; \\
&\quad sr = N[\text{tedsum4}[nTrot, mTrot, newV1, d_1, newV2, d_1, newV3, d_1, newV4, d_1] + \text{tedsum4}[nTrot, mTrot, newV1, d_1, newV2, d_1, newV3, d_1, newV4, -d_1] + \text{tedsum4}[nTrot, mTrot, newV1, d_1, newV2, d_1, newV3, -d_1, newV4, d_1] + \text{tedsum4}[nTrot, mTrot, newV1, d_1, newV2, d_1, newV3, -d_1, newV4, -d_1] + \text{tedsum4}[nTrot, mTrot, newV1, d_1, newV2, -d_1, newV3, d_1, newV4, d_1] + \text{tedsum4}[nTrot, mTrot, newV1, d_1, newV2, -d_1, newV3, -d_1, newV4, d_1] + \text{tedsum4}[nTrot, mTrot, newV1, d_1, newV2, -d_1, newV3, -d_1, newV4, -d_1] + \text{tedsum4}[nTrot, mTrot, newV1, -d_1, newV2, d_1, newV3, d_1, newV4, d_1]]]; \\
&\quad s_1 = s_1 + (sr * \text{dy} * \text{Sin}[\gamma]); \\
&\quad \gamma = \gamma + \text{dy}, \\
&\quad \text{(numIncr)}]; \\
&\quad s_2 = s_2 + (s_1 * \text{db}); \\
&\quad \beta = \beta + \text{db}, \\
&\quad \text{(numIncr)}]; \\
&\quad s_3 = s_3 + (s_2 * \text{da}); \\
&\quad \alpha = \alpha + \text{da}, \\
&\quad \text{(numIncr)}]; \\
&\quad s_4 = \left(\frac{s_3}{\text{numComb} * 2 * \pi^n}\right); \\
&\quad \text{Print}[nTrot * 1000, ",", s_4]; \text{AppendTo[\text{intlist4}, \{nTrot * 1000, s_4\}];} \\
&\quad nTrot = nTrot + \text{inc, \text{numpoints}}]; \\
\end{align*} \]
REFERENCES FOR APPENDIX C


3 Hediger, S. ETH Zürich, Personal Communication, August 1997.

4 Hediger, S. Ph.D. Dissertation, Eidgenössische Technische Hochschule Zürich, Switzerland. 1996.


APPENDIX D

DERIVATION OF EQUATIONS FOR CALCULATING HETERONUCLEAR SECOND MOMENTS IN THE PRESENCE OF MOLECULAR MOTION

The equations necessary for evaluating the $I-S$ heteronuclear second moments for a polycrystalline (powder) sample in the presence of molecular motion are derived in this appendix. These were incorporated in the computer programs described in Appendix E used to locate sorbed $p$-difluorobenzene in the channels of ZSM-5 from $^1$H-$^{29}$Si cross polarization data.
The second moment is in fact invariant to the presence of motion; however the apparent or measured second moment is not, since part of the the resonance is shifted far from the centre of the resonance where it is masked by the spectrometer noise.\textsuperscript{1,2} Michel \textit{et al.}\textsuperscript{3} derived a general expression for calculating the intermolecular contribution to the second moment in the presence of molecular reorientations. An explicit form of this expression for heteronuclear second moments convenient for calculations is derived in this appendix. The approach involves calculating the average value of $M_2(I-J)$ (Eq. D.1) over all orientations of the $I-J$ heteronuclear vector, $r_{ij}$, during the course of the motion. The calculation is over all relevant nuclei and the averaging must be over the motions and then the powder.\textsuperscript{4}

$$<M_2(I-J)>_{\text{rot}} = \frac{\gamma_1^2 \gamma_2^2 \ h^2 \ h_0^2}{(16 \pi^3)^2} \left\langle \left( \frac{3 \cos^2 \vartheta - 1}{r_{ij}^3} \right)^2 \right\rangle_{\text{rot}}$$ \hspace{1cm} \text{(D.1)}

Here $\vartheta_{ij}$ is the angle between $r_{ij}$ and the direction of the external magnetic field $B_0$. Because the terms in front of the cosine expression are all constants, we need only evaluate the average value of Eq. D.2 over all relevant nuclei.

$$\left[ \frac{3 \cos^2 \vartheta - 1}{r_{ij}^3} \right]^2$$ \hspace{1cm} \text{(D.2)}

Eq. D.2 can be re-expressed in terms of Legendre Polynomials $P_j$ as.\textsuperscript{5,6}

$$\left[ \frac{3 \cos^2 \vartheta - 1}{r_{ij}^3} \right]^2 = \left[ \frac{2 \ P_2 (\cos \vartheta_{ij})}{r_{ij}^3} \right]^2$$ \hspace{1cm} \text{(D.3)}

From the addition theorem of spherical harmonics Eq. D.3 can be expressed as Eq. D.4:\textsuperscript{7}

$$\left[ \frac{2 \ P_2 (\cos \vartheta_{ij})}{r_{ij}^3} \right]^2 = \left[ \frac{8 \pi}{5 r_{ij}^3} \sum_{m=-2}^{2} Y_{2m}^*(\theta_{ij},\phi_{ij}) Y_{2m}(\theta_{ij},\phi_{ij}) \right]^2$$ \hspace{1cm} \text{(D.4)}

where $Y_{2m}$ are spherical harmonics, $\theta_{ij}, \phi_{ij}$, and $\theta_2, \phi_2$ are the polar angles describing the orientation of the $I-J$ vector before and after the motion, respectively, and asterix indicates the complex conjugate. Expressions for the spherical harmonics are given in references 7 and 8.
For a given IS spin pair, if the I nucleus occupies \( q \) sites, and the \( S \) nucleus occupies \( p \) sites during the motion, Eq. D.3 becomes:

\[
\left[ \frac{3 \cos^2 \theta - 1}{r^3} \right]^2 = \left[ \frac{8\pi}{5} \sum_{m=-2}^{2} Y_{2m}(\theta, \phi) \left\{ \frac{1}{pq} \sum_{i=1}^{p} \sum_{j=1}^{q} \frac{1}{r_{ij}^3} Y_{2m}(\theta_{ij}, \phi_{ij}) \right\} \right]^2
\]  

D.5

Expanding the associated Legendre polynomials yields Eq. D.6, where the \( < > \) indicates averaging over all possible crystallite orientations in the polycrystalline sample.

\[
\left[ \frac{3 \cos^2 \theta - 1}{r^3} \right]^2 = \frac{1}{(pq)^2} \sum_{i=1}^{p} \sum_{j=1}^{q} \frac{1}{r_{ij}^6} \left\{ \frac{8\pi}{5} \frac{5}{16\pi} (3\cos^2 \theta - 1)(3\cos^2 \theta - 1) \right\}^2 +
\]

D.6

\[
\frac{8\pi}{5} \frac{5}{12\pi} (3\sin \theta \cos \theta \cos \phi)(3\sin \theta \cos \theta \cos \phi) \left[ \frac{8\pi}{5} \frac{5}{12\pi} (3\sin \theta \cos \theta \sin \phi)(3\sin \theta \cos \theta \sin \phi) \right]^2 +
\]

\[
\frac{8\pi}{5} \frac{5}{48\pi} (3\sin^2 \theta \cos 2\phi)(3\sin^2 \theta \cos 2\phi) \left[ \frac{8\pi}{5} \frac{5}{48\pi} (3\sin^2 \theta \sin 2\phi)(3\sin^2 \theta \sin 2\phi) \right]^2 +
\]

For a powder sample all possible crystallite orientations must be accounted for and thus we must average \( \theta_2 \) and \( \phi_2 \) over all space. Averaging these terms yields Eqs. D7-D9.

\[
<(3 \cos^2 \theta_2 - 1)^2> = \frac{4}{5}
\]

D.7

\[
<(3 \sin \theta_2 \cos \theta_2 \cos \phi_2)^2> = <(3 \sin \theta_2 \cos \theta_2 \sin \phi_2)^2> = \frac{3}{5}
\]

D.8

\[
<(3 \sin^2 \theta_2 \cos 2\phi_2)^2> = <(3 \sin^2 \theta_2 \sin 2\phi_2)^2> = \frac{12}{5}
\]

D.9

Substitution of these terms into Eq. D.6 allows Eq. D.2 to be expressed in a convenient form for use in calculations (Eq. D.10).
\[
\left\langle \frac{(3\cos^2 \theta - 1)}{r^6} \right\rangle_{\text{rot}} = \frac{1}{(pq)^2} \sum_{i=1}^{p} \sum_{j=1}^{q} \frac{1}{r_{ij}^6} \left\{ \frac{1}{5} (3\cos^2 \theta_i - 1)^2 + \right. \\
\left. \frac{4}{15} (3\sin \theta_i \cos \phi_i \cos \theta_i)^2 + \frac{4}{15} (3\sin \theta_i \cos \phi_i \sin \phi_i)^2 \\
+ \frac{1}{15} (3\sin^2 \theta_i \cos 2\phi_i)^2 + \frac{1}{15} (3\sin^2 \theta_i \sin 2\phi_i)^2 \right\} 
\]

In the case of zeolite-sorbate complexes, the framework (Si) nuclei are not undergoing motion, so \( p=1 \), and the sum is thus reduced to a sum over the \( q \) positions which the sorbate nuclei (protons) occupy over the course of the motion. We must also consider that each silicon will be dipolar coupled to \( N^1H \) nuclei (each undergoing motion) and must sum the contributions from these interactions. Thus the final form of the equation which must be evaluated for each silicon is:

\[
\langle M(I-S) \rangle_{\text{rot}} = \frac{\gamma_1^2 \gamma_2 \hbar^2 \mu_0}{(16\pi^3)} \sum_{k=1}^{N} \sum_{j=1}^{q} \frac{1}{r_{kj}^6} \left\{ \frac{1}{5} (3\cos^2 \theta_{kj} - 1)^2 + \right. \\
\left. \frac{12}{5} (\sin \theta_{kj} \cos \theta_{kj} \cos \phi_{kj})^2 + \frac{12}{5} (\sin \theta_{kj} \cos \theta_{kj} \sin \phi_{kj})^2 \\
+ \frac{3}{5} (\sin^2 \theta_{kj} \cos 2\phi_{kj})^2 + \frac{3}{5} (\sin^2 \theta_{kj} \sin 2\phi_{kj})^2 \right\} 
\]

REFERENCES FOR APPENDIX D


APPENDIX E

ALGORITHM FOR LOCATING MOLECULES IN ZEOLITE CHANNELS FROM CROSS POLARIZATION DATA

This appendix contains a descriptive outline of the logical sequence of steps necessary for calculations used to determine the location and orientation of the p-difluorobenzene molecule in zeolite ZSM-5 from $^{19}$F-$^{29}$Si and $^1$H-$^{29}$Si cross polarization (CP) data. The actual computer programs were developed directly from this "pseudo-code" algorithm. The approach used was to search for linear correlations between the silicon-fluorine (or silicon-proton) heteronuclear second moments and the $1/T_{CP}$ values of selected silicons in the framework as the rigid sorbate molecule was rotated and translated within the zeolite channel system. Details of the background theory, NMR experiments, fitting of the CP data, and the results of these calculations are discussed in Chapter 6.
E.1 PROGRAM OPTIONS AND DETAILS OF TRANSFORMATIONS USED

Two different programs were written. The first of these (CPF9.PAS) calculated static second moments, while the second (CPH9.PAS) incorporated molecular motions of the sorbate molecules (180° ring-flips about the F-F axis) using the equations derived in Appendix D. The actual programs were implemented using the PASCAL programming language and contained approximately 1800 lines of code. Routines incorporated in the program allowed orthogonal and non-orthogonal space groups symmetries to be used, and also supported non-standard choices of the axes in the different crystal systems. This latter requirement was imposed by the need to use the non-standard settings for the monoclinic phase of ZSM-5 (i.e. space group $P2_1/n.1.1$). The source code was compiled to run under the DOS operating system using the Turbo Pascal software package. The pseudo-code presented here is for analysis of $^{19}\text{F}-^{29}\text{Si}$ CP data but is also applicable for $^1\text{H}-^{29}\text{Si}$ CP data (only the input file had to be modified). A sample input file used for the analysis of a $^{19}\text{F}-^{29}\text{Si}$ CP data set is also included.

The programs allowed the mode of operation to be selected from four possible options:
1. Output atomic coordinates (fractional or Cartesian) for a given rotation and/or translation
2. Output of framework–sorbate distances for a given rotation and/or translation
3. Calculation of second moments and least-squares fit for a given rotation and/or translation
4. Calculation of second moments and least-squares fits for a range of rotations and translations

Option 1 provided coordinates for subsequent viewing in an appropriate graphical environment. The programs ATOMS 4.0² and ORTEP-3 for Windows³ were used for this purpose. The option to output sorbate–framework distances was used to produce the information required for the REDOR and TEDOR simulations (Cartesian coordinates were also output when this option was selected). The program was thoroughly checked by comparing the output distances with those obtained from the PLATON-98⁴ crystallography software, and against manual calculations performed for selected sorbate locations and orientations.

The coordinate transformations used to interconvert between fractional and orthogonal Cartesian coordinates are:⁵
\[ X = M x \quad \text{and} \quad x = M^{-1} X \]

where \( X \) and \( x \) are position vectors written as column vectors, with \( X \) expressed in Cartesian coordinates (dimension of length), and \( x \) in (dimensionless) crystallographic fractional coordinates. The matrices \( M \) and \( M^{-1} \) are valid for all 230 space groups and are defined as: \(^1\)

\[
M = \begin{pmatrix}
\frac{a \varphi}{\sin \alpha} & 0 & 0 \\
\frac{a (\cos \gamma - \cos \alpha \cos \beta)}{\sin \alpha} & b \sin \alpha & 0 \\
\frac{a \cos \beta}{b \cos \alpha} & c & 0
\end{pmatrix}
\]

\[
M^{-1} = \begin{pmatrix}
\frac{\sin \alpha/a \varphi}{1} & 0 & 0 \\
\frac{(\cos \alpha \cos \beta - \cos \gamma)}{b \varphi \sin \alpha} & \frac{1/b \sin \alpha}{1} & 0 \\
\frac{(\cos \alpha \cos \gamma - \cos \beta)}{c \varphi \sin \alpha} & -\frac{1/c \tan \alpha}{1} & 1/c
\end{pmatrix}
\]

where \( a, b, c, \alpha, \beta, \text{and} \gamma \) are the usual cell parameters (lattice constants), and

\[ \varphi = \sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma} \]

Fractional coordinates and details of the crystallographic unit cell parameters for the ZSM-5 framework were taken from the single crystal X-ray structure of calcined ZSM-5 at room temperature reported by van Koningsveld et al. (Monoclinic, \( P2_1/n \), \( a = 20.107 \) \( \text{Å} \), \( b = 19.879 \) \( \text{Å} \), \( c = 13.369 \) \( \text{Å} \), \( \alpha = 90.67^\circ \)). \(^6\) The symmetry operators for this non-standard space group were obtained from reference 7. Different symmetry operators were used for the FROM and TO atom sets to ensure that the central unit cell contained 4 complete (intact) sorbate molecules. The sorbate molecule geometry was fixed to an ideal geometry: a planar, rigid, hexagonal para-disubstituted benzene ring with C–C, C–H, and C–F bond lengths of 1.392 \( \text{Å} \), 1.080 \( \text{Å} \), and 1.328 \( \text{Å} \) respectively.

The matrix \( \mathbf{R} \) used for performing the rotations about three Euler angles \((\phi, \theta, \psi)\) is: \(^8\)

\[
\mathbf{R} = \begin{pmatrix}
\cos \psi \cos \theta \cos \phi - \sin \psi \sin \phi & \cos \psi \cos \theta \sin \phi + \sin \psi \cos \phi & -\cos \psi \sin \theta \\
-\sin \psi \cos \theta \cos \phi - \cos \psi \sin \phi & -\sin \psi \cos \theta \sin \phi + \cos \psi \cos \phi & \sin \psi \sin \theta \\
\sin \theta \cos \phi & \sin \theta \sin \psi & \cos \theta
\end{pmatrix}
\]

where the first rotation is by \( \phi \) about the \( z \) axis, followed by a rotation of \( \theta \) about the \( y \) axis, and finally a rotation about the (new) \( z \) axis by \( \psi \).
Four set of atoms were used. These were subdivided into two groups; the FROM atoms (zeolite framework Si and O), and the TO atoms (F and H atoms in sorbate molecules). In addition to a complete unit cell of Si, O, F, and H atoms, the 26 surrounding unit cells of TO atoms were generated. All FROM–TO distances were checked to ensure that a given translation and rotation did not bring the sorbate too close to the framework atoms (distances less than 2 Å were flagged as "too close"). The second moment calculations were only done for the $^{29}$Si and the TO atoms of interest (e.g. $^{19}$F for $^{19}$F–$^{29}$Si CP data), with any TO-FROM distances exceeding the chosen limit (typically 8-10 Å) omitted. In the case of the $^1$H–$^{29}$Si CP data, two calculations were done; one assuming the rings were stationary (static second moments calculated, i.e. using CPF9.PAS), and another using CPH9.PAS assuming the sorbate was undergoing 180° ring-flips about the F-F axis.

E.2 SAMPLE INPUT FILE

INPUT FILE for CPF9.PAS
TITLE
F-Si CP @ 230K 4 DFB + ZSM-5 (P21/n.1.1 Zeolites 1990,10,235)
Cell parameters
a  
20.107  
b  
19.879  
c  
13.369  
alpha  
90.67  
beta  
90.00  
gamma  
90.00  
"From" Atoms Data
Number of known atoms to calculate distances etc. FROM 24
Gyromagnetic ratio for FROM Nuclei in rad / Tesla sec 53188000
FROM Atoms(label up to 4 chars, No spaces) and FRACTIONAL coords
atom x y z
Si1  0.42056  0.05546 -0.31990
Si2  0.31368  0.03090 -0.16358
Si3  0.27960  0.06249  0.05346
Si4  0.12395  0.06233  0.03674
Si5  0.07678  0.02804 -0.17597
Si6  0.19556  0.05585 -0.31331
Si7  0.42542 -0.17148 -0.31930
Si8  0.31225 -0.12653 -0.17388
Si9  0.27325 -0.17590  0.03597
Si10 0.11895 -0.17634  0.03436
Si11 0.07156 -0.12939 -0.17516
Si12 0.19079 -0.16528 -0.31408
Si13 0.42837  0.44297 -0.33456
Si14 0.31237  0.47305 -0.18814
Si15 0.27704  0.43889  0.02940
Si16 0.12155  0.43563  0.03380
Si17 0.07096  0.47315 -0.17844
Si18 0.18737  0.43778 -0.31743


Other FROM Atoms Data

Number of known atoms to check distances etc. FROM 48

Other FROM Atoms (label up to 4 chars, No spaces) and FRACTIONAL coords

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<tr>
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<td>-0.2169</td>
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<tr>
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<td>0.5530</td>
<td>-0.1913</td>
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<td>0.0851</td>
<td>0.5519</td>
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<tr>
<td>O41</td>
<td>0.4186</td>
<td>0.3714</td>
<td>-0.3885</td>
</tr>
<tr>
<td>O42</td>
<td>0.4154</td>
<td>0.5015</td>
<td>-0.4135</td>
</tr>
<tr>
<td>O43</td>
<td>0.3938</td>
<td>0.6320</td>
<td>-0.4087</td>
</tr>
<tr>
<td>O44</td>
<td>0.1900</td>
<td>0.3711</td>
<td>-0.3847</td>
</tr>
</tbody>
</table>

385
"To" Atoms Data
Number of known atoms to calculate distances etc. TO
2
Gyromagnetic ratio for TO Nuclei rad / Tesla sec
251810000
TO Atoms (up to 4 chars, No spaces) and FRACTIONAL coords
atom x y z
F1 0.500000 0.113163 -0.002379
F2 0.500000 0.386837 0.002379
Number of Other atoms to check distances for (not included in calc)
4
label and fractional coords (x, y, z) for Other atoms
H1 0.393530 0.187819 -0.001081
H11 0.606470 0.187819 -0.001081
H2 0.393530 0.312181 0.001081
H22 0.606470 0.312181 0.001081
Ring Centre (x,y,z as Fractional coords)
0.5000 0.2500 0.0000
Number of "From" Symmetry operations
4
Symmetry Instrucs to generate all FROM atoms in unit cell
Must be same number as above and include X Y Z as FIRST Operator
d1 d2 d3 e1 e2 e3 f1 f2 f3 g h i
1 0 0 0 1 0 0 0 1 0.0000 0.0000 0.0000
1 0 0 0 -1 0 0 0 -1 0.5000 0.5000 0.5000
-1 0 0 0 -1 0 0 0 -1 0.0000 0.0000 0.0000
-1 0 0 0 1 0 0 0 1 0.5000 0.5000 0.5000
Number of "To" Symmetry operations
4
Symmetry Instrucs to generate all TO atoms in unit cell
Must be same number as above and include X Y Z as FIRST Operator
d1 d2 d3 e1 e2 e3 f1 f2 f3 g h i
1 0 0 0 1 0 0 0 1 0.0000 0.0000 0.0000
1 0 0 0 -1 0 0 0 -1 0.5000 0.5000 0.5000
-1 0 0 0 -1 0 0 0 -1 1.0000 1.0000 1.0000
-1 0 0 0 1 0 0 0 1 0.5000 0.5000 0.5000
Number of Silicons with known Tcp values input
8
SiliconTcp (ms)
21 9.674
5 10.248
10 11.716
23 10.341
11 11.149
16 15.566
14 10.271
8 9.766
END
E.3 PSEUDO-CODE LISTING (Static Second Moments)

START PROGRAM
Get information from User about filenames and desired mode of operation
get filenames for Input and Output files
determine whether to do full calculation, single calculation, output distances or coordinates
get limits and step sizes for translations and rotations
get cut-off distance (distances longer than this were excluded from the calculations)

Read in the information from the Input file
get cell constants (a, b, c, α, β, γ)
get fractional coordinates for the 4 sets of atoms (Si, O, F and H)
get symmetry operators
gyromagnetic ratios of 29Si and 19F for second moment calculations
coordinates of ring centroid for rotations
read in TCP data for specific silicons
calculate needed constants

Generate complete unit cell of Si and O atoms
apply symmetry operators to fractional coordinates
ensure they lie within 0 < x < 1, 0 < y < 1, 0 < z < 1
convert to orthogonal Cartesian coordinates

Prepare H and F atoms coordinates for rotations and translations
shift fractional coordinates so ring centroid lies at (0,0,0)
convert H and F coordinates to orthogonal Cartesian
convert coordinates of ring centroid to orthogonal Cartesian
store these coordinates

Open Output file and write header information describing output, limits selected etc.

IF Output Coordinates selected THEN
Perform Rotation and Translations
calculate rotation matrix for selected angles φ, θ, and ψ
rotate Cartesian coordinates
shift ring atoms to proper location using ring centroid coordinates
apply translations along x, y, and z axes in Cartesian system

IF Output Cartesian Coordinates selected THEN
write coordinates to Output file
Close Output file

IF Output Fractional Coordinates selected THEN
convert rotated/translated Cartesian coordinates to fractional coordinates
write coordinates to Output file
Close Output file

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IF Output Distances selected THEN
Perform Rotation and Translations
  calculate rotation matrix for selected angles $\phi$, $\theta$, and $\psi$
  rotate Cartesian coordinates
  shift ring atoms to proper location using ring centroid coordinates
  apply translations along $x$, $y$, and $z$ axes in Cartesian system
Generate 27 complete cells of F atoms
  convert rotated / translated F Cartesian coordinates to fractional coordinates
  apply symmetry operators to fractional coordinates keeping rings intact
  convert to orthogonal Cartesian coordinates
  generate the 26 surrounding unit cells of F atoms
Check and output Si-F and O-F distances
  determine all Si-F and O-F distances
  IF distance is less than the selected cut-off THEN
    write distance and Cartesian coordinates to Output file
  IF distance is less than 2.0 Å THEN add “Too Close” flag
Generate 27 complete cells of H atoms
  convert rotated / translated H Cartesian coordinates to fractional coordinates
  apply symmetry operators to fractional coordinates keeping rings intact
  convert to orthogonal Cartesian coordinates
  generate the 26 surrounding unit cells of H atoms
Check and output Si-H and O-H distances
  determine all Si-H and O-H distances
  IF distance is less than the selected cut-off THEN
    write distance and Cartesian coordinates to Output file
  IF distance is less than 2.0 Å THEN add “Too Close” flag
Close Output file
IF Single Calculation selected THEN

Perform Rotation and Translations
- calculate rotation matrix for selected angles $\phi$, $\theta$, and $\psi$
- rotate Cartesian coordinates
- shift ring atoms to proper location using ring centroid coordinates
- apply translations along $x$, $y$, and $z$ axes in Cartesian system

Generate 27 complete unit cells of H atoms
- convert rotated/translated Cartesian coordinates to fractional coordinates
- apply symmetry operators to fractional coordinates keeping rings intact
- convert to orthogonal Cartesian coordinates
- generate the 26 surrounding unit cells of H atoms

Check Si-H and O-H Distances
- determine distances from every framework atom in unit cell to all H atoms
- IF any of these distances is less than 2.0 Å THEN set “Too Close” flag

IF no H atoms are too close to framework atoms THEN
Generate 27 complete unit cells of F atoms
- convert rotated/translated Cartesian coordinates to fractional coordinates
- apply symmetry operators to fractional coordinates keeping rings intact
- convert to orthogonal Cartesian coordinates
- generate the 26 surrounding unit cells of F atoms

Check Si-F and O-F Distances
- determine distances from every framework atom in unit cell to all F atoms
- IF any of these distances is less than 2.0 Å THEN set “Too Close” flag

IF no sorbate atoms (H or F) are Too Close to Si or O atoms THEN
Calculate Second Moments for each of the unique silicons
- determine all Si-F distances ($r$)
  IF $r < \text{cut-off}$ THEN add $1/r^6$ to sum of $1/r^6$
  multiply sum of $1/r^6$ by appropriate factor to obtain second moment in Hz$^2$

Perform least squares fit of second Moment vs. $1/T_C$ data
- write results of regression ($R^2$, slope, y-intercept) to Output file
- write list of second moments for all silicons to Output file

Close Output file
IF Full Calculation selected THEN

ROTATION LOOP
Increment angles $\phi$, $\theta$, and $\psi$ between selected limits using appropriate steps

Perform Rotation
- calculate rotation matrix for selected angles $\phi$, $\theta$, and $\psi$
- rotate Cartesian coordinates
- shift ring atoms to proper location using ring centroid coordinates

TRANSLATION LOOP
Increment translational shift parameters between selected limits using appropriate steps

Perform Translation
- translate along x, y, and z axes in Cartesian system

Generate 27 complete unit cells of H atoms
- convert rotated/translated Cartesian coordinates to fractional coordinates
- apply symmetry operators to fractional coordinates keeping rings intact
- convert to orthogonal Cartesian coordinates
- generate the 26 surrounding unit cells of H atoms

Check Si-H and O-H Distances
- determine distances from every framework atom in unit cell to all H atoms
- IF any of these distances is less than 2.0 Å THEN set “Too Close” flag

IF no H atoms are too close to framework atoms THEN
Generate 27 complete unit cells of F atoms
- convert rotated/translated Cartesian coordinates to fractional coordinates
- apply symmetry operators to fractional coordinates keeping rings intact
- convert to orthogonal Cartesian coordinates
- generate the 26 surrounding unit cells of F atoms

Check Si-F and O-F Distances
- determine distances from every Si and O atom in unit cell to all F atoms
- IF any of these distances is less than 2.0 Å THEN set “Too Close” flag

IF no sorbate atoms (H or F) are Too Close to Si or O atoms THEN
Calculate Second Moments for each of the unique silicons
- determine all Si-F distances ($r$)
- IF $r <$ cut-off THEN add $1/r^6$ to sum of $1/r^6$
- multiply sum of $1/r^6$ by appropriate factor to obtain second moment in Hz$^2$

Perform least squares fit of second Moment vs. $1/T_C$ data

Check and compare regression results
- check slope is positive
- IF good regression THEN
write results of regression ($R^2$, slope, y-intercept) to Output file
write list of second moments for all silicons to Output file
compare regression results with previous best
IF better regression update “best fit” THEN
   store location, orientation, and regression results

LOOP through all possible TRANSLATIONS

LOOP through all possible ROTATIONS

   Output details of “best” solution
   write results of best regression found ($R^2$, slope, y-intercept) to Output file
   list orientation and translations used to obtain this fit

Close Output file

END PROGRAM

References for Appendix E


2 ATOMS 4.0, Shape Software, 521 Hidden Valley Road, Kingsport, TN 57663 U.S.A. http://www.tricon.net/comm/shape/


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APPENDIX F

SUPPLEMENTARY DATA FOR CHAPTER 6

This appendix contains supplementary data from the low temperature NMR investigations of purely siliceous ZSM-5 loaded with ca. 4 molecules of p-difluorobenzene per unit cell presented in Chapter 6.

Three tables are included:

Table F.1 Occupancies and connectivities within the asymmetric unit of the monoclinic \( (P2_1/n.1.1) \) phase of ZSM-5.

Table F.2 Fractional coordinates for p-difluorobenzene atoms for the best location and orientation found from analysis of the \(^1\)H-\(^{29}\)Si CP data at 230 K.

Table F.3 Fractional coordinates for p-difluorobenzene atoms for the best location and orientation found from analysis of the \(^{19}\)F-\(^{29}\)Si CP data at 235 K.
Table F.1 T-sites, their occupancies and connectivities for the asymmetric unit in the monoclinic (P2₁/n11) phase of ZSM-5. Each T-site is connected to the four sites listed.

<table>
<thead>
<tr>
<th>T-site</th>
<th>Occupancy</th>
<th>Connectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>2 16 17 22</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1 3 6 8</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>2 4 18 24</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>3 5 13 19</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>4 6 11 13</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>2 5 15 21</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>8 16 19 23</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>2 7 9 12</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>8 10 18 21</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>9 11 13 22</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>5 10 12 19</td>
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<tr>
<td>12</td>
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<td>8 11 15 24</td>
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<td>4 5 10 14</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>13 15 18 20</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>6 12 14 16</td>
</tr>
<tr>
<td>16</td>
<td>1</td>
<td>1 7 15 17</td>
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<td>4 7 11 20</td>
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<tr>
<td>20</td>
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<td>14 19 21 24</td>
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<tr>
<td>21</td>
<td>1</td>
<td>6 9 20 22</td>
</tr>
<tr>
<td>22</td>
<td>1</td>
<td>1 10 21 23</td>
</tr>
<tr>
<td>23</td>
<td>1</td>
<td>7 17 22 24</td>
</tr>
<tr>
<td>24</td>
<td>1</td>
<td>3 12 20 23</td>
</tr>
</tbody>
</table>
Table F.2 Fractional coordinates\(^{\dagger}\) of the \(p\)-difluorobenzene atoms found from fitting\(^{\ddagger}\) of the \({}^1\text{H}-{}^{29}\text{Si}\) CP data recorded at 230 K. The linear regression results and the parameters defining the translation and rotation for this solution are listed in Table 6.3

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x/a)</th>
<th>(y/b)</th>
<th>(z/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
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<tr>
<td>F2</td>
<td>0.38092</td>
<td>0.31653</td>
<td>0.05530</td>
</tr>
<tr>
<td>H1</td>
<td>0.50471</td>
<td>0.13032</td>
<td>0.00865</td>
</tr>
<tr>
<td>H2</td>
<td>0.56012</td>
<td>0.30922</td>
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<tr>
<td>H3</td>
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<td>0.19078</td>
<td>0.08610</td>
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<tr>
<td>H4</td>
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</tr>
<tr>
<td>C1</td>
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<td>0.21595</td>
<td>-0.07353</td>
</tr>
<tr>
<td>C2</td>
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<td>0.18261</td>
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<tr>
<td>C3</td>
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<td>0.21665</td>
<td>0.03541</td>
</tr>
<tr>
<td>C4</td>
<td>0.43177</td>
<td>0.28405</td>
<td>0.01369</td>
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<tr>
<td>C5</td>
<td>0.47403</td>
<td>0.31739</td>
<td>-0.05164</td>
</tr>
<tr>
<td>C6</td>
<td>0.52733</td>
<td>0.28335</td>
<td>-0.09525</td>
</tr>
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</table>

\(^{\dagger}\) For monoclinic \(P2_{1}/n.1.1\) symmetry with \(a = 20.107\ \text{Å}, b = 19.879\ \text{Å}, c = 13.369\ \text{Å}\) and \(\alpha = 90.67^\circ\). \(^{\ddagger}\) Static second moments used.
Table F.3 Fractional coordinates\(^\dagger\) of the \(p\)-difluorobenzene atoms found from fitting\(^\ddagger\) of the \(^{19}\text{F}\)-\(^{29}\text{Si}\) CP data recorded at 235 K. The linear regression results and the parameters defining the translation and rotation for this solution are listed in Table 6.3

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x/a)</th>
<th>(y/b)</th>
<th>(z/c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>0.50000</td>
<td>0.09304</td>
<td>-0.03265</td>
</tr>
<tr>
<td>F2</td>
<td>0.50000</td>
<td>0.36671</td>
<td>-0.02789</td>
</tr>
<tr>
<td>H1</td>
<td>0.39353</td>
<td>0.16770</td>
<td>-0.03135</td>
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<tr>
<td>H2</td>
<td>0.60647</td>
<td>0.16770</td>
<td>-0.03135</td>
</tr>
<tr>
<td>H3</td>
<td>0.39353</td>
<td>0.29206</td>
<td>-0.02919</td>
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<tr>
<td>H4</td>
<td>0.60647</td>
<td>0.29206</td>
<td>-0.02919</td>
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<tr>
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<tr>
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<td>-0.03088</td>
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<td>-0.02966</td>
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<tr>
<td>C4</td>
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<tr>
<td>C6</td>
<td>0.55995</td>
<td>0.19486</td>
<td>-0.03088</td>
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</table>

\(^{\dagger}\) For monoclinic \(P2_1/n\) symmetry with \(a = 20.107\) Å, \(b = 19.879\) Å, \(c = 13.369\) Å and \(\alpha = 90.67^\circ\). \(^{\ddagger}\) Static second moments used.
This appendix contains supplementary data from the X-ray diffraction refinement of a single crystal of ZSM-5 loaded with 2.85 molecules of p-xylene per unit cell. Full details of the structure refinement are presented in Chapter 8.

Three tables are included:

Table G.1 Anisotropic displacement factors for Si, O and C.

Table G.2 Bond lengths in the ZSM-5 framework.

Table G.3 Bond angles in the ZSM-5 framework.
Table G.1  Anisotropic displacement parameters ($\AA^2 \times 10^3$) for the low-loaded $p$-xylene / ZSM-5 complex at 180 K. The anisotropic displacement factor exponent takes the form: $-2\pi^2 h^2 a^* U_{11} + ... + 2 h k a^* b^* U_{12}$. \\

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{23}$</th>
<th>$U_{23}$</th>
<th>$U_{13}$</th>
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<tbody>
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<td>0(1)</td>
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<td>6(1)</td>
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<td>0(1)</td>
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<td>Si(3)</td>
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<td>7(1)</td>
<td>7(1)</td>
<td>-1(1)</td>
<td>1(1)</td>
<td>0(1)</td>
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<td>Si(5)</td>
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<td>1(1)</td>
<td>0(1)</td>
<td>1(1)</td>
<td>0(1)</td>
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<td>9(1)</td>
<td>1(1)</td>
<td>1(1)</td>
<td>0(1)</td>
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<td>-1(1)</td>
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Table G.2  Bond lengths for framework atoms in ZSM-5 loaded with 2.85 molecules of \textit{p}-xylene per unit cell at 180 K.

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Table G.3 Bond angles for framework atoms of ZSM-5 loaded with 2.85 molecules of p-xylene per u.c. at 180 K.

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Symmetry transformations used to generate equivalent atoms: x+1/2, y, -z-1/2; -x+1/2, -y, z+1/2; -x+1/2, -y, z+1/2; x-1/2, y, -z-1/2; x, -y, -1/2, z.