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BROAD LINE NMR STUDIES ON WF, SF4.AsF5,

AND IF7.AsF5.

ABSTRACT

A general broad line nuclear magnetic resonance 19 study was made of the 19 F spectra of WF₆ and the adducts IF₇ • AsF₅ and SF₄ • AsF₅ to determine the temperature dependence of the spectra, interpret the line shapes with respect to isotropic and anisotropic chemical shifts and identify non-equivalent fluorine sites in the compounds.

The temperature dependence of the second moment at 30 MHz indicated that rigid lattice conditions probably existed at 77° K for WF₆ and IF₇ · AsF₅ but not for SF₄ · AsF₅. The dependence indicated an nmr transition in the vicinity of 200°K for the first two compounds and one commencing below 77° K for the third. From the second moments in the vicinity of the transitions, activation energies were determined for the average motions involved.

The field dependence of the second moments of the compounds was examined, where possible, at 2, 16, 30, 40, 56.4, and 94.1 MHz at 77° and 295° K. The coumpounds' spectra were resolved, with varying degrees of success, into components. For WF₆ an approximate resolution could be made into two components corresponding to the four equatorial and two axial fluorines in the distorted octahedron at 77° K. The two adducts could both be resolved, especially at 295° K or above, into components which supported the ionic formulations IF_6^+ As F_6^- and SF_3^+ As F_6^- . Non-equivalent fluorine sites within individual ions could not be detected.

From the observed and estimated second moments of the resolved components above and below the transitions, the probable reorientations occuring above the transitions were suggested. The rigid lattice theoretical second moment calculations enabled suggestions to be made for the crystal structures of WF_6 and $SF_3^+AsF_6^-$ and for the bond lengths in $IF_6^+AsF_6^-$. For the first there had been confusion, at least here, about the space group, while the second has not yet been the subject of reported X-ray studies.

Axial symmetry of the chemical shift tensors was assumed. Then, taking account of the relative shifts between the resolved components, average values of the chemical shift anisotropies for each of WF_6 and $IF_6^+ AsF_6^-$ were determined from expressions relating the field squared dependence of the second moment to those quantities.

The mean isotropic shifts of the total 19 F spectra for each compound were measured where possible at each field at 77° and 295°K with respect to CF₃COOH. From those the shifts of the resolved components were calculated relative to HF. Then from the isotropic shifts and the anisotropies, the principal values of the axially symmetric shift tensors were determined. The principal values enabled estimates to be made of I (ionic) and ρ (double bond) characters, neglecting hybridization, in the M-F bonds of the hexafluoride groups. From these values a prediction was made for I and ρ in the axial and equatorial bonds in PuF₆.

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PUBLICATIONS

- M.R. Barr, B.A. Dunell & R.F. Grant 'Premelting Phenomena in Long-Chain Fatty Acids', Can. J. Chem., <u>41</u>, 1188 (1963).
- M.R. Barr, B.A. Dunell 'Proton Magnetic Resonance Absorption in High Temperature Phases of Anhydrous Sodium Stearate' Can J. Chem. <u>42</u>, 1098 (1964).

A ¹⁹F BROAD LINE NUCLEAR MAGNETIC RESONANCE STUDY

of

$$WF_6$$
 , $IF_7 \cdot AsF_5$, $SF_4 \cdot AsF_5$

by

MATTHEW RONALD BARR B. Sc. (Hons.), U.B.C., 1960 M. Sc., U.B.C., 1963

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September, 1967

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Abstract

A general broad line nuclear magnetic resonance study was made of the $^{19}\mathrm{F}$ spectra of WF_6 and the adducts $\mathrm{IF}_7 \cdot \mathrm{AsF}_5$ and $\mathrm{SF}_4 \cdot \mathrm{AsF}_5$ to determine the temperature dependence of the spectra, interpret the line shapes with respect to isotropic and anisotropic chemical shifts and identify non-equivalent fluorine sites in the compounds.

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From the observed and estimated second moments of the resolved components above and below the transitions, the probable reorientations occuring above the transitions were suggested. The rigid lattice theoretical second moment calculations enabled suggestions to be made for the crystal structures of WF_6 and $SF_3^+A_5F_6^-$ and for the bond lengths in $IF_6^+A_5F_6^-$. For the first there had been confusion, at least here, about the space group, while the second has not yet been the subject of reported X-ray studies.

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The mean isotropic shifts of the total 19 F spectra for each compound were measured where possible at each field at 77° and 295°K with respect to CF₃ COOH. From those the shifts of the resolved components were calculated relative to HF. Then from the isotropic shifts and the anisotropies, the principal values of the axially symmetric shift tensors were determined. The principal values enabled estimates to be made of I (ionic) and ρ (double bond) characters, neglecting hybridization, in the M-F bonds of the hexafluoride groups. From these values a prediction was made for I and ρ in the axial and equatorial bonds in PuF₆.

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CHAPTER 1

INTRODUCTION

In the Fall of 1964, a joint project on the investigation of the nuclear magnetic resonance spectra of the solid addition compounds SF₄ \cdot BF₃ , SF₄ \cdot AsF₅ and IF₇ \cdot AsF₅ was undertaken in collaboration with Dr. Neil Bartlett and his co-workers. Exploratory studies showed that an examination of the simpler molecule WFs might be helpful. In the event, it turned out that a complete interpretation of the spectra of any of these compounds was made very difficult by combined isotropic chemical shift and chemical shift anisotropy, both of which were significant, but difficult to separate from one another and from direct dipole-dipole interactions in the solids. Because of the presence in all samples of SF_4 . BF_3 of a narrow, impurity line which grew as each sample aged, attention was focused on the other two adducts. It was obvious that the AsF_5 fluorines would be isotropically shifted from the fluorines in anisotropic shift uncomplicated by isotropic shift, a molecule, solid \mathbb{WF}_6 , in which the fluorines were expected to be equivalent, or very nearly so, was selected. Non-equivalent fluorines, however, were present in WF_6 and a search for a quantitative interpretation of the detail of the molecule's line shape ultimately occupied some two-thirds of the time involved in the research. This thesis then became a general nuclear magnetic resonance study of the fluorine

spectra of $SF_4 \circ AsF_5$, $IF_7 \circ AsF_5$, and solid WF_6 , comprising, where possible, temperature dependence, interpretation of the line shapes with respect to isotropic and anisotropic chemical shifts, and identification of equivalent fluorine atoms.

The two AsF_c adducts are relatively new compounds having been reported only during the last decade. In 1956, Bartlett (1) reported that SF, coordinated with AsF, in the ratio of one mole of each to form a new compound, a white solid. The following year he observed that a displacement reaction involving this adduct was a convenient method for purifying SF, (2). In 1958 Seel and Detmer (3) reported $SF_4 \cdot AsF_5$ and $IF_6 \cdot AsF_5 \cdot They noted that the stable$ solids were a convenient form in which to store gaseous fluoro compounds such as SF_4 . They also used IF_7 . As F_5 as a source of pure fluorine (4). In a longer paper in another journal (5) they discussed the compounds again and suggested an ionic formulation. In 1961, Bartlett (6) reported in greater detail on $SF_4 \cdot AsF_5 \cdot$ Kolditz (7, 8, 9) has also reported adducts of AsF₅ which are ionic. Beaton (10) from infrared and X-ray spectra has shown that the acidbase adduct IF₇ · AsF₅ is indeed the ionic salt IF₆⁺ AsF₅⁻. Tebbe and Muetterties (11) and Young and May (12) also have reported probable ionic adducts of AsF_5 .

The symmetry of hexafluoride molecules has made them of interest to spectroscopists and theoreticians for many years (13 to 30). Thermodynamic values are reported in the preceding references (14, 20, 21, 26, 28) and also separately in other papers (31 to 35). In the

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vapour phase octahedral symmetry appears well established for most hexafluorides (17, 18, 28, 30). Except for UF₆ (36) no detailed X-ray data exist for the metal hexafluorides. Since the bond lengths (37a) and X-ray results (37b) available for WF_6 do not permit determination of the symmetry of the solid, it appeared that this presented an excellent opportunity for broad line nmr. For UF the X-ray data indicate below $+25^{\circ}$ C a tetragonal distortion with four short and two long bonds. Blinc et al (38) undertook a broadline nmr study of polycrystalline UF₆ in which they interpreted the F resonance spectrum below -30 C as a composite arising from the isotropic chemical shifts of two different fluorine sites present in a 2:1 ratio. This is in agreement with the X-ray results. The work was at an external magnetic field of 9400 gauss, at which field anistropic chemical shift of the components could not be detected. Working at higher magnetic fields, Rigny (39) concluded that anistropy was present. Blinc and Rigny (40) later published a joint letter on relaxation through anisotropic chemical shift in UF_{κ} . Prior to the appearance of Rigny's thesis, work was begun on polycrystalline WF_{5} in this laboratory. While the experimental results were being interpreted, Blinc et al (41) published a paper on the nmr and relaxation of hexafluoride, polycrystalline solids which included WF_6 . The Blinc spectra agreed well with those obtained here and the interpretation confirmed what was already known here - that interpretation was difficult. High resolution nmr spectra of liquid MoF₆ and WF have been reported by Cady (26) and

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Rigny (42). In Cady's work the fluorides were also examined below the solid-solid transition (about $-8^{\circ}C$ for both compounds) but the spectra were too broad for the lines to be observed by high resolution. In the liquid state both Cady and Rigny observed in addition to the central peak, six small satellite peaks in the ¹⁹F spectrum of MoF₆ due to the ^{95, 97}Mo - ¹⁹F coupling. For WF₆ Cady observed only a single, central peak. However, Rigny observed two satellites corresponding to the ¹⁸³W - ¹⁹F coupling.

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CHAPTER II

NMR THEORY

Since the first successful nuclear magnetic resonance experiments were reported in 1946 by Purcell, Torrey, and Pound (43) and Bloch, Hansen, and Packard (44) very many papers, reviews, and books on the phenomenon have appeared. For details of the theory one may refer to Bloembergen, Purcell, and Pound (45), reviews by Smith (46), Gutowsky (47, 48) and Pake (49), and books by Bloembergen (50), Andrew (51), Abragam (52), and Slichter (53) among others. Only information to supply a general outline of the theory is given in this section. Unless a specific reference is given, it is to be understood that acknowledgment is made to the above (especially Andrew) for the material in this chapter.

Those nuclei which do not have even mass number and atomic number have a non-zero spin angular momentum $\underline{J}\hbar$ and a dipolar magnetic moment $\mu = \sqrt{J}\hbar$ colinear with it. Prominent among these is the ¹⁹F nucleus. The magnetic moment is also often expressed as $\mu = 9\mu_0\underline{J}$ where μ_0 is the nuclear magneton ($\mu_0 = \frac{e\hbar}{iMc}$) and g is the nuclear g-factor analogous to the Lande splitting factor. In the absence of an external magnetic field the energy of a nuclear "magnet" is independent of the orientation of the magnetic mament. However, in the presence of a field \underline{H}_0 , the moment is subject to a torque $\underline{T} = \mu \times \underline{H}_0$ which tends to align it parallel to the field.

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There is an energy of interaction $E = -\mu H_0$. If H_0 is taken as the z-direction, then $E = -\gamma I_z + H_o = -m\gamma + H_o$ where is the component of the angular momentum vector along H_{o} . I. The values of $\mathbf{I_z}$ or \mathbf{m} , the magnetic quantum number (the more usual symbol for the component of angular momentum) are given by the series I, I-1, ...-(I-1), -I. Hence for 19 F where I= $\frac{1}{2}$, there are two possible orientations for the component and two possible energy levels. The selection rule for transitions between the energy levels is $\Delta m = \pm 1$, therefore for $^{19}F \Delta E = -3 \hbar H_0$. The frequency corresponding to an allowed transition is $\omega_0 = 2\pi v_0 = \delta H_0$. The nuclear moment μ precesses about the external field H_{\bullet} at this frequency, the Larmor precession frequency, ω_o . In the nuclear magnetic resonance experiment, a small, oscillating radiofrequency magnetic field H_i is applied at right angles to \underbrace{H}_{\bullet} . When the frequency of oscillation of $H_{
m c}$ equals $\omega_{
m o}$, a resonance interaction occurs which may flip the nucleus from the upper to lower or lower to upper energy level. In the usual experimental arrangement the oscillator frequency is kept fixed while the external magnetic field \underline{H}_{o} is slowly varied to effect the resonance condition.

The above treatment for a single nucleus may be extended to a system of weakly interacting nuclei. This is an excellent approximation to the conditions in matter in bulk. At equilibrium in an external magnetic field there will be, due to a Boltzman distribution of energies, a slight excess of spins in the state

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m=+½ corresponding to the lower energy level for a ¹⁹F nucleus. There can then be a net absorption of energy by the nuclear system in an nmr experiment. This absorption produces a measurable signal which is characteristic of the system. The net absorption would cease when the populations of the two levels were equalized, but relaxation processes exist whereby the nuclei can dissipate energy to the surrounding lattice.

So far one expects an extremely narrow resonance line. In liquids this is generally realized. (There will of course be uncertainty broadening, which is fundamental to all spectral measurements.) In rigid solids, however, line widths are typically of the order of several gauss. Apart from the trivial cause of inhomogeneity in the external magnetic field, which can be reduced to a negligible value, there may exist for a spin $\frac{1}{2}$ nucleus spin spin, dipolar, and chemical shift broadening mechanisms.

If the nuclei involved are identical, nucleus j produces at nucleus k a magnetic field oscillating at its Larmor frequency and a spin-spin transition involving a mutual exchange of energy may occur. This results in a broadening of the order of \underline{H}_{ℓ} where \underline{H}_{ℓ} is the field produced at nucleus j by nucleus k.

In addition to spin-spin broadening, there will always be a dipolar broadening regardless of whether like or unlike nuclei are present. Each nucleus experiences the resultant effect of the external field \underline{H}_{o} and the local fields \underline{H}_{i} of all the other nuclei. The components of the local fields in the direction of \underline{H}_{o} may

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increase or decrease $\underbrace{H_0}$ with a resultant spread of resonance. In liquids the dipolar broadening effect is removed by the rapid motional averaging of the local fields to zero, but in rigid, diamagnetic solids it is the principal contribution to line width.

Spin-spin and dipolar broadening were strikingly demonstrated by Pake (54) in a classic experiment with gypsum, $CaSO_{\lambda}$ • 2H_2O . Because of the r^{-3} dependence of the dipole interaction, each proton in the gypsum is predominately influenced by its partner in the water molecule. Hence there are two resonance frequencies given by $H_0 = H^* + \mu r^3 (3 \cos^2 \Theta - I)$ where $H^* = h \nu / \lambda \mu$, μ is the proton moment, r is the pair separation, and Θ is the angle between to and (the vector joining the two nuclei). If, as in this case, the nuclei are identical, spin-spin exchange modifies the classical picture to $H_0 = H^{+} \pm \frac{3}{2} \mu F^{-3}(3\cos^2 \Theta - 1)$. The unit cell contains two types of protons with generally different values of $\boldsymbol{\varTheta}$. Depending on the orientation of a single crystal one, two, three or four of the possible resonance lines may be observed. Contributions from distant neighbours will contribute further broadening to the spectrum. If the sample is polycrystalline with the orientation of the dipole pairs isotropically distributed, a line shape function of the form

 $f(h) = (6\sqrt{3}\mu r^{-3})^{-1} [1 + h/(\frac{3}{2}\mu r^{-3})]^{-1/2} \qquad \dots (1)$ where h=H_0-H^{*} and the signs are taken as plus for $-\frac{3}{2}\mu r^{-3} < h < 3\mu r^{-3}$

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and minus for $-3\mu r^{-3} < h < \frac{3}{2}\mu r^{-3}$, can be derived (54). The polycrystalline line shape is a doublet which again is further broadened by the local fields of all other neighbours. This general line shape function will be encountered again.

The line shapes for certain three-spin and four-spin systems have been calculated, but for more general systems the task is extremely difficult and in any case the lack of detail in the spectra makes the effort of little use. Fortunately there exists a technique devised by Van Vleck whereby information can be extracted from the more complicated systems. This method and its applications will be discussed prior to describing the effect of chemical shift on line broadening.

Van Vleck (55) showed that the moments of a resonance spectrum can be readily calculated. If the normalized line shape is the function g(h) where h is the distance from the center of resonance, the h^{th} moment is $S_n = \int_{-\infty}^{+\infty} h^n g(h) dh$. All the oddnumbered moments are zero since g(h) is an even function for magnetic dipolar broadening. Van Vleck calculated second and fourth moments for the general case. For a rigid polycrystalline sample the second moment is

 $S_{2} = \frac{3}{5} I(I+i)g^{2} \mu_{o}^{2} N^{-1} \sum_{j,k} r_{jk}^{-6} + \frac{4}{15} \mu_{o}^{2} N^{-1} \sum_{j,f} I_{f} (I_{f}+i)g^{2}_{f} r_{jf}^{-6} \dots (2)$ where I is the spin number of the nuclei, μ_{o} is the nuclear magneton, g is the nuclear g-factor, N is the number of magnetic nuclei in the system over which the sum j is taken, and r_{jk} is the magnitude

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of the vector joining nuclei j and k. The first term accounts for dipolar broadening by those nuclei whose resonance is being observed. The second term is a contribution to spectral broadening by species of magnetic nuclei other than those at resonance. (In WF_6 for example, ¹⁹F and ¹⁸³W respectively.)

During the course of a broad line nmr investigation of a polycrystalline solid, one normally records the magnetic resonance spectrum over a range of temperatures varying from low (usually liquid nitrogen temperature) up to room temperature or considerably higher as dictated by the nature of the compound. If the lowest temperature corresponds to a rigid lattice condition, then after a correction for zero-point motion of the nuclei has been made (56), the observed second moment, should agree within experimental error with the calculated rigid lattice second moment. Any discrepancy will be due to additional motion in the crystal lattice. If the crystal structure has not been determined a resonable structure may often be worked out by trial from the nmr rigid lattice second moment. Even if rigid lattice conditions do not prevail, quite resonable estimates of the probable structure can be obtained by considering the effect on second moment of possible motions in the crystal lattice. The application of second moments is also useful in determining the positions of protons, which are difficult to locate accurately by X-ray crystallography. Since equation (2) involves r⁻⁶, a highly accurate internuclear distance r can

frequently be obtained. In single crystal spectra bond angles can be obtained in addition to bond lengths.

Motion within the lattice, whether of whole molecules or of substituent groups, contributes to a time averaging of the local fields. The averaged field is less than the steady local field for a rigid system and as motion becomes more pronounced the resonance line becomes narrower as liquid-like conditions are approached. The narrowing of the line may give evidence of molecular motion even though the frequency of reorientation may be quite small for each molecule. A potential barrier obviously exists for this motion and motion takes place when a molecule has sufficient energy to surmount the barrier. A very high barrier produces an essentially rigid structure although even then there may be rotational oscillation. In a reorientation process which can be described by a single frequency or correlation time, the temperature dependence of the correlation time, τ_c , may be described by

 $\tau_c = \tau_0 \exp(\Delta E/RT)$ (3)

where AE is the height expressed in energy per mole of the hindering potential. Then the reorientation rate, ν_c , defined by $2\pi\nu_c = 1$ is

V=V exp(-DE/RT)

The resonance line narrows when the reorientation rate becomes of the order of the frequency of the line width. Calculation of the line shope for a complicated reorienting system is of course even

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more difficult than for a rigid system and again second moments are used. The change in second moment will depend on the nature of the reorientation (57). For a polycrystalline material containing a system or group undergoing a free rotation over an n-fold periodic potential barrier where $n \ge 3$, equation (2) becomes, for the intramolecular contribution only

 $S_{2}^{\mu ren} = \frac{3}{20} I(1+)g^{2} \mu_{0}^{2} N^{-1} \sum_{i,k} (3\cos^{2} g - i)r_{jk} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{jk} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{jk} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{jk} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} (3\cos^{2} g - i)r_{i}^{2} + \frac{1}{15} \mu_{0}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}^{2} N^{-1} \sum_{i} I_{i}(1+)g_{i}$ where γ_{ik} is the angle between the internuclear vector f_{ik} and the axis of rotation. Each term has been reduced by the factor $\frac{1}{4} (3\cos^2 \gamma_{ik} - i)^2$ This is the reduction of only the intramolecular second moment. That for the intermolecular moment is much more complicated since the varies as well. The only case in which the intermolecular contribution can be obtained simply is that for isotropic molecular reorientation of a group about its molecular center (58, 59, 60, 61). The magnetic nuclei are considered to be concentrated at the molecular centers and the distances Tix in equation (2) are replaced by R, the center-center distance between a molecule and its i nearest neighbour. The equation becomes $S_{2}^{\text{INTER}} = \frac{3}{5}I(I+i)g^{2}\mu_{0}^{2}N_{0}\sum_{i}N_{i}R_{i}^{-6} + \frac{4}{15}\mu_{0}^{2}N_{0}\sum_{i}I_{f}(I_{f}+i)g_{f}^{2}N_{i}R_{i}^{-6}$..(6) where N_0 is the number of resonant nuclei in the molecule, N_{\cdot} is the number of i nearest neighbours and the other quantities are as before. The isotropic reorientation averages the intramolecular moment to zero and the calculated sum is the intermolecular contribution. If the reorientation is not isotropic, but about preferred

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axes at random the calculation is more difficult (61, 62, 63, 64a) and the result may differ from that for isotropic reorientation by 5 to 15% (64b).

Activation energies for molecular reorientations may be derived from a log ν_{c} versus $^{1}/T$ plot of equation (4). The correlation frequency in terms of line width in gauss is (based on Gutowsky and Pake (57)

 $\mathcal{Y}_{L} = \frac{\Delta H}{1h} \Delta H / tan \left[\frac{\pi}{2} \left(\Delta H^{2} - \Delta H^{2}_{A} \right) / \left(\Delta H^{2}_{B} - \Delta H^{2}_{A} \right) \right] \dots (7)$ where ΔH is the line width in the transition region, ΔH_{A} is the line width above the transition, and ΔH_{B} is that below the transition, $\boldsymbol{\alpha}$ is a constant of the order of unity, and $\boldsymbol{\mu}$ is the magnetic moment in nuclear magnetons. If the line shape changes during the transition, line width is not a reliable parameter (65). Since second moments are a more reliable indication of temperature effects the correlation time may be expressed according to Powles and Gutowsky (66) in terms of second moment in gauss² as

$$v_{c} = \frac{4\mu}{\ln} \left(S_{2} \right)^{1/2} t dn \left[\frac{\pi}{2} \left(\frac{S_{2} - S_{2}^{A}}{S_{2}^{B} - S_{2}^{A}} \right) \right] \qquad (8)$$

where S_1 is the second moment at any point in the transition region, S_2^A is the second moment above the region, S_2^B is the second moment below the region, and the other symbols are as before. Unless only a single motion is occurring these are average values of \mathcal{V}_2 and $\bigtriangleup E$ which are obtained. Also an added uncertainty arises from the use of the line width or second moment. The intermolecular contributions to the resonance curve may vary with motion and hence with temperature in a different fashion from the intramolecular contribution. Orders

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of magnitude of \mathcal{X} or $\Delta \mathcal{E}$ are probably the best that can be expected. A more reliable approach is to determine correlation times from spinlattice relaxation measurements. This is, however, not always experimentally convenient, while line widths and second moments can always be obtained. Furthermore if the motion taking place is complicated, \mathcal{X} and $\Delta \mathcal{E}$ are, as noted above, average values. Comparison of the observed second moment change with that calculated on the basis of the possible motions occurring gives a more reliable picture of reorientations taking place in complicated cases. The activation energy will, however, provide supporting evidence for the occurrence of the suggested motion.

Chemical shift also contributes to nuclear magnetic resonance line-broadening. In diamagnetic molecules, the most frequent subjects for nmr experiments, the ground state has, in the absence of an external field, no resultant electronic spin or electronic orbital angular momentum (67). An external field induces an orbital motion in the electrons of a molecule which is superimposed on the electrons' motions about their nuclei. The motions constitute effective currents within the molecule which produce at the nucleus additional magnetic fields which are proportional to the external field \underbrace{H}_0 . The resultant field experienced by the nucleus is expressed as (52, Chap. 6; 68, Chap. 1)

where \mathbf{S} is a second rank tensor dependent on the electronic environment of the nucleus considered. The shift is a combination of

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diamagnetic and paramagnetic shielding effects. The diamagnetic term is essentially a Larmor precession, in the field \underbrace{H}_{\bullet} , of the electronic charges in the molecule about the nucleus in question; while the paramagnetic term arises from the polarization of electron shells by \underbrace{H}_{\bullet} (52, Chap. 6).

Slichter (53, p. 84) expressed the shielding after Ramsey (67) as $\begin{aligned} &= \frac{e^{2}}{2mc^{2}} \left(\frac{\Psi_{0}}{\sum} \left[\frac{K}{2} \left(\frac{x_{1}^{2} + y_{1}^{2}}{r_{1}^{3}} - \frac{A}{2} \frac{x_{1}^{2} z_{1}}{r_{1}^{3}} - \frac{1}{2} \frac{y_{1}^{2} z_{1}}{r_{1}^{3}} \right] \right] \frac{\Psi_{0}}{r_{0}} - \frac{e^{2} h^{2}}{2m^{2} c^{2}} \sum_{n} \left[E_{n} - E_{0} \right] \times \left[\left(\frac{\Psi_{0}}{\sum} \frac{1}{r_{1}^{3}} \frac{1}{r_{1}^{3}} + \frac{1}{r_{1}^{3}} - \frac{1}{2} \frac{y_{1}^{2} z_{1}}{r_{1}^{3}} \right] \right] \frac{\Psi_{0}}{r_{0}} - \frac{e^{2} h^{2}}{2m^{2} c^{2}} \sum_{n} \left[E_{n} - E_{0} \right] \times \left[\left(\frac{\Psi_{0}}{\sum} \frac{1}{r_{1}^{3}} \frac{1}{r_{1}^{3}} + \frac{1}{r_{1}^{3}} + \frac{1}{r_{1}^{3}} \frac{1}{r_{1}^{3}} + \frac{1}{r_{1}^{$

where e is the electronic charge, **m** the electronic mass, c the speed of light; $4'_{k}$, $4'_{k}$ and E_{0} , E_{n} the wavefunctions and energies of electrons in the ground and nth excited states respectively; \hat{L}_{j} the total angular momentum operator $\eta \times \rho_{j}$ (where ζ_{j} is the vector from the shielded nucleus to the electron whose coordinates are x_{i} , y_{i} , z_{j} and ρ_{i} is the linear momentum), \hat{L}_{s} is the angular momentum operator $\frac{\pi}{2}(\chi_{\partial j}^{2} - \chi_{\partial s}^{2})$, and r_{j} is the magnitude of ζ_{j} . The sums j and k are taken over the N electrons present and the sum n over the n states. The two terms are of approximately equal magnitude and are respectively the diamagnetic and the second-order paramagnetic contribution. As indicated by equation (10) the diamagnetic term is a ground state contribution. It is in fact (67), the same as Lamb's complete expression for the diamagnetic shielding of single atoms (69). The paramagnetic term is an excited state contribution from the magnetic fields set up by the orbital motions of the valence electrons (70). In the absence of an external static field tha orbital fields have a zero average value but produce instantaneous fields of several thousand gauss at the nucleus. The applied field produces a slight polarization of these large fields and hence an appreciable shielding. Since the valence electrons are more readily polarized, the principal contribution is from them rather than from the closed shell electrons. Ramsey (67) pointed out, however, that the separation into two distinct terms is artificial and that the terms are in fact closely related.

In their discussion of fluorine chemical shifts, Saika and Slichter (70) made a division of the shift into three terms:

(a) the diamagnetic correction for the relevant atom. This is again the Lamb term. It accounts for only about 1% of the range of fluorine shifts observed.

(b) the paramagnetic correction for the relevant atom. This term is principally responsible for chemical shifts in fluorines.

(c) the contributions from electrons in other atoms. The electrons in other atoms are either in closed shells and difficult to polarize or in valence shells in which the electrons although readily polarized are still subject to a $1/r^3$ falling off of the interaction. The contribution from this term is therefore small.

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Although term (b) is the principal contribution to the fluorine shift, in the case of electrons in a purely s state (the electrons exert a zero instantaneous orbital magnetic field at the nucleus, while p and d electrons exert large fields) the terms (a) and (c) would comprise the shift. That is, because of the spherical symmetry of an s state, the angular momentum operators make the second term of equation (10) equal to zero for a purely s state. The paramagnetic term would be zero in completely ionic F^{-} because of the filled L shell, and have its maximum value in covalent F_2 .

Pople (68, Chap. 7) adds a fourth term to Saika and Slichter's: (d) the contribution from interatomic currents. If it is possible for electrons to flow from one atom to another, as for example in aromatic molecules, the interatomic currents can generate additional screening.

Chemical shift broadening of the resonance line may have either isotropic or anisotropic origins or both. If a solid contains nonequivalent nuclei there will be a broadening of the resonance line due to differences in isotropic shift. If there are nuclei in nonequivalent electronic environments, Andrew (71) notes that the following additional contribution must be added to the second moment:

$$H_{u}^{2}\left[\left(\bar{\sigma}_{1}-\bar{\sigma}_{2}\right)^{2}+\left(\bar{\sigma}_{2}-\bar{\sigma}_{2}\right)^{2}+\cdots+\left(\bar{\sigma}_{u}-\bar{\sigma}_{1}\right)^{2}\right] \qquad \dots \qquad (11)$$

where

$$\overline{\overline{\sigma}} = \frac{1}{\mathcal{U}} \left(\overline{\sigma}_1 + \overline{\sigma}_2 + \dots \overline{\sigma}_{\mathcal{U}} \right) \qquad \dots \qquad (12)$$

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 $ar{m{\delta}}_{m{u}}$ is the isotropic mean shift for nucleus $m{u}$

where

 $\overline{\sigma}_{u} = \frac{1}{3} T_{F} \mathcal{O}_{u} = \frac{1}{3} \left(\sigma_{xx} + \sigma_{yy} + \sigma_{yy} \right) \qquad \dots \qquad (12a)$

where 6, 6, 6, and 6, are the principal axes of the shift tensor.

Even if a solid contains only nuclei in identical electronic environments, there may be a chemical shift contribution to line broadening. If the chemical shift tensor, ${\boldsymbol{\varsigma}}$, is asymmetric, a probing external field will encounter different electronic screening depending on the molecular orientation in the field.

The investigation of chemical shift anisotropy in polycrystalline solids is based on the approach employed by Bloembergen and Rowland (72) with thallic oxide. Andrew and Tunstall (71) express the field experienced by a given nucleus in a polycrystalline solid as

 $H = H_0 \left[1 - \left(\lambda_x^2 \mathcal{O}_{xx} + \lambda_y^2 \mathcal{O}_{yy} + \lambda_y^2 \mathcal{O}_{yg} \right) \right]$ where $G_{2x}, \sigma_{3y}, \sigma_{7y}$ are again the principal axes of the shift tensor and $\lambda_x, \lambda_y, \lambda_z$ are the direction cosines with respect to \nexists_o . The average field experienced by all the nuclei if the crystallites in the polycrystalline sample are isotropically distributed is expressed by

..... (13)

 $\overline{H} = H_0 \left[1 - \frac{1}{3} (\sigma_{xx} + \sigma_{yy} + \sigma_{yy}) \right]$ (14)

For axial symmetry about the z-axis $\lambda_{z} = \cos \theta$,

 $G_{xx} = G_{yy} = G_{x}$, and $G_{yy} = G_{y}$ and $H = \overline{H} - h$ (15) where $h = \frac{1}{3} H_{0} (G_{y} - G_{1}) (3 \cos^{2} \theta - i)$ and where H and H are fields at nucleus The normalized line shape is then

The function f(h) is similar in form to equation (1).

The second moment of the line shape given by equation (16) is $f_1(h) = \frac{4}{5}d^2 = \frac{4}{45}H_0^2(G_u - G_1)^2$

(17)

$$S_2 = g_2(h) + f_2(h) = g_2(h) + \frac{4}{45} H_0^2(G_{11} - G_{12})^2 \dots (18)$$

The correct center of moments is not readily apparent in an asymmetric curve, but if first and second moments are computed about a point close to the estimated center (to minimize error) the first moment gives the center of moments directly and the second moment can be transferred to it. If the transferred second moment is plotted against H_0^2 , the absolute value of the anisotropy of

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chemical shift $|6_n-6_1|$ can be determined. The sign can be found from the direction of asymmetry of the curve. The anistropy may be used to provide information about the type of bonding in the solid studied. The intercept of the plot will give $g_n(h)$, the dipolar second moment, and this can be used as a broadening function (gaussian usually) on equation (16) to synthesize a curve for comparison with the experimental curve. The extrapolated "dipolar moment" will of course include any field independent broadening which is present.

If both isotropic and anisotropic shifts are present the second moment equation becomes $S_1 = g_1(h) + f_2(h) + y_1(h)$

 $= g_{R}(J) + \frac{4}{45} H_{0}(G_{1} - G_{1}) + \frac{H_{0}}{U} \left[(G_{1} - \overline{G})^{2} + (G_{2} - \overline{G})^{2} + (G_{2} - \overline{G})^{2} \right] \dots (19)$ Here the expressions $(G_{1} - \overline{G})$ etc. are as in equations (11) and (12) and $(G_{1} - G_{1})$ is an average anisotropy for all the "isotropically" shifted resonant nuclei. Unless the various nuclei are sufficiently shifted from one another to permit a confident resolution of the curve into its components (in which case the individual $(G_{1} - G_{1})^{2}$ s may be determined also) the interpretation of the resonance spectrum may be very difficult.

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CHAPTER III

EXPERIMENTAL PROCEDURE

The $SF_4 \cdot AsF_5$, $IF_7 \cdot AsF_5$, and WF_6 samples supplied by Dr. Neil Bartlett were prepared by Dr. S.P. Beaton. Only pure $SF_4 \cdot AsF_5$ and $IF_7 \cdot AsF_5$ samples were used. For WF_6 both pure samples and samples doped with IrF_6 (up to one part per thousand) were run. In the latter case the paramagnetic impurity was added to shorten the spin-lattice relaxation time, reduce saturation, and improve the signal to noise ratio in the spectrum by permitting the runs to be made at higher rf field (H, field). Spectra were recorded over a two year period using several different samples of each compound. At the end of the study comparisons were made between recent samples and samples stored for more than a year. Between runs samples were stored in a dry-ice acetone bath or liquid nitrogen.

The fluorine magnetic resonance spectra of the compounds were recorded on two Varian 4250-type broad line spectrometers and on a Varian HA100 high resolution spectrometer. One of the broad line spectrometers was a DP60 with a Varian 12 inch electromagnet and a 56.4 MHz V-4311 Fixed Frequency RF Unit. The other broad line spectrometer employed a Varian 6 inch electromagnet and a 30 MHz V-4310A Fixed Frequency RF Unit and a 2-16 MHz V-4210A Variable Frequency RF Unit. The 2000 Hz sidebands of the V-3521A Integrator/

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Decoupler were used to provide sweep modulation on the HA100. Since the resonance lines of the solids were very much wider than 2000 Hz, the resulting spectra were the familiar derivative signals customarily observed in broad line work. Since the normal method of calibrating the modulation amplitude of a lock-in detector by recording the derivative of a liquid line could not be used on the high resolution spectrometer, a minor problem was encountered in determining the amplitude of the modulation. However, when a liquid signal is scanned, the Integrator/Decoupler may be adjusted to give zero amplitude for the center band. Then at that point there is a known modulation index from which the modulation amplitude may be determined (74). This required adjustment of the coarse amplitude control in the interior of the instrument. It was difficult to reproduce this exact value for each series of runs without recording a tedious series of signals on a strip recorder each time. However, it was always simple to ensure that the amplitude was below the point of known amplitude which in itself was safe (about 1.2 gauss peak to peak) and that modulation broadening was absent. A more serious problem was encountered in obtaining a pure absorption derivative of the resonance signal. Balancing and phasing were quite critical and laborious. Operation on wide line diode detection with the introduction of absorption leakage was quicker and surer than phase detection. It also produced a better signal to noise ratio. Standard operating procedures were employed on the two broad line spectrometers.

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The temperature dependence of the fluorine magnetic resonance spectra was studied at 30 MHz for all three compounds from 77° K to above 300 K and for a few temperatures from 173 K to 283 K at 94.1 MHz for a sample of IrF6-doped WF6. For low temperature runs at 30 MHz the temperature was controlled by cooled nitrogen vapour passed through a flow system which has been described by Ware (75). Below about 220°K a liquid nitrogen bath was used to cool the gas. Between 220°K and room temperature a dry-ice acetone bath was used. Above room temperature, heated, compressed air was used in place of the tank nitrogen. The extremely efficient heater was of a doublepass heat exchanger type, incorporating a 600W cylindrical heating coil, designed by W.R. Janzen for his work in this laboratory. Temperature control was approximately $+5^{\circ}$ around 100° K and $+1^{\circ}$ above 150°K. At 94.1 MHz the standard Varian V-4341 Variable Temperature System was used. The temperature range of this system is stated to be -60 to +200°C, but it was found that -100°C could be reached. The maximum temperature variation at the sample is $+1^{\circ}$ C within the specified range and calibration is about $\pm 3^{\circ}$ C.

The H_{\circ} field dependence of the spectrum of each compound was studied at the following temperatures and RF frequencies (H_{\circ} field).

Compound	Temperature K	RF Frequency MHz				
SF ₄ • AsF ₅	295-300	94.1,	56.4,	40,	30	
	77	94.1,	56.4,	40,	30,	16
IF7 · AsF5	295-300	94.1,	56.4,	40,	30	
	77	94.1,	56.4,	40,	30	
WF 6	173	94.1				
	77	94.1,	56.4.,	40,	30,	
		16, 2				

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For both IF₇ • AsF₅ and WF_6 usable spectra could not be obtained at 77[°]K and 94.1 MHz due to the restriction on sample size explained below. However, a 5 mm diameter sample of WF₆ run at 173⁰K and 94.1 MHz using the V-4341 temperature system did produce usable spectra. For the fixed temperature work at 77°K, the samples were immersed in dewars filled with liquid nitrogen. The dewars have been described elsewhere (75, 76). The dewar (5 mm 0.D.) used at 94.1 MHz in the HA100 severely restricted sample size to about 1.6 mm capillaries and had the barely sufferable disadvantage that it would hold liquid nitrogen for only four to six minutes. A dewar with a larger liquid nitrogen capacity, though of course with the same sample size restriction, was made by the Department's glassblower, Mr. Rak. This dewar held nitrogen for more than two hours but could not be removed from the probe without first taking the latter out of the magnet gap.

The samples used were all polycrystalline material, the spectra of which were independent of orientation in the magnetic field $\underbrace{H_0}$. Preliminary spectra were scanned up to 500 gauss on either side of resonance to establish that the resonance was confined to the region studied in expanded scale. Also, at each frequency ($\underbrace{H_0}$ field) preliminary spectra were run to check the rf level for saturation. The field $\underbrace{H_1}$ was varied over a wide range from about 0.05 mgauss to 45 mgauss. When an rf region was found where line widths remained constant as the power was lowered, forward and re-

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verse scans were run to check that line shape was the same for both directions. When an apparently satisfactory level had been found the rf level was further reduced to ascertain that no additional line shape changes occurred. In general, it was found that all three steps were necessary. Since at least two chemically shifted fluorine nuclei were present in each molecule, saturation effects produced sometimes subtle changes in the spectra after an apparently safe power level had eliminated the gross effects. Around 0.5 to 1.0 mgauss was generally a safe region, but spectra were always checked over a range of rf power for signs of saturation.

At 77° K, the restriction placed on the sample size by the dewars meant a poor packing factor in the receiver coil. Since the saturation level was fairly low ($\frac{H}{U}$ under 1.5 mgauss) by the time the rf was reduced below saturation, the signal to noise ratio was poor in some cases. The actual ratio varied depending on sample and sample size, and on the RF unit used and its operating condition. A high sweep modulation could not be used to improve the signal to noise ratio since modulation broadening would have caused a loss of structure which would have totally frustrated attempts to resolve the spectra into their possible components. At the low modulation amplitude used (approximately 0.5 gauss peak to peak), modulation correction to the second moment was negligible, but a relatively low signal to noise ratio had often to be tolerated. Ratios varied from about 4:1 in some unfavourable cases at 77° K to 45:1 under good

conditions at room temperature.

No reference sample was used in the runs with variable temperature equipment or with the large dewar on the HA100, but a CF_3C00H or C_6F_6 reference was used in the H_0 field dependence runs at 77°K and 300°K. Since the purity of the CF_3C00H standard was unknown, its chemical shift relative to Freon 11 was measured at the conclusion of the experiments. The shift was + 76.21 ppm. Two sidebands were imposed on the reference's fluorine resonance with a Hewlett Packard Model 200CD Audio Oscillator. The field H_0 was scanned through one of the sidebands and, while scanning proceeded, the reference was replaced by the sample, the probe rebalanced if necessary and the spectrum recorded. The sample was then replaced by the reference and the other sideband recorded. The position of the reference resonance was taken as the midpoint between the two sidebands.

A minimum of four spectra were recorded at each temperature in the temperature dependence runs. In the $\frac{H}{20}$ field dependence runs, except at 94.1 MHz where machine time was in great demand, at least four referenced spectra were recorded at each frequency at 300° K and ten to twelve at 77° K, the temperature of greatest interest. In addition, at least a dozen non-referenced spectra were run for each sample at each frequency at 77° K and 300° K.

CHAPTER IV

RESULTS & INTERPRETATION

Programs written for the University of British Columbia's IBM 7040 computer played an extensive part in determining and evaluating the results obtained here. The programs are listed together with explanations in Appendix I.

Samples of all three of WF_6 , $IF_7 \cdot AsF_5$, and $SF_4 \cdot AsF_5$ appeared quite stable when stored in dry-ice acetone or liquid nitrogen baths. There was no change exhibited between spectra of the same samples taken after more than one year of storage. Spectra of all samples of the same compound were experimentally consistent whether old or freshly supplied.

WF6

1. Results

Although samples which were doped with paramagnetic IrF_6 could be run at a higher $\operatorname{rf}(H_1)$ with a resultant more favourable signal to noise ratio, both pure and doped samples of WF_6 behaved identically within experimental error. Therefore no distinction is made between pure or doped samples in the results reported.

Figure 1 demonstrates the temperature dependence of the 19 F nmr spectra of 19 F at 30 MH_z. The absorption spectra having a common x-scale and being normalized to constant area, were









TEMPERATURE °K



TEMPERATURE °K

obtained by integration from the derivative curves using Program 2, Appendix I. Reproductions of derivative curves for temperature dependence at 30 MHz and also at 94.1 MHz are given in Appendices IIa and IIb. Figures 2 and 3 show respectively the second moment at 30 MHz (calculated with Program 1, Appendix I using the method outlined there) and the line width at 30 MHz and 94.1 MHz (between extreme maxima and minima of the derivative curve) as functions of temperature.

The second moment remains constant at 9.0 ± 0.4 gauss² from 77°K to approximately 180°K. As seen in Figure 1, throughout this region there is an asymmetry to high field which disappears as the second moment drops between 180 and 220°K to 1.0 ± 05 gauss². During the transition the line changes from a slightly asymmetric derivative at 180-185°K to a symmetric derivative curve at 205 to 210°K. The second moment remains constant at 1.0 gauss² from 220 to 262°K. Beyond this region there is a sudden drop between 262 and 265°K to a value which could not be accurately measured from the derivative curve.

The behaviour of the line width at 30 MHz follows the same pattern over the temperature range. It is constant at 9.8 ± 0.1 gauss from 77 to 180° K, dropping to 3.2 ± 0.1 gauss by 220° K and dropping again (after remaining constant at 3.2 gauss) around 262 to 265° K to a value of 0.1 gauss as measured at 269° K. Although the line width measurement can be made between 265 and 287° K, it

is governed by the depth of modulation which was 0.1 gauss peak to peak. The spectra in this region were similar whether taken above or below the melting point of 276° K (orthorhombic to cubic crystal transition at 265.0° K, melting point at 276.4° K, and boiling point $290.3-290.7^{\circ}$ K (20, 26)) and all had the appearance of liquid-like spectra. However, intensities were less than and lines were broader than that of a liquid signal (CF₃COOH at 298°K) in the same field. The appearance of the spectrum was really more like that of a viscous liquid within this range (265-287°K).

Variable temperature spectra at 94.1 MHz (Appendix IIb) show similar behaviour to those at 30 MHz. Line width is of the order of 12.0 ± 0.3 gauss between 173 and 183° K. By 193° K, asymmetry is still present although it is beginning to disappear, and the line has narrowed to 11.1 gauss. Between 223 and 270° K the derivative curve is symmetrical with line width 3.1 ± 0.1 gauss. Although line widths are plotted in Figure 3 there are not enough points to fix the transitions accurately at 94.1 MHz. The similar behaviour and identical line widths of the spectra taken at 30 MHz and 94.1 MHz in the region above the nmr transition at ~ $185-205^{\circ}$ K indicate the absence of field dependent broadening there.

Above the melting point the 94.1 MHz spectra appear to indicate more liquid-like character than the 30 MHz spectra. This difference may be due to different temperature gradients along the samples in the two cases. In addition all 94.1 MHz spectra in the narrow line region appear to exhibit a small amount of disper-

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sion which could not be balanced out. Initially it was thought this might be a low, broad peak indicating a percentage of molecules undergoing less frequent reorientation than those producing the narrow line. However, the "two components" could not be brought into phase and it was decided that the effect was probably due to the presence of a small amount of dispersion mode in the signal. Since the difficulty was not present at 30 MHz, its origin at 94.1 MHz may lie in an inability in this width region to remove completely the dispersion mode when using the Integrator to provide modulation. At temperatures below the nmr transition the 94.1 MHz spectra were quite satisfactory.

The results agree well, with one exception, with those obtained independently by Blinc (41). His second moment plot (his Figure 8) places the low temperature nmr transition at the same point as found here. His rigid lattice second moment of 9.5 gauss² is of course somewhat higher due to the increased anisotropy at the higher field of his experiment (9500 gauss as against 7500 gauss at 30 MHz). It is even slightly higher than the value of 9.1 gauss² obtained by interpolating our results at 9500 gauss, but is certainly within the reproducibility of an nmr experiment. His line width of about 10 gauss at 7250 gauss field is the same as our value interpolated at the same field and his 3 gauss line width at -41° C at 9500 gauss is again in agreement. (Blinc's line widths were estimated from his Figure 5). However his value of about

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1.8 gauss² (estimated from his Figure 8) for the region above the 200 K nmr transition is significantly higher than our value of 1.0+0.05 gauss². Since the anisotropy has been averaged out in this region, the difference cannot arise from field dependent broadening. Since line widths appear the same in both studies, it is unlikely that the difference arises from saturation or modulation broadening in Blinc's spectra. The alternative that saturation narrowing exists in our spectra is discounted since great care was exercised in controlling the rf (H,) level. The discrepancy may possibly lie in accurately determining the tails of the spectra. The spectra obtained here are in expanded scale and have an excellent signal to noise ratio. The second moments from them are therefore considered quite accurate. The lower second moment makes possible a slightly different interpretation of the motions occurring in this temperature region. This will be discussed later.

Figure 4 shows the field dependence of the centroid of the WF_6 spectrum at $77^{\circ}K$. The chemical shift, measured with respect to an external sample of CF_3COOH at $295^{\circ}K$, is -255 ± 40 ppm. Calculated relative to HF it is -380 ± 40 ppm compared with Blinc's value of -440 ± 20 ppm. This is not really a significant difference when the method used to obtain the shift (see Chapter III) is considered.

In Figure 2 the constant second moment from 77° K to $\sim 180^{\circ}$ K

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suggests that, except for whatever zero point motion of the atoms may be present, the WF₆ lattice is rigid at 77° K. The constancy of the second moment is in itself no absolute guarantee of rigidity, but as will be seen below it is supported by comparison with the calculated theoretical rigid lattice second moment. The anisotropy of the WF_c spectrum can therefore be safely studied at 77°K, some 100° below the transition where motion averages out the effect. The field dependence of the average absorption curves at 77°K is shown in Figure 5 at 2, 16, 30, 40, 56.4, and 94.1 MHz. Appendix IIc gives derivatives typical of the spectra recorded for Figure 5. The absorption curves have a common x-scale and are normalized to constant area. The 16 MHz spectra not quite consistent with the others. Ιn contrast to UF₆ (38, 39, 41) there is virtually no resolution of the spectra except at 94.1MHz. At this frequency, the spectra were actually taken at 173-175 K. However, as is apparent below, this seems to have been sufficiently into the rigid lattice region to obtain a valid spectrum. The spectra at lower frequency appear identical with Blincs. The derivatives at 30 MHz (7500 gauss) and 40 MHz (10,000 gauss) in Appendix IIc are very similar to his 7250 and 9500 gauss spectra. As our spectra and the plot of the field dependence of the line width at 77°K in Figure 6 indicate, there is little change in line width over the entire range of fields from 0.5. Kgauss at 2 MHz up to 23.5 Kgauss at 94.1 MHz. The change as one goes to lower frequency is really only a slight narrowing which has the effect of filling in the shoulder on the high field side

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Figure 6. WF_{6} . Field dependence of line width at $77^{\circ}K$

FIELD (H_o) GAUSS

of the spectra with scarcely any change in height. At initial stages of the investigation it was thought that saturation effects might be involved, but this was later ruled out and the effect shown to be genuine by careful checks of the rf (H₁) level. <u>2. Resolution attempts - Isotropic and Anisotropic Chemical Shifts</u>

It was expected that WF_6 like UF_6 would probably have a distorted structure at low temperatures. There would likely be four short equatorial bonds and two long axial bonds with the chemical shift tensors exhibiting axial symmetry along the bond direction. For such a molecule $\mathbf{\tilde{6}}_1 = \mathbf{\tilde{6}}_2 = \mathbf{\tilde{6}}_3 = \mathbf{\tilde{6}}_4 = \mathbf{\tilde{6}}_e$ and $\mathbf{\tilde{6}}_5 = \mathbf{\tilde{6}}_6 = \mathbf{\tilde{6}}_a$. Equation (19) then becomes

$$S_{2} = g_{a}(h) + \frac{1}{3}H_{o}^{2}\left[\frac{B}{45}(6_{u}-6_{1})_{e}^{2} + \frac{4}{45}(6_{u}-6_{1})_{a}^{2} + \frac{2}{3}(\overline{6}_{a}-\overline{6}_{e})^{2}\right] \qquad (20)$$

 $\mathbf{\tilde{G}}_{a}$ and $\mathbf{\tilde{G}}_{e}$ correspond to the centers of zero first moment of the resolved axial and equatorial components of the total curve. The final term inside the square brackets is the relative chemical shift of the components. This equation is given with an incorrect factor of 6 instead of 2/3 before this term by Blinc (41). It is probably a typographical error since equation (20) applied to his data gives approximately his reported results for UF₆.

The averaged second moments of the spectra taken at 2, 16, 30, 40, 56.4, and 94.1 MHz were plotted against the square of the field (H_0). Figure 7 shows that, as predicted by equation (20), the plot gives a straight line. The experimental value of $g_{\chi}(h)$, the zero field broadening, obtained from the intercept in Figure 7



Figure 7. WF_6 . Field squared dependence of second moment at $77^{\circ}K$

is 8.2 ± 0.2 gauss². This is considerably larger than the rigid lattice second moments published by Blinc (41) for other hexa-fluorides (4 to 5 gauss², but no value was given for WF₆).

Initial attempts at resolution were made prior to running the 2 and 94.1 MHz spectra. It was obvious from the lack of resolution in the 16 to 56.4 MHz spectra that an exact determination of the probable two components would be unlikely. Since the anisotropies of the components, if present, would likely be quite similar it was hoped, however, that at least a relative chemical shift and an average anisotropy could be determined. Thus began a tiresome series of resolution attempts which showed that a large variety of resolutions was possible, some promising and most plausible at one or more fields, but none of which was satisfactory over the full range.

Spectra were run at 2 MHz to determine a good approximation to the zero field line shape. The average second moment was 8.25 gauss², in splendid agreement with the 8.2 gauss² extrapolated value. The line shape was symmetrical but with little change in height or width from the shape at higher fields. When the Varian HA100 and its 23.5 Kgauss field became available, spectra were run at 94.1 MHz. These spectra completed the straight line plot of second moment against field squared. The improved resolution in the spectrum gave promise that there were two components which could be separated one from the other. There was some concern that

since the spectra were run at 173^CK, they might not be within the rigid lattice region, but the averaged second moment lies on the line of Figure 7 and the spectra seem valid.

Unfortunately the 94.1 MHz spectra do not clarify matters at all. They appear (see Figure 8) to define two well resolved peaks each of which is virtually symmetrical about its midpoint and whose area ratios are a quite precise 4 (low field) to 2 (high field). The chemical shift between the peaks is about 270+5 ppm. If in equation (20) the anisotropy is put equal to zero, the slope of the second moment line in Figure 7 gives a maximum value of 220+10 ppm. The agreement between the shifts is perhaps not too bad, but if the WF6 spectrum is composed of two, symmetrical, isotropically shifted peaks, the experimental curve should narrow and increase in height (if constant area is maintained) as the field is lowered. Figure 9 shows curves constructed by shifting the two components resolved at 94.1 MHz by 270 ppm at each field. As the figure indicates the constructed curves do not agree well with the experimental curves and even indicate tailing to low rather than high field. If one accepts the 220 ppm shift and resolves the 2 MHz curve into two similar components of 4:2 area ratios (Figure 9) a constructed curve can be fitted to the experimental curve at 16 and 30 MHz with quite good agreement but fails at higher fields. If a 220 ppm resolution is attempted at



Figure 9. WF6. Symmetrical component reconstruction from 2 MHz spectra



94.1 MHz, the 4:2 area ratio cannot be maintained.

Prior to running the spectra at 94.1 MHz it was considered that in view of the failure to resolve the components, the chemical shift between the axial and equatorial fluorines might be so small that there were six essentially equivalent fluorines present. In this case equation (20) reduces to equation (18) and $|G_{11}-G_{1}| =$ 345 ± 20 ppm. As indicated in Bloembergen (72), Andrew (71) and Abragam (52, p. 206, 220) a curve F(H) may be synthesized for comparison with the experimental curve. The form of the function is

$$F(H) = \int_{\infty}^{\infty} f(H_0 - H^*) s(H - H_0) dH_0$$
 (21)

where $f(Ho-H^*) = -f(h)$ as defined in equation (16), H^* is the applied field at the centroid of the spectrum, H is a general parameter and Ho is the applied field. The asymmetries of the experimental curves tail to high field. Therefore the sign of $|G_{L1}-G_{L}|$ is positive. The determination of $(G_{L1}-G_{L})$ defines $f(Ho-H^*)$ and for the broadening function, S(H-Ho), the experimental curve at 2 MHz is used. Use of the experimental curve should provide a much better approximation to the field independent broadening than the assumption of a gaussian line shape having the extrapolated zero field second moment as has been done previously. The function was calculated using Program 3, Appendix I where it is expressed in a form suitable for computing. The constructed curves are shown in

Figure 10. Because of the relatively small anisotropy and the large (8.2 gauss²) experimental broadening function, the synthesized curves are nearly symmetrical without even a hint of a shoulder. Trials showed that a reasonable approximation to the experimental line shape (up to 56.4 MHz) could be obtained by using a much smaller broadening function. This however was incompatible with the observed 2 MHz line shape. Finally the 94.1 MHz spectra were completely at variance with the concept of six like fluorines exhibiting axial symmetry of their shift tensors. The 94.1 MHz spectra show a minimum, but equation (21) cannot have a minimum within its range and non-equivalent fluorines must be present to account for the line shape. Naturally as the field is decreased the fit of synthesized to experimental curve in Figure 10 becomes progressively better from 30 MHz down until at 2 MHz it fits exactly. This at least demonstrates that the computer program works, The effectiveness of the program was further checked by its quite good fit of Rigny's (39) resolved components of UF_6 .

The most probable of all possibilities was considered to be non-equivalent axial and equitorial fluorines which showed chemical shift anisotropy. However, when resolution was attempted at 94.1 MHz, the only frequency at which it was truly feasible to attempt resolution, the contours of the composite curve produced two components of area ratio 4:2, which were only very faintly asymmetrical, and had a relative shift of about 265 ppm. The shift exceeds the maximum value

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of 220 ppm which is obtained in the absence of anisotropy. The resolution is scarcely different from the attempted resolution into symmetrical peaks. If the relative shift was kept below 220 ppm and the 4:2 area ratio still maintained, some very implausibly shaped components resulted which were disregarded. To anticipate slightly, if an average anisotropy of about 300 ppm is assumed, the relative shift must be about 105 ppm. If two similar curves of 4:2 area ratio are again constructed from the experimental 2 MHz curve then using the above anisotropies and relative shift, a fit to the experimental curve can again be made which is tolerable to 30 MHz but increasingly bad above. The computed component curves are so nearly symmetrical that even opposing their directions of asymmetry makes little change in the shape of the total curve. Indeed, the constructed curves are almost identical with those constructed in Figure 10 for the case of six like fluorines. The experimental 2 MHz broadening function is dominant in both cases.

Resolution was also attempted using opposed asymmetries as in Figure 11. The 94.1 MHz spectrum was resolved into two components an area 4 curve at low field and tailing to high field and an area 2 curve at high field and tailing to low field. This seemed promising at 94.1, hopeful at 56.4, but clearly failing at 40 MHz, and hopeless at lower frequencies, even if the maximum 220 ppm shift was used.

In view of the above failures, non-axial symmetry of the shift tensor must also be considered possible. However separation is

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Figure 11. WF₆. Resolution with opposed asymmetries

certainly not sufficient at 94.1 MHz to permit resolution of these more complicated line shapes. Attempts to do so were no better than in the preceding cases where axial symmetry was assumed.

Resolutions were also attempted with 5:1 and 3:3 area ratios of the components. They were conspicuously less successful even than the preceding attempts. There is also the possibility that there might exist more than two components. If this is the case resolution is utterly hopeless.

There is however one last attempt that can be made. If there is sufficient distortion in the molecule to permit a doublet interaction, both the minor change in line width as the field is varied and the distinct high field peak at 94.1 MHz might be explained. The doublet component must be to high field to produce the high field peak in the 94.1 MHz spectrum. One could not have a very broad doublet which might have its center of moments to low field of the centroid of the spectrum. That would make r, the separation between the nuclei involved impossibly small (from reference 52, p. 220, the doublet splitting in gauss is $3_{\mu}r^{-3}$). Figures 12 and 13 show two possible resolutions at 94.1 MHz involving sets of four and two like nuclei in the components. Both resolutions, in part, produce quite plausible numbers. That in Figure 12 has two components which do not have any apparent anisotropy of chemical shift. Their isotropic shift is 220 ppm, just what is predicted by equation (20) in the absence of anisotropy. The components can be used as indicated





Figure 13. WF₆. Resolution with doublet and asymmetric singlet

in the figure to construct curves whose slopes have some qualitative agreement with the experiment curves and which agreement is certainly no worse than in other attempts. The other doublet resolution, shown in Figure 13, involves a low field peak with a very strange asymmetry indeed. The relative, isotropic shift is about 115 ppm. If the low field, anisotropic component's second moment is plotted against the square of the field a value of $(\mathbf{G_1}, \mathbf{G_1}) = + 333$ ppm is Putting this value into the appropriate anisotropic term found. and remembering that the other anisotropic term is zero since the doublet is symmetrical, one obtains from equation (20) a relative shift of about 135 ppm. This is not bad agreement with the 115 ppm found experimentally. Obviously both of the resolutions involving doublets cannot be correct. In fact neither of them is. The doublet splitting is the same in each case. Estimated from the 94.1 MHz resolutions, it is 3 to 5 gauss giving internuclear separations of about 2.4 and 2.0 Å respectively. In short, the internuclear distances in the doublet will be little different from those in the rest of the molecule and a distinct doublet could not be seen. This was verified using Program 4, Appendix I which is based on Abragam's doublet fitting procedure (52, p. 220). Using the parameters available from this work, the doublet could not be reproduced. There was only a rounded curve with no sign of doublet structure.

Finally it may be stated that the difficulty experienced in attempting the resolution of the WF_6 spectrum can not be attributed

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to electron coupling of the $\begin{array}{c} 19\\ \text{F} \end{array}$ and $\begin{array}{c} 183\\ \text{W} \end{array}$ in the solid. The contribution to the second moment from this splitting according to - Gutowsky (63) is

(22)

 $S_{1} = \frac{1}{3}I_{k}(I_{k}+1)\sum_{k}J_{k}^{*}K$ The coupling constant \mathcal{J}_{WF} measured by Rigny (42) is 43.8 Hz or 0.011 gauss. The addition to the second moment from this source will therefore be negligible.

The resolution trials are most unsatisfactory. None of the attempts gives a sure result and none is really any more plausible than any of the others. Blinc (41) seemingly encountered similar difficulty for, although he does show examples of resolved, asymmetric curves with approximate 4:2 area ratio for WFc, he gives neither values for the anistropics obtained, nor a relative chemical shift for the components, nor a zero field second moment. From T, measurements he does give a value of $|6_n - 6_1| = 500+200 \text{ ppm}$ and states that this agrees within experimental error with the anistropy determined from line width data. The range 500 to 700 ppm is clearly too high since it would give a negative value to the square of the relative chemical shift when applied to our data using equation (20). An upper limit to the average anisotropy is set by the value of 345+20 ppm obtained by assuming six like fluorines. This makes Blinc's lower limit of 300 ppm quite feasible. With our data this gives a relative shift between the components of about 105 ppm as noted earlier. It is not surprising that the curve is difficult to resolve

if this is the case. Orders of magnitude are all that can be expected.

Gur data give an upper limit of 220+10 ppm to the relative shift if there is zero anisotropy. The values of 300 ppm and 105 ppm for $(\mathbf{e_{I}}-\mathbf{e_{I}})$ and $(\mathbf{\bar{e}_{a}}-\mathbf{\bar{e}_{e}})$ are of a resonable order of magnitude therefore. They do not, unfortunately, permit accurate reconstruction of the experimental curves. Moreover, if the chemical shift anisotropy is some three times greater than the isotropic shift between the components, with both phenomena being field dependent, it is surprising that the 94.1 MHz spectra show an actual increase in resolution rather than merely a change in line shape. The doublet spectra in Figure 12 really do behave qualitatively in a fashion very similar to the experimental spectra. Therefore, although it will be assumed that there are two asymmetric components of area ratio 4:2 corresponding to four equitorial and two axial fluorines at low and high field respectively, it would still be very interesting to see the \mathbf{WF}_{6} spectrum at $77^{0}\mathbf{K}$ and 200 MHz.

Even if an experiment were done at 200 MHz, it might not solve the resolution problem in WF₆, however. The attempts have all been based on the premise that if a resolution can be made at one field, the components will retain their distinct identities at other fields and using the observed chemical shift can be summed to give the experimental curves at those fields. In the case of extreme chemical shift as for one "component" arising from fluorine nuclei and another from hydrogen nuclei, there would be a clear resolution at high fields, the "components" would retain their identities at lower fields, and a "total curve" could be derived from the

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"components" using the observed chemical shift. In the other extreme of identical nuclei, there will be no change arising from isotropic shift and the experimental curves can again be reproduced throughout the range of fields available. However, for the intermediate case in which similar nuclei are in components which are chemically shifted by a significant amount which is nonetheless smaller than the dipolar broadening, the component line shapes cannot be disentangled. For WF₆ at low fields there appear to be six essentially equivalent fluorines and at high fields two more or less distinct components with at intermediate fields a confusing mixture of the two extreme cases. The resolution attempts above have been presented in such detail mainly to emphasize one point: if resolution is not present in the experimental spectra it cannot be found by making reasonable attempts. The difficulty arises not from deficiencies in the experiment but from the nature of the interactions involved in intermediate cases of mixed isotropic and anisotropic chemical shifts.

3. Proposed Crystal Structure

A theoretical, rigid lattice second moment can be computed for comparison with the observed zero field or field independent second moment. No X-ray single crystal study of WF_6 has been published. The structure suggested here was based on the W-F bond length of 1.833Å from Weinstock (37a) and crystal structure information in Table 1 supplied by Bartlett (37b) from a private communication from Siegel.
<u>Table 1</u>

Cell Parameters of WF6

273⁰K

273 K cell cubic $a=6.28\text{\AA}$, $V=247.7\text{\AA}^3$, P calc = 3.99 253°K cell orthorhombic $a=9.68\text{\AA}$, $V=434.1\text{\AA}^3$, P calc = 4.56 b=8.81c=5.09

Z=4 space group Pmma?

Attempts to fit the four \mathbb{WF}_6 molecules into the unit cell at 253°K produced what appeared to be unreasonable distortions and a suspicion arose that Pmma might be a transcription error for Pnma. Weinstock (77) may actually state that \mathbb{WF}_6 is Pnma, but it is not quite clear whether he means that all the hexafluorides he discusses are Pnma or only that they are all orthorhombic. In any case it was decided to base the \mathbb{WF}_6 second moment calculations on a Pnma structure for \mathbb{UF}_6 .

Hoarde and Stroupe (36) give the atomic coordinates, cell dimensions and band lengths for UF which are reproduced in Table 2.

- 1	а	ΡŢ	е	2
_	_	_	_	_

Atomic	Coordinates,	Cell	Dimensions,	and Bo	nd Lengths	of UF at 6	298 [°] K
	×		· y		Ż	U-F,A	
U	0,1295		0.2500		0.081	- L	
F ₁ · ·	0.014		0.093		0.250	2.01	
F ₂	0.014		0.407		0.250	2.01	
F3	0.246		0.407	-	0.083	2.01	
F ₄	0.246		0.093	-	0.083	2.01	
F ₅	0.003		0.250	. –	0.250	2.13	
F ₆	0,250		0.250		0.417	2.12	
			٦.		average	2.05	

Orthorhombic, Pnma, Z=4 , scale = 5.06 a=9.80, b=9.00, c=5.20Å

Since the ratios of the cell dimensions for WF_6 and UF_6 are approximately equal for each direction $\left(\frac{9.68}{9.80} \sim \frac{8.81}{9.00} \sim \frac{5.09}{5.20} \sim 0.98-0.99\right)$ and Z=4 for both molecules, the same space group for both may be reasonable. The ratio of WF_6 to UF_6 cell volume is 0.95. The ratio of the respective molecular volumes computed for crude, spherical molecules including fluorine van der Waals radii is 0.82. In both cases the "spherical" volume exceeds the unit cell volume, but in the WF_6 case the excess is relatively less than in the UF_6 case. This would give the WF_6 molecule relatively more freedom to reorient and is consistent with a comparatively low temperature nmr transition at 200° K.

In computing the \mathbb{WF}_6 structure, the coordinates of a uranium atom were chosen as a molecular origin. The atomic coordinates for the fluorine atoms in \mathbb{UF}_6 were adjusted relative to this origin according to the following formulae to give coordinates for the

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fluorine positions in WF_6 .

D

(fluorine atomic coord. in WF₆-origin atomic coord.) (cell dimension WF₆) average W-F bond length

average U-F bond length

· · · · · · · (23)

(fluorine atomic coord. in UF_6^- origin atomic coord.) (cell dimension UF_6)

$$\frac{(X_{F_WF_6} - 0.1295)(9.68)}{(X_{F_{WF_6}} - 0.1295)(9.80)} = \frac{1.833}{2.05}$$

$$\frac{(Y_{F_{WF_6}} - 0.2500)(8.81)}{(Y_{F_{WF_6}} - 0.2500)(9.00)} = \frac{1.833}{2.05}$$

$$\frac{(Z_{F_{WF_6}} - 0.081)(5.09)}{(Z_{F_{UF_6}} - 0.081)(5.20)} = \frac{1.833}{2.05}$$

The value 1.833A given by Weinstock was taken as an approximation to the average of the possibly non-equal bond lengths in the low temperature phase of WF_6 . The atomic coordinates for WF_6 calculated from equations (23) are given in Table 3.

Table 3

Calculated Atomic Coordinates and Bond Lengths for ${}^{\rm WF}_6$ at "253 $^{\rm O}$ K"

	×	У	Z.	W-Ft ^A
Ψ	.1295	.2500	.0810	· _
F,	.0250	.1065	. 2354	1.80
F	°0220	. 3935	.2554	1.80
F ²	.2349	. 3935	0688	1.80
F ,	.2349	.1065	0688	1,80
F ⁴	.0150	.2500	2213	1.90
F ^D	.2386	.2500	.3879	1.90
D			average	1.83

Orthorhombic, Pnma, Z=4 9=9.68, b=8.81, c=5.09Å

The positions are not of course accurate to the number of significant figures retained in this table.



Figure 14. WF_{6} . Proposed unit cell (along c-axis)

ATOMIC COORDINATES OF TUNGSTEN | 0.13, 0.25, 0.08 2-0.13, 0.75, 0.08

3 0.37, 0.75, 0.58

4 0.63, 0.25, 0.42

O 5Å CIRCLES INDICATE

FLUORINE Van der Waals radii

Pnma a = 9.68 Å b = 8.81 Å c = 5.09 Å The symmetry operations of the Pnma space group give the other three positions in the unit cell. Figure 14 shows the proposed structure of WF_6 viewed along the c-axis.

4. Theoretical Rigid Lattice Second Moment

To provide nuclear positions for the second moment calculation a simple linear transform program (Program 5, Appendix I) was written. It translates the nuclear positions in one unit cell into positions in a block of unit cells around the original cell. In the computation of the rigid lattice theoretical second moment there is in addition to the assumption that a reasonable WF_6 structure at 253 K can be derived from the UF $_{\rm K}$ structure at 298 $^{\rm O}{\rm K}$, the additional assumption that the results will be valid at 77°K. The two hexaluorides are similar molecules and the temperatures at which the X-ray results are quoted are in each case rather roughly the same distance below the melting points of the respective compounds. The first is not an unreasonable approximation. The assumed WF6 structure, however, is for a temperature above the nmr transition but is used at temperatures below the transition. This too is acceptable. X-ray spectroscopy and nmr spectroscopy are sensitive to different motional frequencies. As far as X-ray is concerned, the structure is essentially rigid and the nuclear positions at 253 ⁰K may give a reasonable approximation to the positions at 77 K if contraction of the lattice is not too great. As will be noted later, thermodynamic evidence rules out the possibility of a crystal structure change between 77 and 253 ⁰K (28).

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Equation (2) gives the theoretical dipolar second moment for a rigid, polycrystalline solid. The first term applies to the F-F interactions, the second to the W-F interactions. The respective numerical coefficients are 316.8 and 0.27. When the 14% natural abundance of W, the only isotope of tungstan with a magnetic moment, is considered, the U-F factor becomes \sim 0.04. The contribution from W-F interactions is negligible and only F-F interactions need be summed in equation (2). The summation was carried out on the IBM 7040 using Program 6, Appendix I using the nuclear coordinates generated by Program 5 and was extended to a radius of 6Å from molecule number one (any one of the four) in the unit cell. Because of the r^{-6} dependence of the second moment, it is sufficient to assume the remainder of the nuclei are uniformly distributed with known density throughout the rest of the sample (51, p. 160). If the number of nuclei between r and r+dr is $4n^2\rho$ dr, where ρ is the number of nuclei per unit volume (A), the additional contribution is given by

 $S_{2,add} = (numerical factor) 4TTp \int r^{-4} dr = (3/6.8) 4TTp$ (24)

The contributions to the total, theoretical rigid lattice dipolar second moment of 8.14 gauss 2 are given in Table 4.

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Table 4

Rigid Dipolar Second Moments of WF_c at 77 K

Total Intramolecular Second Moment 4.40 G² Total Second Moment within 6A 7.80 G² Contribution Outside 6A .34 G² Total Theoretical Second Moment Experimental Second Moment

Moderate distortion makes little difference to the second moment. The intramolecular moment calculated on the basis of six equal W-F bonds of length 1.833Å each is 4.31 gauss². The moment calculated for four short equatorial (1.80Å) and two long axial (1.90Å) bonds is 4.40 gauss² only slightly different.

 $8.14 G^{2}$ $8.2+0.2 G^{2}$

The crystal structure assumed here receives some passive support from the count of internuclear interactions. The theoretical second moment program indicates that within a range of 6°_{1} from the molecule chosen as origin, there are 152 F-F interactions. Of these, 12 interactions involve nuclei with separations of less than 2.70 $^{\circ}_{1}$, twice the fluorine van der Waals radius. However, these interactions are all intramolecular. At least the structure has the advantage of having no intermolecular interactions less than the van der Waals radius. This of course does not say that other structures equally favourable do not exist. Considering that the structure is based on X-ray results obtained at 298°K, adjusted to 253°K, and applied at 77°K where thermal contraction might be significant, the very close agreement between theoretical and experimental second moments is perhaps fortuitous. Nonetheless it is encouraging.

5. Reorientation in the Solid

Above the nmr transition around $180-210^{\circ}$ K, the puzzling WF₆ line shape becomes symmetrical. Between this transition and the next around 265° K, the line width has a constant value of about 3.2 gauss at both 30 and 94.1 MHz. Clearly whatever field dependent broadening existed below 200° K, it is now averaged out. The second moment plot in Figure 2 shows a drop from approximately 9 gauss² (8.2 gauss² at zero field) below the lower transition to 1.05±0.05 gauss² above the transition. Since the WF₆ molecule is approximately sperical, this drop in second moment to about 1 gauss² may be due to the onset of isotropic rotation of the molecule about its center of gravity. In this case the intramolecular second moment averages to zero and the only remaining contribution is from the intermolecular second moment (51, p. 173). For WF₆, the appropriate form of equation (6) for isotropic reorientation is

 $S_{2 \text{ iso. Heor.}} = 316.8 N_0 \sum_{i=1}^{\infty} N_i R_i^{-6}$ (25)

Since this calculation concentrates the fluorine nuclei at the molecular centers, the sum is computed using Program 6 with the coordinates of the tungsten nuclei as the centers. The result corrected for nuclei at distances greater than 6Å is 1.06 gauss². This is excellent agreement with the experimental value of 1.05±.05 gauss², but Smith (64b) points out that random (non-isotropic) jumps between equivalent positions can give a second moment different from the isotropic value by as little as 5 to 15%. Since the experimental value itself varies by 5%, it is impossible to state positively that an isotropic reorientation is taking place.

Weinstock (37a, 77) considers rotation in the solid is unlikely at the solid-solid phase transition (265 $^{\circ}$ K for UF₆). He believes that for all the hexafluorides there is little difference between the cubic solid phase and the liquid, a belief which our results support, but that free rotation occurs in neither phase. The nmr results, however, appear to indicate a very considerable reorientation not only in the cubic phase, but also in the orthorhombic phase, some 65° below the solid-solid transition to the cubic phase. Admittedly there appears no sign of the transition in the vicinity of 200 K from thermodynamic data. The heat capacity curve for WF_{6} is smooth with no break from 4 $^{\circ}K$ to the point at which the transition to the cubic structure takes place (28). Since there is no change in thermodynamic properties, the second moment drop cannot be due to a change of crystal structure at 200°K. It must arise from reorientations which, considering the approach of the second moment to a value indistinguishable from that for isotropic reorientation, average out not only the two different fluorine sites, but also to a considerable degree the local fields as well. As Figure 14 and the count of internuclear distances in the theoretical second moment calculation demonstrate, the molecules in the WF6 unit

cell interlock but do not overlap. There is clearly room for considerable restricted reorientation. Approximating the molecules as spheres of radius 3.18Å (W-F = 1.83 + van der Waals F radius = 1.35) gives a separation of 6.36Å between molecules for complete clearance. The separations between the centers of molecules 1, 2, 3, and 4 are 1-2, 5.68Å; 1-3, 5.60Å; 1-4, 5.14Å; 2-3, 5.90Å; 2-4, 8.92Å; 3-4, 5.70Å. The overlap encountered during isotropic reorientation would not be impossibly large but is rather substantial.

Weinstock's (77) evidence against a high degree of motion in the solid states of the hexafluorides is based in part on thermodynamic grounds. He gives the entropies of fusion for UF6, NpF6, and PuF as 13.6, 12.8, and 13.7 eu respectively. Since these values exceed Timmermans' (78) limit of 5 eu for plastic globular compounds, he concludes that rotation below the melting point is unlikely for these hexafluorides. Cady (26) gives the entropy of fusion for WF6 as 1.45 eu. This value, which is well within the Timmermans limit, would suggest that free rotation is possible. Weinstock points out that PtF_6 has an entropy of fusion of 3.2 eu and would on this basis qualify as a plastic crystal and its solid-solid transition might be a consequence of the onset of rotation. However, the total entropy change associated with the two transitions, solid-solid and fusion, is only 7.7+3.2=10.9 eu which is considerably less than the rotational entropy of the molecule in the vapour phase (22.1 eu at the fusion point). Since the 10.9 eu total will include other as well as

rotational entropy, the total rotational entropy below the vapour phase will be even smaller than 10.9 eu. He believes that there is relatively little difference, with regard to rotation, between the cubic solid and the liquid and that free rotation does not occur in either case. Rotation at a lower transition would be even less likely then. Hence for WF_6 where the entropy of the solid-solid transition is 5.28 eu and the entropy of fusion is 1.45 eu for a total of 6.73 eu against a vapour phase rotational entropy of 21.8 eu, the same objections would apply.

However, both the 5d transition series hexafluorides, \mathbb{WF}_6 and PtF₆, for which nmr results are available show "nmr transitions" well below their solid-solid transitions at 265°K and 276°K respectively. Blinc (41) places the \mathbb{WF}_6 transition at about 200°K, as do we, and the PtF₆ transition at about 250°K. From equation (7) or (8) average frequencies \mathbf{Y}_6 of molecular reorientation may be obtained. From an Arrhenius-type plot of $\ln(\mathbf{\gamma}_6)$ against $1/T^{\circ}K$, an activation energy for the reorientation may be determined. For the transition at 200°K there is an activation energy of 10.0±0.4 Kcal from second moment data and 15.0±0.9 Kcal from line width data. In accord with Powles (65), the value derived from second moment data is considered more reliable. The calculations were made using Program 7, Appendix I which was modified from Smith (79). The program gives a least squares fit to the experimental line width

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data as used by Smith or to the second moment data as used here. The value 10.0 Kcal will include a slight error due to the anisotropy of the second moment, but it seems a very reasonable activation energy for molecular reorientation. It is in good agreement with the value of about 9 Kcal obtained by Blinc with T, measurements. Because of the abrupt nature of the transition at 265° K neither equation (7) nor (8) gives a meaningful activation energy for that change.

The thermodynamic and nmr results are not contradictory. The phenomena are responsive to different frequencies of reorientation. For the nmr experiment, a high degree of reorientation implies a frequency of reorientation of the order of the nmr line width, i.e. $10^4 - 10^5 \text{ sec}^{-1}$; whereas the frequency of the reorientations must be of the order of $10^{11} - 10^{12} \text{ sec}^{-1}$ to affect the thermodynamic properties. It is consistent therefore for nmr to observe a transition which indicates a high degree of reorientation well below the solid-solid phase transition. Blinc's value of 1.8 gauss² above the nmr transition suggests that there may not be isotropic reorientation taking place above 200° K in WF_6 . The value of 1.05 ± 0.05 gauss² obtained here suggests that as far as an nmr experiment can detect, isotropic rotation can not be ruled out and, from the activation energy calculation, is occurring through a hindering potential barrier of 10 Kcal par mole.

The AsF₅ Adducts

In the case of the two AsF_5 adducts, there will obviously be non-equivalent fluorine nuclei present. As will be seen below, the equivalent fluorines are grouped as IF_6^+ and AsF_6^- in the $IF_7 \cdot AsF_5$ adduct and as SF_3^+ and AsF_6^- in the $SF_4 \cdot AsF_5$ adduct. There may well be non-equivalent fluorines within these groups, but there is no possibility of identifying them in a broad line nmr experiment when even the major non-equivalences are so small compared to dipolar broadening.

A. IF7 · AsF5

1. Results

Figure 15 shows the temperature dependence of the $IF_7 \circ AsF_5$ fluorine absorption spectrum at 30 MHz. As for the previous compound, the curves have a common x-scale and are integrated to a constant, arbitrary area from the derivatives. Reproductions of typical derivatives are given in Appendix IIIa. Figure 16 is a plot of the averaged second moments of the derivative curves. The second moment is constant at 11.6 ± 0.6 gauss² from 77° K up to about 205° K at which point the moment begins dropping until 2.1 ± 0.2 gauss² is reached at 235° K. It then remains constant up to 295° K, the highest temperature recorded. A preliminary line width study indicated no other transition from 77° to above 370° K (79a). At 77° K the spectrum tails to high field. By 174° K the spectrum appears to be approximately symmetrical and at 217° K, within the transition





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region, it marrows and begins to tail to low field. At 295°K the spectrum is much narrower and has a slight yet distinct asymmetry towards low field. As may be seen by examining the higher field spectra at 77 and 295°K, this effect is indeed real. It does, however, present a distinct difficulty in deciding what is the line width between maximum and minimum on the derivative curve and for this reason no variable temperature line width plot is given.

2. Resolution into Components. Isotropic and Anisotropic Chemical Shifts

Figures 17a and 17b show the field dependence of the $IF_7 \cdot AsF_5$ absorption spectra at 300° and 77°K. Typical derivatives of the spectra are given in Appendices IIIb and IIIc. As Figure 17a demonstrates the spectrum at 94.1 MHz and 300°K can be resolved into two quite symmetrical components. There is, a comparatively broad component to low field and a narrow component at high field. The relative areas of the components are 1.1:1 and the isotropic chemical shift between them is 153 ± 10 ppm. The components are equidistant on either side of the centroid of the total curve, which, from Figure 18, has a chemical shift of -54 ± 8 ppm with respect to our CF_3COOH standard at 295-300°K. The figure indicates that the shift of the centroid with respect to the reference at 300°K is the same whether the adduct is at 77 or 300°K.

The l.l:l ratio of the areas of the components implies that the twelve fluorines known to be present in the IF_7 • AsF₅ adduct are

Figure 17a. $IF_{6}^{\dagger}AsF_{6}^{-}$. Field dependence of absorption spectra at 295 K







arranged in two distinct groups of six fluorines each at 300° K. (For IF₇ and AsF₅ the ratio would have been 1.4:1). This supports the ionic formulation IF⁺₆ AsF⁻₆ suggested by Seel and Detmer (5) and confirmed by Beaton (10).

Figure 19 gives the field dependence of the line width at 77 and 295°K. For the 295°K spectra the slope of the plot is 140+25 ppm in agreement with the chemical shift determined from the resolved curves at 94.1 MHz. This confirms that the resolution does involve components which are not completely overlapped and which have not asymmetry. For IF_6^+ As F_6^- we may take $\bar{\mathbf{6}}_1 = \bar{\mathbf{6}}_2 = \bar{\mathbf{6}}_3 = \bar{\mathbf{6}}_4 = \bar{\mathbf{6}}_5 = \bar{\mathbf{6}}_6 = \bar{\mathbf{6}}_{As}$ and $\bar{\mathbf{6}}_7 = \bar{\mathbf{6}}_8 = \bar{\mathbf{6}}_9 = \bar{\mathbf{6}}_{10}$ $\bar{\mathbf{6}}_{11} = \bar{\mathbf{6}}_{12} = \bar{\mathbf{6}}_1^-$ where $\bar{\mathbf{6}}_{As}^-$ and $\bar{\mathbf{6}}_1^-$ denote the mean isotropic shifts for fluorine atoms bonded to arsenic and iodine respectively. If, as the resolution at 94.1 MHz and Figure 19 suggest, the asymmetry in the components is averaged out, equation (19) becomes

$$S_2 = g_2(h) + \frac{H_0^2}{4} (\bar{G}_{A_s} - \bar{G}_{I})^2$$
(26)

The relative positions of $\mathbf{\tilde{s}}_{As}$ and $\mathbf{\tilde{s}}_{I}$ with respect to high or low field cannot be determined from this equation, but may be deduced from other considerations. It will be indicated later that the As-group is to high field of the I-group. From equation (26) and the slope of the 295°K line in Figure 20, which shows the field squared dependence of the second moment, the relative chemical shift between the components is

 $(\vec{e}_{As} - \vec{e}_{I}) = 135+8$ ppm. This is quite reasonable agreement with

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the value of 153 ± 10 ppm from the resolution and confirms both the absence of anisotropy at 295° K and the accuracy of the resolution.

In Figure 17a, the broken curve has been constructed by shifting the two components resolved at 94.1 MHz relative to each other with a shift of 153 ppm. Although at low fields the constructed curve is taller than the experimental curve, line width is about the same and the constructed and experimental curves have very similar shapes. Evidently, in the region 235-295 K, the spectrum is composed of two distinct curves whose area ratios are a quite definite l.l:1. From comparison of the line shapes of the components with those of the $SF_4 \cdot AsF_5$ adduct, it is concluded that the tall component (second moment 0.7 gauss²) to high field is the AsF_6 grouping and the short component (second moment 2.0 gauss²) to low field is the IF_6^+ grouping. Confirmation comes from Christe et al (80), from whom a chemical shift of -126.6 ppm with respect to HF can be obtained for AsF_6 in HF solution. In our work the shift of the centroid of the total IF_6^+ AsF curve is -54+8 ppm with respect to CF_3COOH . The AsF⁻ peak is to high field and the mean shift between the components is 143+10 ppm. (The estimates of the shift range from 135+8 through 140+25, to 153+10 ppm). This places the AsF_6 peak in solid $IF_6^+AsF_6$ at -100+20 ppm relative to HF in fair agreement with Christe's value. The IF_6^+ group will be at -243+20 ppm relative to HF.

For the 77[°]K spectra to tail in the opposite direction to the high temperature spectra, anisotropy of chemical shift almost

certainly must be present at the lower temperature. As will be seen below when the IF_6^+ AsF $_6^-$ crystal structure is mentioned, the I-F and As-F bond lengths are quite similar. The groups are nearly identical in size and shape (there is a slight distortion in the As-group). When they are at 77°K where, because of the constancy of second moment between 77° and 205°K, they are both presumably rigid, they will have probably closely similar second moments of about 10.7 gauss² each, the same value as the extrapolated zero field, dipolar second moment. This is verified below following Table 7 with the theoretical rigid lattice calculations of the second moment. (If all other factors are identical, the I-group should have a slightly greater second moment because of the greater magnitude of the F-I than the F-As interaction.) The line shapes too will be quite similar at 77 K and, in the absence of anisotropic shift, the total curve would be symmetrical. The direction of the asymmetry - to high field - gives a positive value to the anisotropies or at least to their net effect. They will almost certainly both be positive.

Figure 18 showed that the relative shift of the centroid of the total curve with respect to CF_3COOH was the same at 77° and $300^{\circ}K$. If we make the reasonable assumption that the relative shift between the components remains the same at both temperatures, an estimate can be made of the chemical shift anisotropy at $77^{\circ}K$ by applying the equation

 $S_1 = g_2(h) + \frac{4}{45} H_0^2 \left(\overline{\mathfrak{S}_{11}} - \overline{\mathfrak{S}_1}\right)^2 + \frac{H_0^2}{4} \left(\overline{\mathfrak{S}_{A3}} - \overline{\mathfrak{S}_1}\right)^2$ (27)

to the 77° line in Figure 20. From the upper limit of the relative shift of 153+10 ppm, the average shift of 143+10 ppm, and the lower limit of 135-8 ppm, average anisotropies of about 310, 333, and 355 ppm respectively are obtained. How closely the anisotropies of the individual groups approach the average value is difficult to say. The average itself appears to be of a reasonable magnitude since it is quite similar to the approximate 300 ppm for WF_c . The broken curve in Figure 17b shows curves reconstructed from two equal components of 10.7 gauss second moment, having 333 ppm anisotropies, and with relative shift of 143 ppm. Since a gaussian broadening function has been applied to equation (16), the constructed curve is perhaps too narrow. Compared to the gaussian curve of the same second moment, the experimental zero field curve found for WF₆ was rather wider towards the top, but without such extensive wings. This would make the constructed curves in Figure 17b in somewhat better agreement with the observed shapes. However, the qualitative agreement with the experimental line shape is not bad considering the assumptions involved.

3. Crystal Structure

Beaton (10) has determined the structure of $IF_6^+AsF_6^-$ from powder X-ray data, presumably at room temperature. His information is summarized in Table 5.

Table 5

		X-Ray P	owder	Structure of $IF_6^+ AsF_6^- \sim 295^{\circ}K$
	Space Gro	up Pa3		$cubic a_{0} = 9.4935 \pm 0.0005 Å$
			•	atomic parameters
As I F F	in 4(a) in 4(b) in 24(d) in 24(d)	(D, (¹ / ₂ , (x, (x,	0, 0) ½, ½) y, z) y, z)	x=0.0980; y=0.1377; z=-0.0489 x=0.6001; y=0.6431; z=0.4411
		ьо	nd dis	stances and angles
As. 1 ·	-F 1.67 ^{Å*} -F 1.75 ^{Å*}			F-As-F = 86.5° F- 1-F = 90°
		i	ntermo	plecular distances

(3) F...F at 2.81A (3) F...F at 2.95Å (3) F...F at 2.97Å (3) F...F at 3.04A

*These distances may be too small. See text below.

Beaton points out that the bond lengths derived from his X-ray data may be rather short, the As-F length in particular. He ascribes this to his neglect of thermal motion when determining the bond lengths and suggests that such a correction might be 0.1A or more. As evidence he cites Copeland et al (81) who found in a salt of AsF that the As-F band length corrected for thermal motion was 1.77^{0}_{7} and uncorrected was 1.65A. Trotter (82) considers that this appears a rather large correction for thermal

motion. However, if one arbitrarily applies a correction of 0.1^{M} to each of Beaton's bond lengths, both of them are still within the ranges given in the Interatomic Distances Supplement (83). There, values of 1.71, 1.85, 1.80, and 1.83 are given for I-F bond lengths in IF, and 1.80±0.05Å for the As-F bond lengths in AsF₆. In this last, the F-As-F angle is given as 88.3°±2.1°. In Table 6 the first column of atomic coordinates contains Beaton's values, the second contains his coordinates adjusted for the 0.1Å increase in bond length. Only the first "molecule" in the unit cell is given, the symmetry operations will of course give the other three.

Table 6

				<u> </u>		
	Beaton	x Thermally Adjusted Beaton	Beaton	y Thermall Adjusted Beaton	y Beaton	z Thermally Adjusted Beaton
As	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
1	0.0980	0.1039	0.1377	U.146U	-0.0489	-0:0518
¹ 2	-0.0489	-0.0518	0.0980	0.1039	0.1377	0.1460
F	0.1377	0.1460	<u>-</u> 0.0489.	-0.0518	0.0980	0.1039
F,	-0.0980	-0.1039	-0.1377	-0.1460	0.0489	0.0518
Fg	0.0489	0.0518	-0.0980	-0.1039	-0.1377	-0.1460
F	-0.1377	-0.1460	0.0481	0.0518	-0.0980	-0.1039
I	0.5000	0.5000	0.5000	0.5000	0.5000	0.5000
F,	0.6001	0.6058	0.6431	0.6513	0.4411	0.4377
F'	0.4411	0.4377	0.6001	0.6058	0.6431	0.6513
F	0.6431	0.6513	0.4411	0.4377	0.6001	0.6058
F, 7	0.3999	0.3942	0.3569	0.3487	0.5589	0.5623
F	0.5589	0.5623	0,3999	0.3942	0.3569	0.3487
F_{12}^{11}	0.3569	0.3487	0.5589	0.5623	0.3999	0.3942

Atomic Coordinates for IF_6^+ AsF $_6^- \sim 295^{\circ}K$

(1) "Thermally adjusted Beaton" means that the coordinate listed under "Beaton" has been increased to allow for an estimated +9.1A thermal correction to the bond length.

(2) It is not meant to imply accuracy to four significant figures in this table.

4. Theoretical Rigid Lattice Second Moment

For $IF_6^+ AsF_6^-$, equation (2) for the theoretical rigid lattice second moment will have a third term similar to the second. The numerical factors will be 316.8, 23.4, and 74.3 for the F-F, F-As, and F-I sums respectively. Table 7 gives the second moment contributions from calculations based both on Beaton's atomic coordinates adjusted for thermal motion and on his unadjusted coordinates. For Beaton's uncorrected values only the total second moment is shown. In calculating the second moments it has been assumed that the coordinates at 295°K will be in reasonable approximation to those at 77°K.

Table 7

Rig	id Lattice Second Moment Contributions to IF ⁺ AsF ⁻ 6							
From Bea	ton's adjusted coordinates	Second Moment Gauss ²						
•		F-F	F-As	F-I	Total			
IF ⁺ AsF 6 6	Total (including integral contributions over 6A of 0.35, 0.00,	8.78	0.39	0.98	10.40			
TE ASE	and U.UI gauss) INTRA	4.75	0-38	0.93	6,06			
6 6	• O .	- - - - - - - - - - -	0.00	0.00	0,00			
Asf 6	TOTAL (to 6A)	4.71	0.38	0.04	5.13			
AsF ₆	INTRA	2.71	0.38	0.00	3.09			
IF ₆	TOTAL (to 6Å)	4.07	0.01	0.93	5.01			
IF ⁺	INTRA	2.04	0.00	0.93	2.97			
From Bea	ton's coordinates (10)							
IF ⁺ AsF ⁻ 6	TOTAL (including above integral contributions)	10.68	0.54	1.34	12.56			
Extrapol	ated Zero Field							
Second	Moment				10.7			
Note: Al IF al	l contributions in this tab + AsF- unit. N in equation 6 6 1 groups.	le are t (2) has	based on 5 been 1	i a 12-f taken a	fluorine s 12 for			

Zero point vibrational motion would decrease the theoretical second moment somewhat, but contraction of the crystal lattice between 295°K, where the structure was determined and 77°K where it was applied to the calculation of the theoretical moments would increase the values somewhat more. The good agreement between the theoretical second moment based on the adjusted coordinates and the zero field second moment indicates that the "thermal correction" was probably of the right order. The probable bond lengths therefore are of the same order as those listed in the Interatomic Distances Supplement as Beaton suggested, and are longer than those he reported.

The contributions of the IF_6^+ and Asf_6^- groups to the total second moment (up to 6Å radius from the center of the relevant group) are 5.01 and 5.13 gauss² respectively. Since these are based on a 12 fluorine unit, the values must be multiplied by $1^2/6$ to obtain the second moments the individual components would have if they could be resolved out at $77^{\circ}K$. This gives 10.20 and 10.44 gauss² respectively when the contribution for distant nuclei is included. Both values are in good agreement with the 10.7 gauss² assumed above for the attempted reconstruction of the experimental curves in Figure 17b.

5. Reorientations in the Solid

Above their respective nmr transitions all three of the IF_6^+ , AsF_6^- , and WF_6 groups exhibit symmetrical spectra. Below the transition the WF_6 spectra exhibit asymmetry presumably both because of anisotropy of the shift tensors and because of the non-equivalent sites of the axial and equatorial fluorines in the molecule. In WF_6

above the transition, motions average out both the chemical shift anisotropy and the mean isotropic shift between the non-equivalent fluorines, to give a single, symmetrical line. Similar motions are likely involved above the transition in $IF_6^+ AsF_6^-$ which is also around $200^{\circ}K$. In the case of the salt, there are two symmetrical, but distinct components above the transition. Whatever motions occur can average out only the anisotropic shift and non-equivalences (if present) within each different ion. The differences between the fluorines attached to the cation and those attached to the anion are a consequence of their bonding to the respective I and As atoms and are not averaged out. The relative shift between the ions therefore remains regardless of the degree of reorientation.

With regard to the actual reorientations which are occurring above the transition, it appears that that AsF_6^- is undergoing mora extensive motion than the IF_6^+ ion. Its second moment at $295^{\circ}K$ is about 0.7 gauss², a value quite consistent with isotropic reorientation about its center of mass. The IF_6^+ component, however, has a broader line and a greater second moment, 2.0 gauss². In explaining or at least rationalizing the rigid lattice line shape, we stated that both the IF_6^+ and AsF_6^- component line shapes would probably be similar since the two ions were similar in size and geometry. This is satisfactory in the rigid lattice, but would appear true also at higher temperatures since the two groups presumably will experience and be influenced equally by the same barrier to reorientation. The more frequent reorientation exhibited at $295^{\circ}K$ by the AsF_6^- than the

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 IF_6^+ group may be a consequence of the shorter As-F bond length. About any axis of rotation, the moment of inertia of the AsF_6^- ion is some 10% less than that for the IF⁺₆ ion. This estimate was made using regular octahedra. In fact the AsF_6 octahedra are distorted (10). The compression, however, is along a $\overline{3}$ axis. The effect merely squeezes the faces of the octahedra together and the centers of mass still coincide with those of the As atoms so that the As atoms still make no contribution to the moments of inertia. Although the moment of inertia is increased for rotation about the 3 axis, it is reduced for rotation about an axis at right angles to the 3 axis along which compression occurs. Since qualitatively one expects a reorientation to occur preferentially about the axis with the least moment of inertia, then it will take place about this last axis where the moment is even less than in the undistorted case. Hence the AsF_6^- ion undergoes more frequent reorientation at 295 K than the IF ion.

The above view is confirmed by Das (84) who points out that the probability of transition from one potential well to the next over an n-fold barrier is

$$\mathbf{W} = \mathbf{W}_{\mathbf{c}} + \mathbf{W}_{\mathbf{T}} \qquad \dots \qquad (28)$$

where W_{c} and W_{T} are the probabilities for classical rotation over the barrier and quantum mechanical tunneling through the barrier respectively. Since for all rotating groups other than those involving only protons W_{T} is negligible, the probability reduces to

 $W = W_c = \frac{n}{2\pi} \left(\frac{V_0}{T_{col}}\right)^{1/2} e^{-\frac{V_0}{kT}}$

..... (29)

where I_{eff} is the effective moment of inertia and where Vo, the activation energy or height of the hindering potential barrier, may be determined from equation (8). From equation (29), it is obvious that the smaller I_{eff} , the greater is the probability of reorientation. Hence the AsF⁻₆ group can logically be expected to undergo more frequent reorientation than the IF^+_6 group at a given temperature, provided that the temperature is high enough for the motion to occur. Although the above qualitatively predicts a higher probability for AsF⁻₆ reorientation, the actual probabilities differ by less than 10%. It may be that, contrary to the assumption above, the groups do encounter different barriers with the AsF⁻₆ barrier to reorientation being the lesser.

The narrow $\operatorname{Asf}_{6}^{-}$ line with its 0.7 gauss² second moment can be accounted for at 295°K by assuming isotropic reorientation of the group as noted earlier. The broader line of the $\operatorname{IF}_{6}^{+}$ component has a second moment of 2.0 gauss², however, which is clearly much higher than the 1 gauss² value predicted for isotropic reorientation. It is too high also for reorientation at random about the symmetry axes of the octahedral group. This would have the effect that each fluorine spent 1/6 of its time at each position and would reduce the second moment to a value only slightly larger than that for isotropic reorientation (63). As noted in equation (5), reorientations about a single symmetry axis reduce each contribution to the intragroup dipolar broadening by a factor $\frac{1}{4}$ (3 $\cos^2 \lambda_{jk} - i$)² where λ_{jk} is the angle between the internuclear vector Γ_{ik} and the axis of rotation.

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This factor holds for stepwise reoriantation about an n-fold axis with $n \ge 3$ and for classical rotation about any axis (57). For the IF_6^+ ion there are two - , three - , and fourfold symmetry axes about which reorientation might occur. The intragroup second moments for IF_6^+ are 2.04, 2.17, and 1.93 gauss² respectively for reorientations about the C $_2$, C $_3$ and C $_4$ axes. In addition to this intragroup contribution there will be an intergroup contribution. The AsF_6 group appears to be undergoing an isotropic reorientation in which its intragroup second moment would be averaged to zero. Therefore its 0.7 gauss² second moment is due entirely to intergroup interactions and can be used to estimate an intergroup second moment for the similar IF_6^+ group. This makes the total second moments of the cation 2.74, 2.87, and 2.63 gauss 2 for C $_2$, C $_3$, and C, reorientations. All these exceed the experimental value of 2.0 gauss² by more than 30%. The actual motion which IF_6^+ is undergoing must therefore be less than reorientation about octahedral axes at random but greater than reorientation about a single axis. Perhaps the motion is a combination of reorientation about one axis and simultaneous oscillation about another. This implies that different reorientational barriers may exist for the IF_6^+ and AsF_6^- ions.

The average activation energy for the combined motions was determined from an Arrhenius plot of equation (8) to be 19±4 Kcal per mole. This energy is very high. Because of the scatter in Figure 16 of the points just below the transition; it is possible that the change in second moment as drawn is sharper than it really is. A less

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abrupt transition would have a lower activation energy. If the transition is indeed this abrupt, the activation energy found may not be valid. Instead of a change in motion within a solid phase of fixed crystal structure, the transition may mark an actual crystal transition.

$$B_{\circ}$$
 $SF_4 \cdot AsF_5$

1. Results

Figure 21 shows the temperature dependence of the SF_{A} • AsF₅ absorption spectrum at 30 MHz. The absorption curves have the same x-scale and are integrated to a constant, arbitrary area from the derivative curves. Appendix IVa contains reproductions of the actual derivatives including some for temperatures higher than the highest value shown in Figure 21. Figure 22 is a plot of the temperature dependence of the averaged second moments at 30 MHz. The second moment does not appear to achieve a rigid lattice value by 77°K, the lowest temperature reached in the study. At 77°K the second moment is 5.9+0.3 gauss². From that temperature it drops gradually in a smooth curve to 1.85+0.1 gauss 2 around 200 K. The second moment remains constant at this value until 336 K. Throughout the region from 77 to 336 K, the 30 MHz absorption spectra are almost symmetrical, with a slight tailing to low field. Above 336 K the absorptions were so narrow that the integrated spectra were not plotted. The derivative curves in Appendix IVa show a marked increase in motion beginning at 336 K. The derivative at 320 is similar to that at 295 K, which shows a shoulder on the low field half of the

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to Follow Page 69
derivative. The spectra at 336° have a very general similarity in shape and a similar second moment to those at 320° , but the shoulder has now become a narrow component. Second moment drops at 336° to a value of about 0.1 gauss² by 342° K. Between 342° and 373° K, the highest temperature recorded, the second moment remains constant. By 342° K there is an almost complete resolution of the spectrum into two components with an isotropic chemical shift of 97.5 ± 5 ppm. The resolution is slightly better at 373° K, but the chemical shift is exactly the same.

Appendix IVa as noted above shows the temperature dependence of the derivative line at 30 MHz. The gradual shift of the low field shoulder towards high field changes the line shape in a manner which makes it difficult, as with $IF_6^+AsF_6^-$, to define a consistent peak to peak line width from the derivative. For this reason no plot of variable temperature line width is given.

The chemical shift for the total curve with respect to CF_3COOH is given in Figure 23. Although it appears that there might be a temperature dependence of the shift relative to CF_3COOH at $300^{\circ}K$, the scatter is so great that it cannot be established. The shift determined from Figure 23 is -40+15 ppm.

 Resolution with Components (see Results also). Isotropic and Anisotropic Chemical Shift.

Figures 24a and b show the field dependence of the absorption spectra at 300° K and 77° K. Appendices IVb and IVc give the derivative curves for these spectra Figure 24a demonstrates that one can make a



FIELD (H,) GAUSS



Field dependence of absorption spectra at 300°K





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resolution of the curve at 300 K and 94.1 MHz. The ratio of the area under the tall, high field peak to that under the short, low field peak is 2.2:1, from which it is concluded that there are twice as many fluorines involved in the high field peak as in the low field. Hence at 300° K the SF₄ • AsF₅ adduct is probably the ionic salt SF_3^+ AsF_6 for the experimental ratio of areas under the components is greater than 6:3, not between 6:3 and 5:4. The high field component has a second moment of about 0.9 gauss² and the low field component one of 1.1 gauss². The relative chemical shift between the two components as resolved at 94.1 MHz and 300°K is 105+10 ppm in agreement with the value determined in the 30 MHz spectra at 342°K and above. The components at 300°K obtained from the resolution of the 94.1 MHz spectrum, are each symmetrical about their centers with no suggestion of asymmetry. As shown by the broken lines in Figure 24a the components, with a shift of about 100 ppm, give a reasonable reproduction of the experimental spectrum at each lower frequency investigated. From the approximate 100 ppm shift between the components and the -40+15 ppm shift of the total curve with respect to CF3COOH at 300°K, the shifts of the components with respect to any standard can be determined. Relative to HF the high field component is at -107+20 ppm and the low field component at -207+20 ppm. Since the AsF ion is common to both the AsF adducts, it is undoubtedly the peak found at about -100+20 ppm in each. The cation in each adduct is then the low field component in each case.

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It is also possible to make a resolution into components at 94.1 MHz and 77° K. The resolution was based on the contours of the curve and the assumption that the line shapes of the components would be roughly similar at 77 and 300° K. Two fairly symmetrical components are obtained with a relative shift of 185 ± 20 ppm which might be "squeezed" to 160 ± 20 ppm but no more. As indicated later even this value may be too great. The area of the taller, high field curve (AsF⁻₆) to that of the shorter, low field curve (SF⁺₃) is 1.9:1, again providing support for the 2:1 area ratio required by the ionic formulation of the adduct. The AsF⁻₆ component has a second moment of 2.8 gauss², the SF⁺₃ component one of 4.7 gauss². Shifting the two curves appropriately gives a reasonable reproduction of the line shapes at lower frequencies as indicated by the broken curves in Figure 24b.

Figure 25 shows the field squared dependence of the second moment at 300° and 77°K. Since there was no asymmetry evident in the resolved components at either temperature, the field squared dependence of the second moment must be due entirely to the mean, isotropic chemical shift. Since $\mathbf{\bar{G}}_1 = \mathbf{\bar{G}}_2 = \mathbf{\bar{G}}_3 = \mathbf{\bar{G}}_5$ and $\mathbf{\bar{G}}_4 = \mathbf{\bar{G}}_5 = \mathbf{\bar{G}}_6 = \mathbf{\bar{G}}_7 = \mathbf{\bar{G}}_8 =$ $\mathbf{\bar{G}}_9 = \mathbf{\bar{G}}_{As}$ where the S and As refer to the fluorine shift in SF⁺₃ and AsF⁻₆ respectively, and there is no detectable anisotropy present, equation (19) becomes

$$S_{2} = g_{2}(h) + \frac{2}{9} H_{0}^{2}(\bar{e}_{A_{s}} - \bar{e}_{s})^{2}$$
(30)

From equation (30) the 300° K line gives a value of the relative shift of 87 ± 10 ppm in good agreement with the two other values for 295° K and



above. Indeed, because of the small slope of the second moment line, a change of only +0.2 gauss² in the average second moment at 94.1 MHz would bring this shift up to about 100 ppm in even closer agreement with the values found by resolution of the spectra. From the 77° K line on isotropic shift of 110 ± 10 ppm is obtained. This agreement with the value at 300° K confirms that there is no anisotropy at 77° K. It also suggests that the resolution at 77° may be in error. Although the shape of the experimental curve appears to dictate components with a shift of at least 160 ± 20 ppm, in the absence of resolution in the experimental curve itself, there is certainly room for error. Probably the 110+10 ppm value from Figure 25 is more reliable.

3. Proposed Crystal Structure

No X-ray study is available for $SF_3^+ AsF_6^-$. Some information is available for $SF_4 \cdot SbF_5$, enough to make a guess at the structure of $SF_3^+ AsF_6^-$. In the absence of a rigid lattice second moment for comparison with the theoretical moment for the model, the guess must be rather tentative.

Bartlett (6) has determined a crystal structure from powder data for $SF_4 \circ SbF_5$. The determination was not fully completed but the symmetry suggested an ionic formulation $SF_3^+ SbF_6^-$. Muetterties (85) also suggested the ionic formulation for the adduct as the most likely of two possible structures. Bartlett's information is summarized in Table 8.

Table 8

X-Ray Data for SF⁺₃ SbF⁻₆ at 291[°]K

Simple cubic

 $a = 5_{0.002}$

= 178
$$\stackrel{03}{A}$$
, $\rho_{obs.}$ = 3.1 ± 0.1, $\rho_{calc.}$ = 3.03, Z=1

The Interatomic Distances Supplement (83) gives an Sb-F (single crystal) bond length of 1.78^o, and in the bond length range noted earlier an As-F (powder) length of 1.80Å. The SbF and AsF groups will have nearly the same symmetry and volume then and the SF_3^+ SbF_6^- structure may be a reasonable approximation to the SF_3^+ As F_6^- structure. However the atomic coordinates are not known for SF_3^+ SbF_6 and a further approximation must be made. The AsF_6 groups may be placed at the corners of the simple cubic cell. They could be approximated for the purposes of a second moment calculation as spheres (86) since the orientations of the octahedra in the cell are unknown. However, Program 6 is designed to use nuclear coordinates and the (0, 0, 0) AsF_6 group from $IF_6 + AsF_6$ was chosen after considerable trial and error with a model. Octahedra having this orientation were placed at the four corners of the cell. The SF⁺₃ group will be in the center of the cell at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, but it is unlikely (82) that the sulfur atom will be at the exact center. The group was placed so that the three fluorines were in an equilateral triangle centered on $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and parallel to the a-b plane of the Then the sulfur atom and its lone pair can fit along the cell. vertical axis passing through $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. In the model it appeared t hat the SF_3^+ group could rotate quite freely about the C_3 axis through the **S** atom and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Table 9 gives the atomic coordinates calculated for the assumed SF_3^+ AsF₆ unit cell at "291[°]K" and applied at 77[°]K. In determining the coordinates for the AsF₆ groups, As-F bond lengths of 1.77Å, as for the previous adduct, were used. Figure 26 shows a view

Estimated	Atomic Coor	dinates for S	$F_3^+ AsF_6^-$	at "291 ⁰ K"
As	0.000	0.00	00	0.0000
F,	0.1754	0,24	64	-0.0874
F ₂	-0.0874	0.17	/54	0.2464
F ₂	0.2464	-0.08	374	0.1754
F ³	-0.1754	-0.24	64	0.0874
F	0.0874	-0.17	754	- 0 . 2464
F	-0.2464	0.08	374	-0.1754
ຮັ	0.5000	0.50	000	0,4074
F,	0.3693	0.27	736	0.5000
F.	0.7614	0.50	000	0.5000
۴å	0.3693	0.72	264	0.5000

Table 9

It is not meant to imply accuracy to four significant figures.

down the a-axis for the proposed structure.

 Theoretical Rigid Lattice Second Moment and Reorientations in the Solid.

The theoretical rigid lattice second moment for $SF_3^+ AsF_6^-$ calculated by Program 6 from the above coordinates in 9.4 gauss². Only contributions from F-F and F-As interactions need be summed since the natural abundance of ³³S, the only stable, magnetic isotope of sulfur is so low (0.74%) that F-S interactions are negligible. There are a great many assumptions involved in the calculation and no experimental value is available as a Figure 26. $SF_3^+AsF_6^-$. Proposed unit cell (along a-axis)



PROPOSED POSITION OF As AT CORNERS

PROPOSED POSITION OF 'S AT(1/,1/,1/)

CIRCLES INDICATE FLUORINE Van der Waal's radii check. Indeed the count of internuclear distances which Program 6 can provide shows that the SF_3^+ ion is somewhat crowded in its assumed position. There are four SF_3^+ intergroup contacts with surrounding AsF_6^- ions. Two are not too severe being 2.5 and 2.6Å, but the other two are 2.2Å well under twice the 1.35Å fluorine van der Waals radius. Inspite of this the calculated second moment seems of a reasonable magnitude. The various contributions to the total second moment are listed in Table 10.

Table 10

			Secon	d Mome	2 nt Gauss
SF ⁺ ₃ AsF ₆	TOTAL	(including integral contribution over 6A of 0.31 gauss ² to F-F)	8.80	0,52	9.42
SF3 AsF6	INTRA		4.72	0.51	5.23
AsF ₆	TOTAL	(to 6 ^A)	5,96	0.51	6.47
AsF ₆	INTRA	· · · · · · · · · · · · · · · · · · ·	3.62	0.50	4.12
SF ⁺ 3	TOTAL	(to 6 ^P)	·2.63	0.01	2.64
SF ⁺ ₃	INTRA		0.77	0.00	0.77

"Rigid Lattice" Second Moment Contributions to $SF_3^+ AsF_6^-$

Note: All contributions in this table are based on a 9-fluorine unit SF_3^+ AsF $_6^-$. N in equation (2) has been taken as 9 for all groups.

5. Reorientations in the Solid

One thing to notice in Table 10 is that total second moment for the component SF_3^+ curve, if it could be resolved out, is

2.64 x $\frac{9}{3}$ = 7.9 gauss² while its intragroup second moment is only 0.77 x $\frac{9}{3}$ = 2.3 gauss². In determining positions in the SF⁺₃ ion, it was assumed in agreement with Bartlett (6) that because of the electron lone pair on the sulfur, the ion would have an opproximately tetrahedral configuration. Therefore S-F bond lengths of 1.56Å (83) and F-S-F angles of 109⁰ 28' were used. The presence of a lone pair will repel the three bond pairs somewhat more than a bond pair (7). The bond angle will therefore be somewhat less than the tetrahedral angle. This would reduce the intra-group F-F distances of 2.5A and would hence reduce the rather heavy proportion of inter (7.9 - 2.3 = 5.6 gauss²) to intra-group second moment (2.3 gauss²) in the SF_3^+ ion. A position in the unit cell which tilted the ion away from its assumed position would also change the second moment. However, reducing the tetrahedral angle would reduce the effective volume of the ion and give.it more freedom in the AsF_6 "cage" consistent with its considerable motion as low as

The calculated zero field rigid lattice second moment is about 9.4 gauss² yet the experimental moment at 30 MHz and 77°K, which includes a contribution from isotropic chemical shift, is only 5.9 gauss². The theoretical zero field anion and cation resolved curves would have second moments of about 6.47 x $\frac{9}{6} = 9.7$ gauss² and 7.9 gauss² respectively if they could be measured at their rigid lattice

 77° K. The most probable motion at 77° is reorientation about the C₃

axis. The shrinkage of the ion due to the smaller bond angle would

the ion's ability to reorient.

also reduce the moment of inertia about this axis and further enhance

temperature. Their actual resolved components at 77° K and 30 MHz have moments of 2.8 gauss² and 4.7 gauss². Obviously by 77° , the motion in the groups is sufficient not only to average out the anisotropy (since the components are symmetrical), but also to partially average out the dipolar interactions. By 220°K the total second moment of the experimental 30 MHz curve has fallen to about 1.9 gauss². Since there is no anisotropy in this region above the transition; the resolution into components made at 94.1 MHz and 300°K will be valid here too (there is virtually no change in line shape from 200 to 295°K at 30 MHz). The second moments are 1.1 gauss² and 0.9 gauss² for the SF⁺₃ and AsF⁻₆ ions respectively. The anion surely and the cation very likely are undergoing isotropic or near isotropic recrientation above the transition.

In the absence of a rigid lattice second moment, it is impossible to obtain a reliable activation energy for the transition. One can of course estimate a reasonable value for the experimental rigid lattice second moment at 30 MHz (at which frequency the temperature dependence studies were made) and eventually arrive at an activation energy. This was done and an energy of about 1 Kcal per mole obtained. It is of course an even cruder estimate than one normally obtains from second moment studies.

The transition between 336 and 342°K is too abrupt to give a meaningful activation energy. The value of the total second moment

is about 0.1 gauss² which includes the contribution from relative shift between the ions. Diffusion of the ions is probably taking place through the solid. Although the sample is rather plastic looking at 373[°]K, it remains solid and does not melt even when held at that temperature for several hours.

CHAPTER V

SUMMARY AND DISCUSSION

It is difficult to obtain precise results for the three compounds studied. This is particularly so with WF . The most probable resolution of that compound is into two components separated by a mean isotropic shift of 105 ppm and each with an average anisotropic shift of 300 ppm. Since no accurate resolution could be made, no values were quoted for the zero field, dipolar broadening of each. From the theoretical rigid lattice second moment, the contributions of the axial and equatorial fluorines to the total second moment for the molecule are 2.71 gauss and 5.44 gauss respectively. Weighted according to the relative numbers of fluorines involved in each, they would give 8.14 gauss² for each component if they could be resolved out. These second moments are virtually identical to the second moment of the observed zero field curve (actually at 2 MHz) which was used as a broadening function (components weighted 4:2 by area) in the attempted reconstruction based on the shifts mentioned immediately above. It was assumed that the individual line shapes would be similar to that of the total curve at zero field. The second moment, however, says nothing about line shape. Line shapes are much more difficult to predict than are second moments, which, of course, is the difficulty here.

For the two AsF_5 adducts resolution into components can be made and relative shifts determined. However, even for $IF_6^+AsF_6^-$ only average anisotropies could be estimated for the two components. No reliable value at all could be obtained for $SF_3^+AsF_6^-$ since a rigid

lattice was not found within the temperature range of the investigation.

All three of the compounds showed a transition in the second moment curve around 200[°]K from which activation energies of varying reliability were determined for the probable reorientations occurring. The type of reorientation was deduced from the magnitude of the change in the second moment of the total curve or resolved component.

Table 11 summarizes what are considered to be the best values obtained here for the isotropic and anisotropic shifts, second moments, transition temperatures, and possible reorientations in the solids. All these have been discussed in detail earlier.

Finally, it is possible from the anisotropic and mean isotropic chemical shifts to draw some conclusions about bond character in the hexafluoride groups. For fluorine, the principal contribution to chemical shift is from the paramagnetic term in equation (10) according to Saika and Slichter (70) and Karplus and Das (88). Following their treatment, Andrew (71) has expressed the chemical shift in terms of localized bond parameters I, ρ , and s which are respectively the ionic character, double bond character, and degree of sp hybridization in the bond orbital. Then for a fluorine atom bonded in the z-direction, the principal values of the paramagnetic contribution to the chemical shift tensor are

$$\begin{split} & \mathbf{G}_{xx} = \frac{3}{2} \mathbf{G}_{o} \left[1 - \mathbf{s} - \mathbf{I} + \mathbf{I}\mathbf{s} + p_{y} \left(\mathbf{s} + \mathbf{I} \right) \right] \\ & \mathbf{G}_{yy} = \frac{3}{2} \mathbf{G}_{o} \left[1 - \mathbf{s} - \mathbf{I} + \mathbf{I}\mathbf{s} + p_{x} \left(\mathbf{s} + \mathbf{I} \right) \right] \\ & \mathbf{G}_{12} = \frac{3}{2} \mathbf{G}_{o} \left[p_{x} + p_{y} - p_{x} p_{y} \right] \end{split}$$

.....(31)

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Table 11

Summary

Compound or Group		A ppm	B ppm	C GAUSS ²	D GAUSS ²	° K	F Kcal/mole	G
WF ₆		-380+40		8.25+0.2	1.0+0.05	180-210	10.0+0.4	Isotropic or near isotropic
equatorial	F	-435 <u>+</u> 40	~300	8.14 ¹				
axial	F	-325+40	~300	8.14 ¹		• .		
IF ⁺ AsF ⁻		-170 <u>+</u> 8		10.7 <u>+</u> 0.2	2.1 <u>+</u> 0.2	205-235	19 <u>+</u> 4`	
IF ₆ +		-245 <u>+</u> 20	~33 3	10.20 ¹	2'• 0		•	Reorientation about one axis and simultaneous oscillation
AsF		-100 <u>+</u> 20	~ 333	10.44	0.7			about another. Isotropic or near isotropic
$SF_3^+ AsF_6^-$		-155 <u>+</u> 15		$5.9+0.3^{2}$	1.9+0.1	<77-200	ل یہ	
sr ⁺	•	-205 <u>+</u> 20		9.41 4.7^2 7.01	1.1			Isotropic or near isotropic
AsF ⁷ 6		-105 <u>+</u> 20		2.8 ²	0.9			Isotropic
SF ⁺ AsF ⁻ 6				9.71	342 -373⁰K Q.1	336-342		Diffusion

- A. Mean isotropic chemical shift to nearest 5 ppm relative to HF.
- B. Anisotropy of Chemical shift $(\boldsymbol{s}_{11} \boldsymbol{s}_{1})$.
- C. Zero field second moment 77°K.
- D. Second moment at 295°K.
- E. Transition temperature range.
- F. Activation energy.
- G. Possible reorientation above transition temperature.

- 1. Calculated for theoretical, rigid lattice.
- 2. Not a rigid lattice.

The expressions \int_{x} and \int_{y} relate to \mathbf{n} -bonding in the xz and yz planes. Such \mathbf{n} -bonds may be formed by the overlap of the fluorine p_{x} and p_{y} orbitals with the d_{xz} and d_{yz} central atom orbitals. The chemical shift is expected to vary, according to the ionic character of the bond, from HF the most ionic down to F_{2} the most covalent. Although hybridization could have the same effect as ionic character, Saika and Slichter neglected it because of the difficulty of making a numerical estimate. Although Andrew has taken account of hybridization, we shall follow Saika and Slichter and also Rigny (39) in ignoring it.

When hybridization is neglected, then, in the case of axial symmetry of the chemical shift tensor where $G_{zz} = G_{ll}$ and $G_{xx} = G_{vv} = G_{l}$, equations (31) reduce to

 $6_{II} = \frac{3}{2} 6_{o} (2\rho - \rho^{2}) \qquad (32)$ $6_{I} = \frac{3}{2} 6_{o} (1 - I + \rho I)$

where $\rho_x = \rho_y = \rho$ and ρ and I are as above. From Karplus and Das the coefficient $\mathcal{O}_0 = -863$ ppm. They point out, however, that the exact value of \mathcal{O}_0 is not important since it does not affect the trends calculated and it is the trends, not the actual values, which are of primary significance.

The mean isotropic chemical shift may be written

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or for axial symmetry of the shift tensor

$$\vec{6} = \frac{1}{3}(26_1 + 6_n)$$
(34)

If \tilde{G} is measured relative to HF, then the knowledge of $(G_n - G_n)$ enables individual values of G_n and G_n to be obtained for substitution into equations (32). Only average values of $(G_n - G_n)$ are available here, but Blinc (41) reports values of 640 ± 50 and 670 ± 50 for UF₆ and 1300 ± 100 and 1380 ± 100 ppm for PtF₆ for the axial and equatorial components respectively. In our case, therefore, the average anisotropies are probably good approximations to the values for the individual components. Values of ρ and I for the hexafluoride groups studied here and also for UF₆ are plotted in Figure 27 as a function of mean isotropic shift with respect to HF.

From Figure 27, values of $\rho = \sim 0.01$ and I = ~ 0.8 can be estimated for the S-F bond in SF⁺₃. However, Karplus and Das caution that such plots be considered only as applying to groups of similar compounds. Figure 27 will be taken only as holding for hexafluoride groups. Indeed even the value of ρ for the UF₆ axial component deviates widely from the plot although the value for I is in good agreement. Also neither axial nor equatorial component of PtF₆ can be fitted to the plot. Both components lie far outside the range of shifts found here and give meaningless values of ρ and I. However, although Blinc (41) was unable to determine the anistropies of the components in PuF₆, he was able to estimate mean isotropic chemical



MEAN ISOTROPIC SHIFT PPM

shifts of -440 and -1070 ppm relative to HF for the axial and equatorial components respectively. These shifts do lie within the range of shifts in Figure 27. From the figure we can predict $\rho = 0.1$, I = 0.6 for the axial fluorine bonds and $\rho = 0.38$, I = 0.03 for the equatorial bonds.

APPENDIX I

COMPUTER PROGRAMS.

All the programs in this appendix have been written in or adapted to Fortran IV as compatible with the University of British Columbia's IBM 7040 (now temporarily 7044) computer. Some of the programs have been tidied up slightly from the form in which they were used. However this merely involved changing notation that might have been confusing. Some quantities which really could be input as data still appear instead in the programs themselves. These are obvious, however, and can easily be changed by any one wishing to adapt the programs for his own use. Program 1. Calculation of Experimental Second Moments from Derivative Curves.

This program is for the general case of an asymmetric derivative curve. For an asymmetric curve the second moment is $SM = S - (FM)^2$. SM is the second moment about the centroid of the curve, S is the second moment computed about any point (taken at the estimated centroid to minimize error), and FM is the first moment computed about the same point. For the derivative curve the second moment is

$$SM = \frac{1}{3}(scale)^2 \frac{\Sigma x^3 y}{\Xi x y} - \left(\frac{1}{2}(scale) \frac{\Sigma x^2 y}{\Xi x y}\right)^2 - \frac{(\Delta Hm)^2}{4}$$

where scale = gauss per division. The last term in the equation for SM is Andrew's (89) correction for medulation broadening. is one-half the peak to peak modulation. In the measurement of the experimental curves, the x - axis of the spectrum is divided into convenient, equal divisions, for which a calibration has been determined, and the corresponding y values measured in arbitrary units. The y values are written directly on computer data sheets and the remainder of the determination of the second moment is carried out by the computer.

		•
N	=	the identification number of the derivative curve or TRACE
Nl	=	total number of data points on trace N
N2	=	total number of data points on the first half of the curve
		including the cross-over point in the middle.
SCALE	=	gauss per division
PMOD	=	\wedge Hm = $\frac{1}{2}$ peak to peak modulation
TEMP	=	temperature in degrees
IY	=	y amplitude in arbitrary units for each of the N1 equal
		divisions
SM, S,	, a	and FM are as described above.

It is immaterial at which end of the spectrum measurement is commenced. However to avoid confusion as to field direction in Program 2, if integrating derivatives which are only slightly asymmetric, it is recommended that a consistent policy be followed. Start always at the low field end and choose the sign of IY positive in that half of the spectrum.

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			•	
				· · ·
			•	
\$FOI	RTRAN	*****		
С	EXPERIMENTAL SECOND MOMENT			
	DIMENSION IY(200),C(9)			
1	FORMAT (1914,4X)			
2	FORMAT (314, F7.4, F6.2, F5.0, 8A6)			
3	FORMAT (1X,5HTRACE,4X,1HT,5X,1HS,10X,2HFM,10X,2HSM)			
	WRITE (6,3)			
4	FORMAT (1X, I5, F6, 1, F9, 2, 1X, F8, 2, 5X, F6, 2, 5X, 8A6)			
5	READ (5,2)N,N1,N2,SCALE,PMOD,TEMP,(C(I),I=1,8)			
6	READ (5,1) (IY(I),I=1,N1)			ŕ
	KFM = 0		· .	•
	IS=0 ;			C3
				9
	DO IO J =I•NI			•
ana an			at ge verdensklasse stande, so dy en nyersed, feldelikkersprog – so of sis	• • • • • • • • • • • • • • • • • • • •
1 ^	$10 - X^{*} + 10$			· · · · · · · · · · · · · · · · · · ·
10	$\frac{1}{2} = \frac{1}{2} + \frac{1}$			
	A = IA			
allela mir 1944-dan osanlada. Angeledda fe endia fe endiadalladar da '	Γ FM=KFM	al bull caracterization and tangen allogers and y total can be charger	ny nano kalalahan sa sa kala dagi ka bina di kala manaki , k _{an} a - sa kanaki .	
	FM = -5 * FM * SCAL F/A			
	S = SCAL F * SCAL F * SUM / (A * 3)	•		
	SM=S-FM*FM25*PMOD*PMOD			
	WRITE (6,4) N,TEMP,S,FM,SM,(C(I),I=1,8)			
	GO TO 5			•
nyn felgela, ar wywar fy drigt offel familian from afaalla felyn, afaalle wra on	END	Automotive and the second		
\$EN	TRY			
· .				
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(1)11 11112 - 1307626 (* 17)10 - 1917 (* 1916) - 1917 - 1918 - 1910) - 1910 - 1910 - 1910 - 1910 - 1910 - 1910		ب منطقه ما من وي المحمد برخم و الرام		

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Program 2. Integration of Derivative Curves to Absorption Curves.

This program integrates the derivative curves to absorption spectra using the data punched for the second moment calculations. The integration is performed using rectangular strips which, when small enough, are sufficiently accurate for broad line nmr.

NMBR = identification number of derivative curve N = total number of data points SCALE = gauss per division (on the derivative curve) IY = y amplitudes of the N points on the derivative curve

In the body of the program the G(I)'s are the amplitudes of the absorption curve at points separated one from another by the distance SCALE. BL is a correction parameter applied to G(I) to ensure that G(I) approaches zero at both limits of the integration. Z, the DEVIATION, gives an estimate of the accuracy of the integration. It is expressed as a percentage in terms of G(N) and X the maximum amplitude of the absorption curve. FNORM normalizes the spectra to constant arbitrary area for comparison with each other. The punch instruction produces data for use in Program 2^{*}. This last program outputs the data from Program 2 on an X-Y plotter. The program was written to give a constant x-scale to all the absorption curves so that comparison could be made directly between the area-normalized curves. Since the program calls special routines which were written expressly for the computer here by the computing center staff, it cannot be used elsewhere.

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ana jaya na katala na	SEODTRA		 				³
	C	INTEGRATION OF DERIVATIVE CURVE					0 64
		$DIMENSION \qquad G(100) \cdot TITIF(9) \cdot IY(100)$					U
	20	READ(5,1)NMBR,N,SCALE,(TITLE(I),I=1,9)	 				 21
	1	FORMAT(A4, I4, 4X, F7.4, 6X, 9A6)					ķ
		READ($5,2$) (IY(I), I=1,N)					
	2	FORMAT(19I4,4X)					111
		H=0.					
		<pre>)RTRAN INTEGRATION OF DERIVATIVE CURVE OIMENSION G(100).TITLE(9).IY(100) READ(5,1)NMBR,N.SCALE.(TITLE(I),I=1,9) FORMAT(44,14+4X,F7.4+6X.9A6) READ(5,2) (IY(I), I=1,N) FORMAT(1914+4X) H=0. DO 10 I=1,N H=H+FLOAT(IY(I)) G(I)=H*SCALE Z=G(N) WRITE(6+12)NMBR,(TITLE(I),I=1,9) BL=G(N)/FLOAT(N) DO 29 I=1,N G(I)=G(I)=FLOAT(I)*BL X=0 Y=0 DO 30 I=1,N IF(G(I)-FLOAT(I)*BL X=0 Y=0 DO 30 I=1,N IF(G(I).GT.X)X=G(I) IF(Y.GT.G(I))Y=G(I) CONTINUE IF(X.LT.(-Y))X=Y Z=Z*100./X AREA=0. DO 100 I=1,N 0 AREA=AREA+G(I)*SCALE FNORM=1000./AREA DO 110 I=1,N 0 G(I)=G(I)*FNORM WRITE (6+11) (G(I),I=1N) PUNCH 1.NMBRN,SCALE PUNCH 11, (G(I),I=1,N) FORMAT(10F8.2) FORMAT(10F8.2) FORMAT(10F8.2) FORMAT(10F8.2) FORMAT(107.9A6) GO TO 20 END</pre>	 			· · · · · · · · · · · · · · · · · · ·	
		H=H+FLOAT(IY(I))					
	10	G(I)=H*SCALE					
Mentional (state projekti projekti stati (stati and stati stati stati stati stati		Z = G(N)	 				
	•	WRITE(6,12)NMBR,(TITLE(I),I=1,9)		•	۲۲۱	ŧ	
		BL=G(N)/FLOAT(N)			ro		
	20	$\frac{\text{DO} 29}{\text{C(1)} \text{C(1)} \text{C(1)}}$	 		03		
	29	G(I) = G(I) - F LOAT(I) * BL			ស្ន		
		X=0				. 1	
	nt and countries and there by millionian interest	D = 20 $I = 1.01$	 	· · · · · · · · · · · · · · · · · · ·			
·		IE(G(I),GI,X)X=G(I)					
		IF(Y,GI,G(I))Y=G(I)					
	30	CONTINUE	 				
		$IF(X \cdot LT \cdot (-Y))X = Y$					
. •		Z=Z*100•/X					
anayo harrand mark - krayburd a de	in an all and a substitution of the provident	AREA=0.					
		DO 100 I=1,N				· .	
	100	AREA=AREA+G(I)*SCALE	 			faat also als darf and a first die warman is an die beste	
;		FNORM=1000./AREA					
•		DO 110 I=1,N					
ngga pangang palan seten pelekungkan secara kan delem seten pertekungkan se	110	G(I)=G(I)*FNORM	 	·····			'
•	1.0	WRITE (6,40) AREA,2					
	40	FORMAT(70X)5HAREA=)F10.195X)10HDEVIATION=)F10.4)	· .				
		$\frac{WRIE(6,11)(G(1),1=1,0)}{DUNCU2,000000000000000000000000000000000000$	 				
							. ; y
	רר	FORMAT (10F8.2) = (10F8.2)					1111
and an and a state of a state of a part of a state of a	12	$FORMAT(3X \cdot \Delta 4 \cdot 10X \cdot 9\Delta 6)$	 	ala anga Malaya da - Pangalan Jandanasa			
. 3	<u>له</u> د.	GO TO 20	•			· .	30
		END					J.
	SENTRY		 		.	· · · · · · · · · · · · · · · · · · ·	2'

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	D I D F I C	REMEMBER LAST SPEC.N.SCALE CARD MUST BE	BLANK TO CALL	PLOTND	•	
		DIMENSION $X(100) \cdot Y(100)$				
		CALL PLOTS		· · · · · · · · · · · · · · · · · · ·		
	1	READ (5,2) SPEC,N,SCALE		•		•
	2	FORMAT (F4.0,14,4X,F7.4)	and the second structure and a state state of the second structure structure and the second structure and the s			
		IF(N.LE.O) GO TO 100				
	: 3	READ $(5,4)$ $(Y(I), I=1,N)$				
	4	FORMAT (10F8.2)	*			· · · •
		DEEX=SCALE/2.54				
		DEEY=0.03				
a y gygga an da y y dag yn dynai (y dy y da ywy nyw fael ha y da y yn yw	Anal Part State of the case of the case of the state of the	S=FLUAT(N-1)*DEEX	is self-admitischen andersachten der andersachten aller sit. Som der gestren geste die teil der Stade bleich dame d		- #	
	1.0	$\begin{array}{c} \text{DU} 1 \text{U} 1 = 1 \text{ in} \\ \text{V}(1) = \text{ELOAT}(1) \text{ indef } \\ \end{array}$			۲ ^م	1
•	10				30.	~
	مريح ما المحمد الم	$\frac{1}{1} = \frac{1}{1} = \frac{1}{1}$		· · · · · · · · · · · · · · · · · · ·		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
•	11	$IE(Y(I) = \{-0, 25\}) + Y(I) = (-0, 25)$			am	
	* *	CALL NUMBER $(5 \bullet 98 \bullet 90 \bullet 14 \bullet SPEC \bullet 0 \bullet \bullet -1)$			N	1
y a pytholotokia (2006-06160)	1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1	DO 12 I=1,N	аналарын каланаларын жана жана каланда жана жана калана калана калана тарык тарык тарала калан калана калана к Каланда калана тарык тарак калана калана калана к			
	12	CALL SYMBOL (X(I),Y(I),0.14,3,0.,-1)				
	,	CALL PLOT ((S+2.),0.,-3)				
Constraint of the second states of the second		GO TO 1				
	100	CALL PLOTND				•
ants of the said these	n kanalah di pantuku mahangku naha nangku panuka utaku utaku aku u ku ku	STOP	libruar a vana - Minansis in un un un un un un annun annun annun annun annun an annun an annun a		a to there and the statement	
•		END				
	\$ENTRY					
* *)						
	an angalan nagara asal kenyangan arta tertetakan kenyangan kenyangan kenyangan kenyangan kenyangan kenyangan k		nelle ar minin versenen kann ar Mr. – ritteraaraaster al is ee astel an re			
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			an a bulan na mangang atau kabupatèn di kabupatèn di kabupatèn di kabupatèn di kabupatèn di kabupatèn di kabup			
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Program 3. Line Shape Function F(H).

This program synthesizes a curve F(H) using experimentally determined values of $(\sigma_{11} - \sigma_{1})$ and the zero field dipolar second moment. It is written for the case of equivalent nuclei exhibiting axial symmetry of their shift tensors. If non-equivalent nuclei are present, two or more synthesized curves appropriately shifted relative to each other may be used. F(H) is given by equation (21). Since the centroid of the synthesized curve will be superimposed on that of the experimental curve, H^* will be identical in each case and may be chosen equal to zero for the program. Therefore

$$F(H) = \int_{-\infty}^{+\infty} f(HO)S(H-HO)DHO \qquad (A)$$

where

$$f(Ho) = \left(\left| + \frac{HO}{ALPHA} \right)^{-\frac{1}{2}} \right.$$
(B)

and the constant in equation (B) is omitted since the function F(H) will itself be normalized in the program.

Two programs, 3a and 3b, are given below. For 3a the experimental line shape at 2 MHz has been used as the broadening function S(H-HO) and for 3b the broadening function is a gaussian function having the same second moment as the extrapolated zero field second moment. The former was used with WF_6 and the latter with $IF_6^+AsF_6^-$

Program 3a.

ALPHA = the "a" defined under equation (16) SCALE = separation in gauss between the data points on the experimental broadening function (ebf.). Program 3a Contd.

NY	=	the number of data points, including the centroid,
		on the left half of ebf.
NM	=	total number of data points on ebf.
Y(I)	=	an amplitude on ebf.
H and DHO	=	(where DHO = dHo) are as defined under equation (21).
Amp	=	the maximum amplitude of the experimental curve. If
		the curve consists of two or more components, the
		synthesized curve must be normalized to the area,
		not the height of the experimental curve.

Program 3b.

ALPHA is as for 3a. BETA is the square root of the extrapolated zero field dipolar rigid lattice second moment. H, DHO, and AMP are as for 3a.

Both programs output values of F(H) - labelled F(K) here - for values of H - labelled G(K) here.

• • • •

Note that in the actual programs SH(H-HO) is written as SH(HO).

	SIRFTC						
	C	ANISOTROPIC FUNCTION WITH EXPERIMENTAL BROADENING FUNCT	TION			•	
,	C	DIMENSION E(00)-G(100)-Y(100)					
		COMMON ALPHA SCALE NY NM Y HODHO					
		READ (5.1) NM					
	1	$FORMAT (4X \cdot I3)$					
		READ (5,2) (Y(I),I=1,NM)					
	2	FORMAT (10F8.1)					
	-	WRITE $(6,2)$ (Y(I), I=1, NM)					
	3	READ (5,4) ALPHA, SCALE, NY, AMP					
	4	FORMAT (4X,2F12.4,4X,13,4X,F12.4)					
		WRITE (6,4) +LPHA, SCALE, NY, AMP					
ilia Maritik ermanisi	e Milijaniyaniyaniyangin geresayar som persameneriyanis-Marina	H = -20	annoran - nan alam nan kanan kana kana kana ka		··	1	
		DH=0.5			ř	1	
•		DHO=0.1			 	<u></u>	
		DO 11 K=1,80			_ H	ν.	
		F(K)=0.			E		
		H=H+DH	المحاول المحافظ المحافظ والمحافظ المحافظ والمحافظ المحافظ المحافظ المحافظ المحافظ المحافظ والمحافظ و		<u></u>		
		G(K)=H			φ		
		HO=-ALPHA+0.01					
		IF(H.GT.20.) GO TO 3					
		DO 10 L=1,2000					
		HO=HO+DHO					
	sumply a score the get easy concernentially sub-	IF(HO.GT.(2.ALPHA)) GO TO 11	Larre energy recommendation of the	and the state lines of the Pratic day do not			
	10	F(K) = F(K) + FH(HO) * SH(HO)	· .				
	11	FMAX=0.					
		DO 20 N=1,80					
		IF(FMAX.LT.F(N)) FMAX=F(N)					
	20	CONTINUE					
		FMAX=AMP/FMAX					
		DO 21 N=1,80					
	21	F(N) = F(N) * FM + X					
		WRITE (6,22) (G(K),F(K),K=1,80)					
	22	$FORMAT (1X) 2F12 \cdot 4)$					
		GO TO 3					
1 1 4 7 Bar an a 100 Bar a las an 1 . • • •	F		No. 11.00.000 (1999) 1. 1. 2.1.00 (1. 1999) 1. 1999			·	
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\$ IBFTC	FH	арадын байла жаларын байл тараларын тарат арын байлаган байлага унун болбоор байлан байлан байлан байлан байлан Тарат	antaran kanan mananan anya kanan kanan T	
	FUNCTION FH(HO)		· ·	
	COMMON ALPHA, SCALE, NY, NM, Y, H, HO	nalisaan artiin tah maaanti bahkin maaayaa aa		
·	DIMENSION Y(00)			
	FH=1.+HO/ALPHA	•		•
s Na mang manang manan	FH=1./SQRT(FH)			n a a such an a bang i yang ngangan nga sa sang an tang an tang an tang an tang an tang an tang a tang
SIRFIC	SH SH			
\$1011C	EUNCTION SH(HO)			ana yang sa
•	COMMON ALPHA, SCALE, NY, NM, Y, H, DHO	· ·		
	DIMENSION Y(100)			
namenta en la secono de la constructiva de la construcción de la construcción de la construcción de la constru Namenta en la construcción de la co	FEJ=FLOAT(NY)+(H-HO)/SCALE			
	J=FEJ			1
ning ang mang mang mang mang mang mang man	IF (J.LE.0) GO TO 110			
	IF(J.GE.NM) GO TO 110			Ğ
	BELOW=Y(J)			
n gen genom het genomen hannen versterer file gegenbern vorschrittenske state gener. D	ABOVE = Y(J+1)			l
	CO TO 111			
1.10	SH=0.			
	GO TO 112			
111	SH=BELOW+FINK			
112	CONTINUE			
	RETURN			
	END			
na je na politika za zako, na konstantika i kali ka se teken na seri kan na seri i Marka i Marka i Marka i Kali	· · · · · · · · · · · · · · · · · · ·		<u>_</u>	
ander af fan de faffen fer er meder of an en eller provinsie fan fan de fan de fereder faffen an er fan er fan		hadalan ang ang ang ang ang ang ang ang ang a		and an an an analysis borry is a massive on the brokens. So the same has been
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C SKIN	ANISOTROPIC FUNCTION WITH GAUSSIA	N BROADENING EUNCTIC) NI	
	DIMENSION E(100).G(100)	I BROADENING FONCTIO		
na har hanna fan star a sa fan har far far an star ann fan star star star star star fan star fan har fan har fa	COMMON ALPHA.BETA.H			-
. 1	READ (5.2) ALPHA.BETA.AMP			
2	$FORMAT (1X_3F12_4)$	· · ·		
NATIONAL TOTAL CONTRACTOR CO	WRITE (6.2) ALPHA.BETA			nya na mangana na mangana na mangana na manganan ang pananan ang panganan na pangana na ng panganang ang pang m
	$BETA=1 \cdot / (2 \cdot *BETA*BETA)$			
	H = -20.			
a gamma mandana ayang karang ada karang karang karang kanang kanang kanang kanang kanang karang karang karang k	DH=0.5			nana a mahamman na pangan na pa
	DHO=0.1			
• · · · · ·	DO 11 K = 1,80			
a Source and the second	F(K)=0.			
	H=H+DH			ان بر
	G(K) = H			
nandersten fersakternetiften ner metten ist mensek terne i hjerer på har at banen sjoner at ander ander	HO = -ALPHA + 0.01			
· · ·	IF(H.GT.20.) GO TO 1			щ
	DO 10 J=1,2000			W 1
nanaranan menan menan kerinta kerinta dari para terandar menan metar metari dari di sebagai dari para dari para T	HO=HO+DHO	анандан улуман килинин килинин килинин калана к Калана калана	yy nana takin dina dinangana kati ka dalam katangkan ing pangangangkat yi kuta nangat dinasi ing mangangkan katang ta na kupi yi	σ'
	IF(HO.GT.(2.*ALPHA)) GO TO 11	· · · ·		,
10 .	F(K) = F(K) + FH(HO) + SH(HO)			
11	FMAX=0.	renne ander en ander a		nen menandakan kerana keranakan keranakan keranakan peranakan ana
• •	DO 20 N=1,80			•
	IF(FMAX.LT.F(N)) FMAX=F(N)			
20	CONTINUE			 An of other capy cape is series. The Pre-Man is the birth in the series of the series o
	FMAX=AMP/FMAX			
	DO 21 N=1,80			
. 21	F(N) = F(N) * FMAX			
	WRITE (6,22) (G(K),F(K),K=1,80)			
22	FORMAT (1X,2F12.4)			۰ ۱۰
•	GO TO 1	· · · · · · · · · · · · · · · · · · ·		
	END			
				•
والمحافظة والمنافقة والأرواني والمرار والمتحد والمتحد والمتحافظة والمحافظة والمتحد والمحافظة والمحافظة				

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SEOPTRA										
JI UNINA	FUNCTION EH(HO)									•
	COMMON ALPHA, BETA, H									
W A MARKATATATATATATATATATATATATATATATATATATA	FH=1.+HO/ALPHA									
1	FH=1./SQRT(FH)		· .							
niyaasiyoo ay ahaa kaalaa daga ya ahaaya, jaayaa ya yaa ahaa ahaa ya ya yaa ahaa ahaa ahaa ahaa ahaa ya ya ya y	RETURN				n gan im metre manga per sam biliper bili derget. So. 3 %					
	END									
\$FORTRA	N									
ay ay an anna baala at baaba tha baabaa ay aanaa ay ahay ay ahay ay ahaana gabba tha canaa ka anaa ahaa ahaa ah	FUNCTION SH(HO)									
	SHEEXP(-(H_HO)*(H_HO)*	BETAN								
	RETURN	DLIAI								
δοδο τη μετροπείο το στο στο μαροδιατική ματα το ματά το	END		ra mende a lana (all'hellen) blik, hell menanja er rem mer ne jerenga (a a ser (aan jel) - menit)	, <u>and a second s</u>	an an a larna - ann an Mala I Maladana a Mha	1 10 10 10 10 11 10 10 10 10 10 10 10 10	ante autre descendentes des la larg		na ana a satunggangkupun interne natu	
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۰. , Program 4. Doublet Fit.

This program is from Dr. P. Raghunathan of this Department and is based on Abragam (52, p. 220).

ALPHA and BETA are related by $SM = \frac{4}{5} \alpha^2 + \beta^2$ where SM is the second moment of the experimental curve and $\alpha = \frac{3}{4} \delta^2 \hbar^{-3}$ where r is the estimated doublet splitting. H is again a general field parameter.

X is the HD of Program 3 and Abragam (52, p.220).

The program puts out amplitudes, SUM, for values, H. These in the existing program (which was written for a single use and never put into "polished" form) are scaled by hand to the amplitude of the experimental curve for comparison of line shapes. Different values of r are tried until a fit is obtained.
	• •				
A Millio ar et designi for particulation and o fai i Millio foi	SIRFT	$\boldsymbol{\mathcal{C}}$	rada, bada dalahili da ang udan unaka ng ang ng kana k		······································
	¢10(1	DOUBLET EIT			3
	<u> </u>	DIMENSION C(14)			ī
Malakati wa Munda wa wali ini aka ma wana ma wa maja a shija		COMMON ALPHA,BETA,X	· · · · · · · · · · · · · · · · · · ·		
	21	READ(5,22)(C(I),I=1,14)			,
	22	FORMAT(1X,13A6,A1)			
geig und spinlicht spinlift der fullagte sum fan Brite, bann, f		WRITE(6,22)(C(I),I=1,14)		ander die er offen dage oder bestende zu besten erstende	
		PRINT 10			
	10	FORMAT(1X,34HDOUBLET LINESHAPE FIT ABRAGAM P219)			
•		READ(5,1) ALPHA,BETA			
		DX= 0.0125			
		X = 2.*ALPHA			- Landing and Market - Tability as in a pixely - Apple and pixely
· ,		H=0.			1
		DO 100 I=1,1000			ليت
	Anto ya Gangani kana di kata yanga malangani kana ya	H= H+(40.*DX)		*****	S
· .		IF(H•EQ•ALPHA) H=(40•*DX) + H			, O
	•	SUM = 0.			1
		$D = -3 \cdot * ALPHA$		ulante - mandridade communication and an empire of	•
		DO 90 J = 1,4000			
		D = D + DX	· .		
Ballati, Carrollar - Store Spir Physical Sciences and a california		<u>IF(D.GI.(3.*ALPHA)) GO IO 91</u>			
		I = H - D			
		$IF(D \bullet L(\bullet (-ALPHA))P = FH(D)$			
agge that was added to as as has a special base as		$IF(D \circ GI \circ ALPHA)P=FQ(D)$	The sector sector sector contains to the sector sector sector description of the sector sector of the	n ann an 12 a an Iaddana air an Iadain an 1999	
	0.0				•
	90	CONTINUE			
	71		······································		
	۰ ٦	FORMAT(2E12,8)			
2	2	FORMAT(1X, 2HH=, F12, 8, 10X, 5HF(H)=, F13, 4)			
· · · · · · · · · · · · · · · · · · ·		$IF(H_{\bullet}GT_{\bullet}(3_{\bullet}*BETA)) = GO_{\bullet}TO_{\bullet}TO_{\bullet}$	anna an an a' anna anna a' an anna a' cuire a' cuire an annan an an anna a' anna a' anna a' anna a' a' an		
û -	100	CONTINUE			
- } -	101	CONTINUE			,
-		GO TO 21			
, · · ·		END			5 5 1 1
					1 A A A A A A A A A A A A A A A A A A A
ganta ha saanaan shiiy afashiin a nigaana maana a dhaan	arila nanas mingersifinata patrion		ւրացնուցուները, ազգահետում՝ եւներ միջեւ բետք լենեցներներները, որը արվել ենչին հետորվեն։ Դու		
					õ
\$. <u></u>					

	. · · ·	
\$IBFTC FHD		
FUNCTION FH(D)		
COMMON ALPHA, BETA, X	•	
IF(D.1 T.X)FH=0.		
$IF(D \circ GT \circ X)FH=(-D/AIPHA+1)**(-0.5)$		
RETURN	·	
FND		n (m. ann f ffin fan st i sanstig swittin Afrikansk m
\$IBFTC_SHT		
FUNCTION SH(T)		
COMMON ALPHA, BETA, X	ann <mark>Balling an an Angele Manager ann an an ann an ann an ann an ann ann</mark>	
SH = $EXP(-T*T*0.5/(BETA*BETA))/(BETA*2.505)$		
RETURN		
	нала раки актоловарана каката ви манито пала се одитот, подитот, коа коа и белеволоски, по нако и алек и кака и Вила баки актоловарана каката ви манитот нака се одитот, подитот, коа коа и белеволоски, по нако и алек и кака и	
SIBFTC FLD		
FUNCTION FL(D)		1
COMMON ALPHA, BETA, X		E E
A= D/ALPHA		
FL = (-A+1•)**(-0•5)+(A+1•)**(-0•5)		L
RETURN		
END		
SIBFTC FQD		
FUNCTION FQ(D)		
COMMON ALPHA,BETA,X		
IF(D.GT.X)FQ=0.		
$IF(D \cdot LT \cdot X)FQ = (D+1 \cdot) * * (-0 \cdot 5)$		
RETURN		
END		
\$ENTRY		
	r a , , , , , , , , , , , , , , , , , ,	
		· .
		12 and 1 at 110 at 11 at 11 at 11
	·	

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Program .5. Transformation of Coordinates.

This program generates blocks of unit cells around a cell
[labelled (0, 0, 0)] from which it is desired to compute interactions. It gives the coordinates of all nuclei within the cells.
AI, BI, CI is the designation of the cell from which the
 program starts (not 0, 0, 0. Starting from
 0, 0, 0 would give the cells in only one half
 of the block).
AM, BM, CM is the designation of the cell at which the
 program finishes.
XA, YB, ZC are the unit cell dimensions in angstroms.
XI, YI, ZI are the atomic coordinates of the nuclei
 in the unit cell.
NUC labels the unit cell nuclei if desired.

The punched output X, Y, Z (the A, B, C, and NUC are merely labelling) is used in Program 6 for the theoretical second moment calculation.

•			· · ·		
• •		· · ·			
\$FOR	TRAN				
С	RECTANGULAR COORDINATES				
1	FORMAT(6F5.0)		x		
3	FORMAT(3F8.4)				
. 4	FORMAT(3F10.4,A6)				
. 7	FORMAT(1H0)		,		
50	FORMAT(5X,3F8.4,5X,3F5.0,A6)				y na sa
	READ(5,1) AI, BI, CI, AM, BM, CM				
,	WRITE(6,1) AI, BI, CI, AM, EM, CM				
a 1.4. per 1.6. per	READ(5,3) XA,YB,ZC	peperina ja da Mika Irra antakin kina ata (dalami kina da Kata)	an an ann a bhairda na anns a dh' na shear ann ann ann ann an bhairte a' faith a' fh' airte ann an bhairte ann	,	
	WRITE(6,3) XA,YB,ZC				
8	READ(5,4) XI,YI,ZI,NUC				
	WRITE(6,4) XI,YI,ZI,NUC				
	A = A I				
	B=BI				
	C=CI				i
	GO TO 100				
10	CONTINUE		·		H
	C=C+1.				4
	IF(C.GT.CM) GO TO 11				
	<u>GO TO 100</u>			unanen sem unanen un subjus 1 - a - manima productiona de la service de segue a service - man	I
· 11	CONTINUE				
	C=CI				
	B=B+1.		•		
	IF(B.GT.BM) GO TO 12				
	: GO TO 100				
12	CONTINUE				
	C=CI				
	B=BI			•	
`	A = A + 1 •		•		
•	IF(A.GT.AM) GO.TO 101			· .	
. 100	CONTINUE -				
	X = (XI + A) * XA				
	Y = (YI + B) * YB				
•	Z = (ZI + C) * ZC				
an na manana karana karana kana mana kana karana	WRITE(6,50) X,Y,Z,A,B,C,NUC				
	PUNCH 50, X,Y,Z,A,B,C,NUC				
	GO TO 10			· ·	
101	CONTINUE		19 - 19 19 19 19 19 19 19 19 19 19 19 19 19	gantu u kanada afangana jamananakan kang ad ayanggi - ad bagkan se kan di sebu	-
• •	WRITE(6,7)				
	GO TO 8				
	END				

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Program 6. Theoretical Rigid Lattice Second Moment Calculation.

This program computes the theoretical rigid lattice second moment using the nuclear coordinates (in angstroms) generated by Program 5. It was adapted from W.R. Janzen's original program written for the IBM 1620.

LS = 1, 2. 1 instructs the computer to read in a new set of data cards and do calculations. 2 instructs it to do further calculations with the data.

RMAX = distance in angstroms up to which the sum is carried. FACT = the factor

in equation (2) as is applicable.

NN=DEN = N as in equation (2).

NVAN = count of interactions between nuclei separated by less than the van der Waals radius.

NMB = the count of interactions within the distance RMAX. NI, NM is list of data cards read in.

JI, JM is the list of parameters j in rjk in equation (2).
KI, KM is the list of parameters k in rjk in equation (2).
X(I), Y(I), Z(I) are the nuclear coordinates in angstroms
generated by Program 5.

SM = theoretical rigid lattice second moment.

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	SIBFT C	C THEORETICAL SECOND MOMENT		
	. 55. 74	DIMENSIONX(2000),Y(2000),Z(2000),A(2000),B(2000),C(2000),NUC(2000) FORMAT(1H1,7X,26HTHEORETICAL SECOND MOMENTS,22X,14HPROG 4 WRJ MRB) FORMAT(12,F3,0,F7,2,715,24H		
	75 88 99	FORMAT(I5,I5,F11.8) FORMAT (5X,3F8.4,5X,3F5.0,A6) FORMAT(10HOTHEO SM =,F6.2,8X,I5,14H R LESS THAN ,F4.1,2H A)		
	100 101 104	FORMAT(1H0) FORMAT(24X,15,21H R LESS THAN 2.70 A///) FORMAT (5X,F10.4)		· ·
, educardo indestituted of solar of	80	WRITE(6,55) WRITE(6,100) READ(5,74) LS,RMAX,FACT,NN,NI,NM,JI,JM,KI,KM		
	nangen kan generation of the second secon	RMS = RMAX*RMAX DEN = NN J = O		i 1
		NVAN=0 NMB = 0 SUMR = 0.0	· .	06 •
	1	WRITE (6,74) LS,RMAX,FACT,NN,NI,NM,JI,JM,KI,KM GO TO (1,2),LS DO 10 I = NI,NM		
· .	10 2	READ(5,88) $X(I),Y(I),Z(I),A(I),B(I),C(I),NUC(I)$ DO 30 J = JI,JM DO 30 K = KI,KM		
	15	$IF(K \cdot EQ \cdot J) GO TO 30$ DZ = ABS(Z(K) - Z(J)) $IF(DZ \cdot GE \cdot RMAX) GO TO 30$		2010 (1997) - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -
	16	DY = ABS(Y(K) - Y(J)) IF(DY.GE.RMAX) GO TO 30		· ·
12 10 9	18	$DX = ABS(X(K) - X(D))$ $IF(DX \cdot GE \cdot RMAX) GO TO 30$ $RS = DX*DX + DY*DY + DZ*DZ$ $IE(RS \cdot GE \cdot RMS) GO TO 30$		
0 7 6	40	IF(RS.GE.7.29) GO TO 40 NVAN=NVAN+1 CONTINUE		
5 4	20	SUMR = SUMR + 1./(RS*RS*RS) NMB = NMB + 1	and the processing the conserve of	
الد. 	<u> </u>	CONTINUE		



Program 7. Activation Energies.

This program is Smith's (79) program for the calculation of activation energies from line widths in nmr transition regions. It is listed here as adapted for the IBM 7040 by Dr. Raghunathan. It is, as noted, written for line widths as in equation (7). However it can be used without modification for second moments as in equation (8) provided $(SM)^{\frac{1}{2}}$ and SM are used instead of AH and AH².

,					{
	\$15F	TC MOD BPP			
	C	IF YOU DO ALL THESE CALCULATIONS BY HAND AND PLOT THEM IT IS EASTER TO			
	C	SEE WHAT IS GOING ON.			
	С	MODIFIED BPP LINE NARROWING ANALYSIS			
	C	DIFFERS FROM ORIGINAL CASE BY INCLUSION OF TERM AG IN NUMERATOR OF			(j
	<u>`C</u>	BPP EQN PHYS REV 1948 VOL73 P679.FOR PROTONS AG=767.5			!
	С	THIS PROGRAM USES THE MODIFIED BPP EQN TO DERIVE THE CORRELATION			2
	C ·	FREQUENCY, MAKES A LEAST SQUARES FIT OF LN(COR.FRQ) TO A ST.LINE			ر
	C	WHEN PLOTTED VS.1/RT, DERIVES THE ACTIVATION ENERGY AND INF.TEMP.			
,	C	CORREL'.FREQ.FROM THE FIT.PROGRAM THEN REVERSES THE PROCESS TO GIVE			
	С	THEORETICAL FIT TO THE LINEWIDTH VS.TEMP.DATA PLOT.			
	٢C	DEFINITIONS-INPUT			
	C j	ALPHA=DATA COMMENTS E.G. NAME OF COMPOUND,DATE.			
	С.	TEMP• IN DEG•KELVIN•,DELTAH=LINEWIDTH(GAUSS) IN NARROWING REGIO5			
	C	(LESS THAN C, GREATER THAN B).C= AVG.LINEWIDTH BELOW TRANSITION.			****
	С	B=AVG.LINEWIDTH ABOVE TRANSITION. AG=PARAMETER DEPENDENT ON NUCLR	•	t.	•
	Ċ	SPECIES,=767.6 FOR H. DELMIN= MIN LINEWIDTH IN REGION OF THEORETIC			
	С	FIT, GREATER THAN B.DELMAX=MAX LINEWIDTH IN REGION OF THEORETICFIT,			
	С	LESS THAN C. DELINC= LINEWIDTH INCREMENT FOR THEORY FIT.N=NO. OF		0	
	С	DATA POINTS.			
	C	CALCULATED QUANTITIES- OUTPUT		I	
	С	CORFRQ= DERIVED CORREL. FREQ. RECIPT=1/TEMP. XLNFRQ=LN OF CORFRQ.			
	С	RCPRT =1/(R*TEMP), WHERE R= 1.9869 CAL/DEG-MOLE.			
	чC	EACT = ACTIVATION ENERGY(CAL/MOLE), EREACT= ERROR IN SAME, FRQMAX =			
,	С	INF.TEMP. CORREL.FREQ. IN THEOR.FIT. ERFRQ=ITS ERROR.THDEL= LINE-			
	С	WIDTH IN THEOR.FIT. THTEMP= TEMP.IN THEOR.FIT. THFRQ= CORREL.FREQ			
	. C	IN THEOR. FIT.			
1999 14 1999 14 1999 14 1999 14 1999 14 1999 14 1999 14 1999 14 1999 14 1999 14 1999 14 1999 14 1999 14 1999 14	marjana iy kalaitan yan ya kiyolog'yiy a din	DIMENSION TEMP(500), DELTAH(500), CORFRQ(500), RECIPT(500),			
		1XLNFRQ(500),XSIN(500),XCOS(500),XTAN(500),RCPRT(500),ALPHA(12),			
		2THERQ(500),THTEMP(500),THDEL(500),THSN(500),THCO(500),THTAN(500)			
		PRINT 10			
	10	FORMAT(1X,49HNMR LINEWIDTH DATA TREATED ACCORDING TO G.W.SMITH)	*		
	ī 5	READ (5,20) (ALPHA(I), I=1,12)			<u>,</u>
	20	FORMAT (12A6)			
		WRITE (6,30)(ALPHA(I),I=1,12)			
	30	FORMAT (1X,12A6)			
	35	READ (5,40)N,C,B,AG			,
	40	FORMAT (15,3F15.5)			- 11 11 11
		READ (5,50)(TEMP(I),DELTAH(I),I=1,N)		· ·	21.7
a ngaging na ang pang pang pang pang pang pang	50	FORMAT (6F12.5)			2
		DO 60 I=1,N			ô
		XSIN(I)=SIN(1.5707*(DELTAH(I)**2-B**2)/(C**2-B**2))			.,

•				÷		۹. ۲ (
,	a a na an	XCOS(I) = COS(1.5707*(DELTAH(I)**2-B**2)/(C**2-B**2))				
· ·		XTAN(I) = XSIN(I) / XCOS(I)				í
•		CORFRQ(I)=AG*DELTAH(I)/XTAN(I)				ş
		XLNFRQ(I)=ALOG(CORFRQ(I))				
		RECIPT(I)= 1./TEMP(I)		•		(
		RCPRT(I)=1./(1.9869*TEMP(I))				_ !
	60	CONTINUE				7
	65	WRITE(6,70)N,C,B,AG				
	70	FORMAT(1H0,5X,2HN=,15,5X,25HRIGID LATTICE LINEWIDTH =,F10.5,5X,20H				
	•	INARROWED LINEWIDTH =,F10.5,5X,4HAG =,F15.5)				6
		PRINT 80				
ngg hang ay in Spirit to the All Science and	8.0	FORMAT (1H0,1X,16HTEMP(DEG KELVIN),4X,16HLINEWIDTH(GAUSS),4X,				
		114HCOR.FREQ.(CPS),10X,6H1/TEMP,10X,13HLN(COR.FREQ.),11X,4H1/RT)				
1 - A		WRITE(6,90)(TEMP(I),DELTAH(I),CORFRQ(I),RECIPT(I),XLNFRQ(I),				
ganda (tarda 1) or J -tarday (-tarday a)	adjastijaši urtedrova – referejovejsko filosofija	1RCPRT(I), I=1, N)	*****			
	90	FORMAT(1H ,2X,F12.5,8X,F12.5,7X,E14.6,9X,F10.7,9X,F12.7,9X,F10.7)	•		i	
		SUMX = 0.0				
		SUMY = 0.0				
		DO 200 J=1,N			ю	
		SUMX = SUMX+ RCPRT(J)				
		SUMY = SUMY + XLNFRQ(J)				
	200	CONTINUE				
		CALL LSQFITTN,RCPRT,XLNFRQ,SUMX,SUMY,Q,P,STDERQ,STDERP,XAV,				
		$\frac{114V}{100}$				
		FROMAX - EXPLOY				
•		ERFRU = EAPTUT * STDERU				
		$\frac{1}{1} = \frac{1}{1} + \frac{1}{1} + \frac{1}{2} = \frac{1}{2} + \frac{1}$				
		WRITE (6.210)EROMAX.ERERO.EACT.EREACT				
	210	$FORMAT (1H0.25HCOR, FRQ, AT INF, TEMP, = F12.5.2X_7HERROR = F12.5.$				
i;	<u> </u>	15X, $12HACTIV$, EN, =, F12, 5, 7HCAL/MOL, $2X$, 7HFRROR =, E12, 5, 7HCAL/MOL)				
	,	READ (5,220) DELMAX, DELMIN, DELINC				
2	220	FORMAT(3F10.5)				
1		NOINC= (DELMAX - DELMIN)/DELINC +0.001			<	
0		NSW = NOINC+1				
i .		DO 230 K= 1,NSW				
}		AK = K				<u> </u>
7	• •	THDEL(K)=DELMIN+(AK-1.)*DELINC	1			1
	•	CB = C**2 - B**2				3
5	nagyaganan dan kanan ang mbangga panagbangan nagi	THSN(K)=SIN(1.5707*(THDEL(K)**2-B**2)/CB)				NIA.
1		THCO(K)=COS(1.5707*(THDEL(K)**2-B**2)/CB)				ō
3		THTAN(K)=THSN(K)/THCO(K)				ر ني

· ·		
4 2014 m. Canar and . Communication fights. 2017 (Const. Const. Co	THFRQ(K)=(AG*THDEL(K))/THTAN(K)	
	THTEMP(K)=EACT/(1.9869*ALOG(FRQMAX/THFRQ(K)))	
230	CONTINUE	
NEAR THE PARTY OF	PRINT 240	1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1
240	FORMAT(1H0,34X,47HTHEORETICAL MODIFIED BPP LEAST SQUARES DATA FIT)	
	PRINT 250	· ·
- 250	FORMAT(1H0,6X,28HTEMPERATURE (DEGREES KELVIN),17X,18HLINE WIDTH(GA	
-	1USS),17X,27HCORRELATION FREQUENCY (CPS))	
	WRITE(6,260)(THTEMP(K),THDEL(K),THERQ(K),K=1,NSW)	
260	FORMAT(1H +14X+F11+5+30X+F10+5+28X+F14+6)	anna ghair ann a tha in iomrain ann ann an ang an thirt ainm
200	60 TO 15	
SIBET		
01011	SUBROUTINE ISQEIT(N•X•Y•SUMX•SUMY•B•C•STDERB•STDERC•XAV•YAV•NOGO)	
	DIMENSION X(500) Y(500)	
ann an an Sann Malaisteach a' Sann an Ann an Annaisteach ann	$IF(N-2) = 1050 \cdot 1050 \cdot 1000$	
1000		1
.2000	X = X = X	I'
-	V = S = M	
· .	DIEXX=0	
		t
gadets partpa-it lay by hay no year tarr a ny phononyper ny ay	D = 1 + 1	······································
	DIEXY - DIEXY $\pm (X(I) = X(V) + X(V) + X(I)$	
	DIFXT = DIFXT + (X(0) = XAV) * (0)	
1010	CONTINUE	Name and the task of the second carrier and the second second second second second second second second second
1010		
an factoria at ange as at ang it card-assauly dae bare		1
	DC = DC +	
	$V_{0} = V_{0} + V_{0$	
	XSU = XSU + X(J) * * 2	
1020		
	$O = SOR \left\{ \left(D SO \right) \left(A N - 2 \right) \right\}$	
	$U = A N \pi X S U = (A N \pi X A V) \pi \pi Z$	
2.000		
T030	WUVKID= W/SWRI(DEE)	, a
	$SIDERC = QUVRID \otimes SQRI(AN)$	
radire ballentites beaters from tweever for agree addeeds and	SIDERB= QOVRID*SQRI(XSQ)	
	NUGU = 1	
	PRINT 1040	· .
1040	FORMAI(1H •52HNOGO = 1• THEREFORE LSQFIT HAS MADE A SUCCESSFUL FIT	-

10 CT 100 CT	1050	1) GO TO I NOGO =	1100												
	1060	FORMATI IR = 0,	1060 (1H, 8 OR T(84HNOC O N LE	50 = 2 : SS THA	LSQFI	T UNSUC	CESSFUL	DUE T	O DEE	LESS T	HAN	0		
	1100 \$ENTR	RETURN END Y										,			
			• .												
ануулан тайтай тайта	na the curve and in reflective constraints	1100-000-000-000-000-000-000-000-000-00			and the second secon					/2 m - 7 + 1994 tanas, con 4 m - 9 a - 9 a - 9 a - 9 a - 9 a - 9 a - 9 a - 9 a - 9 a - 9 a - 9 a - 9 a - 9 a -					1
	· .							9,0 <u>01</u> , 01, 01, 02, 00, 03, 04							يد ۱
	анаралан алын алын анаралан алын алын алын алын алын алын алын	νι ταπατικά ματό το τους το τους το τους το τους το τους τους	er til Men för Frankrikkelskalande av de		an an fa fan de fan de generate an	чл тур на чила на сел так		, and a second	anna - an is lof fig and		riters and any gave serving interest disaptime in 1994				
			-												
unti otzani perse de secondorizadore				· .											
			•												
			, and a second secon											•	
,	1,			a ga ina ga dalama ya kata ya ma da kata na i	an a							4. 41 H H H H H H H H H H H H H H H H H H		 	



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References

(1)	N. Bartlett & P.L. Robinson, Chemistry & Industry, 1351 (1956).
(2)	N. Bartlett & P.L. Robinson, Proc. Chem. Soc. (London), 230 (1957).
(3)	F. Seel & O. Detmer, Angew. Chemie, <u>70</u> , 163 (1958).
(4)	F. Seel & O. Detmer, Angew. Chemie, <u>70</u> , 470 (1958).
(5)	F. Seel & D. Detmer, Z. Anorg. Allgem. Chem., <u>301</u> , 113 (1959).
(6)	N. Bartlett & P.L. Robinson, J. Chem. Soc., 3417 (1961).
(7)	L. Kolditz, D. Weisz, & U. Calov, Z. Anorg. Allgem. Chem., <u>316</u> , 261 (1962).
(8)	L. Kolditz, & E. Roesel, Z. Anorg. Allgem. Chem., <u>341</u> , 88 (1965).
(9)	L. Kolditz & W. Rehak, Z. Anorg. Allgem. Chem., <u>342</u> , 32 (1966).
(10)	S.P. Beaton, Ph.D. Thesis, University of British Columbia, Sept. 1966.
(11)	F.N. Tebbe & E.L. Muetterties, Inorg. Chem., <u>6</u> , 129 (1967).
(12)	A.R. Young, II, & D. May, Inorg. Chem., <u>6</u> , 178 (1967).
(13)	H, Braune & P. Pinnow, Z. fur Physik Chemie <u>35-36</u> , 239 (1937).
(14)	J. Bigeleisen, M.G. Mayer, P.C. Stevenson, & J. Turkevich, J. Chem. Phys., <u>16</u> , 442 (1948).
(15)	S.H. Bauer, J. Chem. Phys. <u>18</u> , 27 (1950).
(16)	K.N. Tanner & A.B.F. Duncan, J. Am. Chem. Soc., <u>73</u> , 1164 (1951).
(17)	T.G. Burke, D.F. Smith, & A.H. Nielsen, J. Chem., Phys., <u>20</u> , 447 (1952).
(18)	J. Gaunt, Trans. Farad. Soc., <u>49</u> , 1122 (1953).
(19)	J. Gaunt, Trans. Farad. Soc., <u>50</u> , 546 (1954).
(20)	B. Weinstock & J.G. Malm, J. Am. Chem. Soc., <u>80</u> , 4466 (1958).
(21)	B. Weinstock & J.G. Malm, "Some Recent Studies with Hexafluorides", <u>Proceedings of the Second U.N. Int. Conf. on the Peaceful</u> Uses of Atomic Energy, 28, Geneva, 1958.

22)	C.W.F.T. Pistorius, J. Chem. Phys., <u>29</u> , 1328 (1958).
23)	J.W. Linnett, C.J.S.M. Simpson, Trans. Farad. Soc., <u>55</u> , 587 (1959).
24)	H.H. Claassen, J. Chem. Phys., <u>30</u> , 968 (1959).
25)	8. Weinstock & H.H. Claassen, J. Chem. Phys., <u>31</u> , 262 (1959).
26)	G.H. Cady & G.B. Hargreaves, J. Chem. Soc., 1563 (1961).
27)	E. Meisingseth & S.J. Cyvin, Acta Chem. Scand, <u>16</u> , 2452 (1962).
28)	B. Weinstock, E.F. Westrum, & G.L. Goodman, "Heat Capacities & Electronic Spectra of the Platinum - Metal Hexafluorides Down to He Temperature", <u>Proceedings of the Eighth Int</u> . <u>Conf. on Low Temp. Physics</u> , London, 1963, p. 405.
29)	L.S. Bartell, R.M. Gavin, Jr., H.B. Thompson, & C.L. Chernick, J. Chem. Phys., <u>43</u> , 2547 (1965).
30)	B. Weinstock & G.L. Goodman "Vibrational Properties of Hexa- fluoride Molecules", I. Prigogine, ed., <u>Advances in</u> <u>Chemical Physics</u> , vol. 9, London, Interscience Pub., 1965, p. 169-319.
31)	B. Weinstock & R.H. Crist, J. Chem. Phys., <u>16</u> , 436 (1948).
32)	F.G. Brickwedde, H.J. Hoge, & R.B. Scott, J. Chem. Phys., <u>16</u> , 429 (1948).
33)	S. Sundaram, Z. fur Physik. Chemie Neue Folge, <u>34</u> , 225 (1962).
34)	P.A.G. O'Hare & W.N. Hubbard, J. Phys. Chem., <u>70</u> , 3353 (1966).
35)	N. Bartlett, S.P. Beaton, N.K. Jha, Chem. Commun., 168 (1966).
361	The Heard & T.D. Stroups "The Structure of Crystalling

(

- (36) J.L. Hoard & J.D. Stroupe, "The Structure of Crystalline Uranium Hexafluoride", J.J. Katz & E. Rabinowitch, eds., <u>Chemistry of Uranium</u>, vol. 1 Oakridge, Tenn., United States Atomic Energy Commission Technical Information Service Extension, 1958, p. 325.
- (37a) B. Weinstock, Rec. Chem. Progress, 23, 34 (1962).
- (37b) N. Bartlett (private communication from S. Siegel)
- (38) R. Blinc, V. Marinkovic, E. Pirkmajer, I. Zupancic, & S. Maricic, J. Chem. Phys., <u>38</u>, 2474 (1963).

123. -

- (39) P. Rigny, Ph.D. Thesis, University of Paris, April, 1965.
- (40) R. Blinc, E. Pirkmajer, I. Zupancic, & P. Rigny, J. Chem. Phys., <u>43</u>, 3417 (1965).
- (41) R. Blinc, E. Pirkmajer, J. Slivnik, I. Zupancic, J. Chem. Phys., <u>45</u>, 1488 (1966).
- (42) P. Rigny & A. Demortier, Comptes, Rend. Sc. Paris, <u>263</u>, 1408 (1966).
- (43) E.M. Purcell, H.C. Torrey, & R.V. Pound, Phys. Rev., <u>69</u>, 37 (1946).
- (44) F. Bloch, W.W. Hansen, & N.E. Packard, Phys. Rev., <u>69</u>, 127 (1946).
- (45) N. Bloembergen, E.M. Purcell, & R.V. Pound, Phys. Rev., <u>73</u>, 679 (1948).
- (46) J.A.S. Smith, "Nuclear Magnetic Resonance Absorption", <u>Quarterly Reviews</u>, vol. VII, London, The Chemical Society, 1953, p. 279.
- (47) H.S. Gutowsky, "Nuclear Magnetic Resonance", G.K. Rollefson, ed., <u>Annual Review of Physical Chemistry</u>, vol. 5, Stanford, Annual Reviews, Inc., 1954.
- (48) H.S. Gutowsky, "Analytical Applications of Nuclear Magnetic Resonance", W.G. Berl, ed., <u>Physical Methods in Chemical</u> <u>Analysis</u>, vol. 3, New York, Academic Press, Inc., 1956.
- (49) G.E. Pake, "Nuclear Magnetic Resonance", F. Seitz & D. Turnbull, eds., <u>Solid State Physics</u>, vol. 2, New York, Academic Press, Inc., 1956, p. 1.
- (50) N. Bloembergen, Nuclear Magnetic Relaxation, D. Pines, ed., <u>Frontiers in Physics</u>, New York, W.A. Benjamin, Inc., 1961.
- (51) E.R. Andrew, Nuclear Magnetic Resonance, N. Feather & D. Shoenberg, eds., <u>Cambridge Monographs on Physics</u>, Cambridge U.P., 1958.
- (52) A. Abragam, <u>The Principles of Nuclear Magnetism</u>, N.F. Mott, & E.C. Bullard, & D.H. Wilkonson, eds., <u>The International</u> <u>Series of Monographs on Physics</u>, Oxford, Clarendon Press, 1952.

124 -

(53)	C.P. Slichter, <u>Principles of Magnetic Resonance</u> , F. Seitz, ed., <u>Harper's Physics Series</u> , New York, Harper & Row, 1963.
(54)	G.E. Pake, J. Chem. Phys., 16, 327 (1948).
(55)	J.H. Van Vleck, Phys. Rev. <u>74</u> , 1168
(56)	H.S. Gutowsky, G.E. Pake, & R. Bersohn, J. Chem. Phys., <u>22</u> , 643 (1954).
(57)	H.S. Gutowsky & G.E. Pake, J. Chem. Phys., <u>18</u> , 162 (1950).
(.58)	E.R. Andrew & R.G. Eades, Proc. Roy. Soc. A, <u>216</u> , 398 (1953).
(59)	D.J. Kroon, Philips Res. Rept., <u>15</u> , 501 (1960).
(60)	D.W. McCall & D.C. Douglas, J. Chem. Phys., <u>33</u> , 777 (1960).
(61)	L.V. Dmitrieva and V.V. Moskalev, Sov. Phys Solid State, <u>5</u> , 1623 (1954).
(62)	V.V. Moskalev, Sov. Phys Solid State, <u>3</u> , 2218 (1962).
(63)	G.R. Miller and H.S. Gutowsky, J. Chem. Phys., <u>39</u> , 1983 (1963).
(64a)	G.W. Smith, J. Chem. Phys., <u>36</u> , 3081 (1962).
(64b)	G.W. Smith, J. Chem. Phys., <u>42</u> , 4229 (1965).
(65)	J.G. Powles, Proc. Phys. Soc. (London), B69,281 (1956).
(66)	J.G. Powles & H.S. Gutowsky, J. Chem. Phys., <u>23</u> , 1692 (1955).
(67)	N.F. Ramsey, Phys. Rev., <u>77</u> , 567 (1950); <u>78</u> , 699 (1950).
(68)	J.A. Pople, W.G. Schneider, & H.J. Bernstein, <u>High-resolution</u> <u>Nuclear Magnetic Resonance</u> , McGraw-Hill Series in Advanced Chemistry, Toronto,
(69)	W. Lamb, Phys. Rev., <u>6</u> , 817 (1941).
(70)	A. Saika & C.P. Slichter, J. Chem. Phys., 22, 26 (1954).
(71)	E.R. Andrew & D.P. Tunstall, Proc. Phys. Soc., <u>81</u> , 986 (1963).
(72)	N. Bloembergen & T.J. Rowland, Acta. Metallurgica, <u>1</u> , 731 (1953).
(73)	D.G. Hughes & D.K.C. MacDonald, Proc. Phys. Soc., <u>78</u> , 75 (1961).

۰.

125 -

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- (74) W.I. Orr, ed., <u>The Radio Handbook</u>, 16th ed., New Augusta, Indiana, Editors & Engineers, Ltd., 162, p. 316.
- (75) D.R. Ware, M. Sc. Thesis, University of British Columbia, July, 1964.
- (76) W.R. Janzen, M. Sc. Thesis, University of British Columbia, Sept., 1963.
- (77) B. Weinstock, J. Phys. Chem. Solids, <u>18</u>, 86 (1961).
- (76) J. Timmermans, J. Phys. Chem. Solids, <u>18</u>, 1 (1961).
- (79) G.W. Smith, "Some Computer Programs for Calculation of Nuclear Magnetic Resonance Parameters", General Motors Research Publication, GMR-540, Research Laboratories, Warren, Michigan, 1966.
- (79a) C.R. Eaton, B. Sc. Thesis, University of British Columbia, May, 1966.
- (80) K.O. Christe, J.P. Guertin, A.E. Pavlath, & W. Sawodny, J. Inorg. Chem., <u>6</u>, 533 (1967).
- (B1) R.F. Copeland, S.H. Conner, & E.A. Meyers, J. Phys. Chem., <u>70</u>, 1288 (1966).
- (82) J. Trotter, U.B.C., private communication.
- (83) "Interatomic Distances", Special Publication No.11, The Chemical Society (London), 1958; Supplement, Special Publication No. 18, 1965.
- (84) T.P. Das, J. Chem. Phys., 27, 763 (1957).
- (85) A.L. Oppegard, W.C. Smith, E.L. Muetterties, & V.A. Engelhardt, J. Am. Chem. Soc., 82, 3835 (1960).
- (86) A. Fratiello & D.C. Douglass, J. Chem. Phys., 41, 974 (1964).
- (87) R.J. Gillespie & R.S. Nyholm, "Inorganic Stereochemistry", Quarterly Reviews, vol. XI, London, The Chemical Society, 1957, p. 339.
- (88) M. Karplus & T.P. Das, J. Chem. Phys., <u>34</u>, 1683, 1961.
- (89) E.R. Andrew, Phys. Rev., 91, 425 (1953).