EXPERIMENTAL SOLID STATE NMR OF GAS HYDRATES: PROBLEMS AND SOLUTIONS

Igor Moudrakovski*
Hailong Lu
John Ripmeester
The Steacie Institute for Molecular Sciences
National Research Council of Canada
100 Sussex Drive
Ottawa, Ontario, K1A OR6
CANADA

Rajnish Kumar
Robin Susilo
Department of Chemical and Biological Engineering,
University of British Columbia,
Vancouver, BC, V6T 1Z3
CANADA

Manja Luzi
GeoForschungsZentrum Potsdam (GFZ),
Telegrafenberg, 14473 Potsdam,
Germany

ABSTRACT

Solid State NMR spectroscopy has taken a very prominent place among the many spectroscopic techniques employed for the characterization of clathrate hydrates. Exceptionally high sensitivity of the spectra to the molecular environment and dynamic processes, together with the ability to provide accurate and quantitative data make NMR spectroscopy a highly desirable and versatile approach for studying hydrates. Application of the method to its full capacity, however, requires some extensive instrumental developments to adapt it to the specific experimental requirements of hydrate studies, for example, very low temperatures and high pressures.

In this presentation we will give an overview of recent Solid State NMR advances in various areas of hydrate research. Examples will include analysis of the composition and structure of mixed gas hydrates prepared from multi-component mixtures of hydrocarbons, characterization of the natural gas hydrates from different sources, and evaluation of formation conditions and properties of mixed hydrogen hydrates. ^{13}C NMR with Magic Angle Spinning (MAS) at -100C has been the main approach in the first two examples. We will discuss the requirements and the necessary instrumental developments to make the experiments of this type successful. The detailed characterization of mixed hydrogen hydrates required low temperature ^1H MAS. Problems of quantification in these experiments will be discussed. We expect that all these recent experimental developments will prompt wider application of Solid State NMR in hydrate research.

Keywords: Solid State NMR, gas hydrates, structure, cage occupancy, composition

---
* Corresponding author: Phone: +1 613 993 5638 Fax +1 613 990 1555 E-mail: igor.moudrakovski@nrc-cnrc.gc.ca

NOMENCLATURE

BD Bloch Decay
CP Cross Polarization
CS Chemical Shift [ppm]
CSA Chemical Shift Anisotropy
HPDEC High Power Proton Decoupling
I intensity of a signal
I_0 total intensity of a signal
M nuclear magnetization
M_0 nuclear magnetization in equilibrium
MAS Magic Angle Spinning
NMR Nuclear Magnetic Resonance
ppm part per million
PXRD powder X-ray diffraction
RF Radio Frequency [Hz]
THF tetrahydrofurane
TBME t-butylmethylether
t time [s]
T_1 spin-lattice relaxation time [s]
$T_{1\rho}$ spin-lattice relaxation time in rotating frame [s]
T_{CH} cross-polarization time [s]
T_2 spin-spin relaxation time [s]
τ mixing time in CP experiment [s]

INTRODUCTION

Solid state NMR is a well established spectroscopic technique with numerous applications in different areas of material sciences. The very high sensitivity of NMR to the local environment, the capability to distinguish between different structural types of hydrates, its quantitative nature, and potential for both in-situ and time resolved experiments, make it a very appropriate technique for hydrate research. The applicability of solid state ^{13}C NMR to hydrates was demonstrated some 20 years ago [1], but due to experimental difficulties the method has been used rather sparsely.

The main challenges of NMR in gas hydrate research stem from the instability of the materials at ambient conditions. The experiments may need to be performed at a very low temperature (down to 77K) with cold loading of the samples, and fast - 2 to 5 kHz – magic angle spinning (MAS [2,3,4]) of the samples, or/and at high pressure, as may be required by *in-situ* and time resolved experiments. The total number of publications with the use of high resolution solid state NMR in hydrate research remains relatively small and still in the low tens [4-29]. Most of the publications come from just four or five research group throughout the world. One may note, however, that in recent years the number of NMR studies of hydrates has been growing steadily. The studies have also become noticeably more complex [4, 7, 8, 10, 12, 15, 29].

Although the application of high resolution solid state NMR to gas hydrates has some very distinct experimental features, nothing has been published specifically on solid state NMR experimental details relevant to hydrate studies. The main purpose of this work is to illustrate the applications of solid state NMR for compositional and structural studies of hydrates with emphasis on experimental techniques and possible ways of overcoming the technical difficulties. First the quantification in the ^{13}C spectra of hydrates will be discussed with examples from natural and synthetic gas hydrates. The problems of the signal assignments and quantification in gas hydrates of different structural types (Structure II and Structure H) will be exemplified on a number of mixed hydrates. Along the way we will discuss the effects of dynamics on quantification in C-13 spectra. Experimental difficulties of ^{1}H NMR and in-situ studies will be considered in relation to mixed H_2/CO_2 hydrates.

EXPERIMENTAL CONSIDERATIONS

Traditionally this part of the publication reports only experimental details relevant to a particular study. In this work we would like to use this space for discussion of general experimental requirements and the choice of an NMR instrument and probes. The first and most obvious characteristic of the NMR instrument is its operational magnetic field. Solid state NMR instruments can come in a rather broad range of magnetic fields, most commonly between 4.7 and 14 T (Larmor frequencies for protons 200 and 600 MHz, respectively). The selection of the magnetic field can be very important for a successful experiment.

The sensitivity, signal separation and chemical shift anisotropy (CSA) all strongly depend on the strength of magnetic field (sensitivity $\sim B_0^{7/4}$, separation and anisotropy scale linearly with the

field). All three parameters increase with field, but the increased anisotropy will require higher MAS speed to achieve complete averaging [2,3]. In some situations with large anisotropies (i.e. CO_2 or CO) that could be a limitation. An incomplete averaging of the CSA results in a splitting of the signal into a comb of spinning sidebands [3], which effectively reduces the signal intensity and complicates the analysis. Due to increased spread of the proton frequencies, the higher magnetic fields will also require an increase in proton decoupling power. Application of a composite pulse decoupling scheme (i.e. TPPM [30]) is highly recommended and can be realized easily on any modern instrument.

The most important requirement for the NMR probes is the capability of cold loading. The probe is generally expected to have a broad operating temperature range, usually between 163 and 293K, for at least several hours. In most experiments with gas hydrates, cold loading of the sample and MAS at low temperatures is required to prevent decomposition. Cold loading and the requirement for low temperatures favor instruments with wide bore NMR magnets (diameter of the probe is over 60 mm). Since the best resolution and sensitivity can be achieved only with proton decoupling, the probes are normally expected to be double resonance. Not all probes are well suited, and some are better than others. In our opinion the probes with the top loading of a spinner (Bruker) are particularly well suited for work with hydrates since they can don't need to be removed from the magnet to insert the samples. This reduces the time of sample exposure to room temperature during its transfer to the probe. To prevent accumulation of ice inside the probe during experiments, the use of dry nitrogen gas is necessary both for the spinning and cooling of the samples.

To ensure preservation of the samples, the hydrates are commonly packed into the MAS spinners in liquid nitrogen and then heated to the required temperature inside the probe. A development of specialized tools to simplify the packing may be necessary. Instead of plastic caps that are normally used in MAS experiments (to drive the spinner) the use of ceramic caps is highly recommended due to a reduced shrinkage at low temperature and better spinning stability.

Generally *in-situ* and kinetic NMR experiments on gas-hydrate formation can not be performed on a spinning sample since pressurization of the sample and a continuous gas supply are required. In isolated cases, particularly in studies of the decomposition of hydrates, the use of sealed samples may prove to be very useful [8]. One needs to keep in mind, however, that an explosion of a sealed glass container can lead to a severe damage of the probe and costly repairs.

Due to the very high concentration of carbon-containing substances in gas hydrates, it is expected that ^{13}C NMR should be quite feasible even for materials with natural abundance of the ^{13}C isotope (1.1%). In some situations, especially for in-situ studies and kinetic measurements, it is desirable to use ^{13}C enriched materials. Most of the simple hydrate forming gases (CH_4, C_2H_6, C_2H_4, CO, CO_2, C_2H_4) are inexpensive and easily obtainable in C-13 enriched form, when more complicated molecules are needed, this may require a special order.

In our work we use a Bruker DSX-400 instrument (magnetic field of 9.4T, wide bore magnet). All MAS experiments are performed on a Bruker BL7 triple resonance probe (7 mm OD spinners). Spinning speed and the temperature inside the probe are controlled using standard Bruker equipment.

Tetramethylsilane (TMS) is an accepted reference both in ^{1}H and ^{13}C NMR (0 ppm). In practice the signals of adamantane (29.51 and 38.56 ppm) and glycine (43.72 and 176.52 ppm) are often used as secondary standards.

During processing of the experimental data it is often desirable to do some sort of fitting, deconvolution or simulation of the experimental spectra. Standard processing software from the instrument vendors often provides some tools for integration or deconvolution of the spectra. In many situations a more specialized NMR simulation or processing software may be required. In our work we use DMFit [31], WinSolids [32] and the NMRTools [33] add-on package for Origin® plotting software.

EXPERIMENTAL RESULTS AND DISCUSSION

^{13}C MAS NMR in compositional and structural studies of gas hydrates. Using a set of examples from our laboratory practice we will discuss the variety of experimental situations arising in studies of gas hydrates by solid state NMR.

The most common and straightforward application of NMR to gas hydrates is for structural and compositional identification (structural type of hydrate, cage occupancies / hydration number). Structural assignment is usually done based of the position of the ^{13}C signals observed in experimental spectra and compared to those in the samples with known structure. ^{13}C chemical shift of methane in the 5^{12} cages of Str.I, Str.II and Str. H hydrates are usually found between -4.1 and -4.5 ppm, when the CH$_4$ in $4^3 5^6 6^3$ medium cage of Str.H produces a signal at -4.7 to -4.9 ppm . Such a small range of the shifts requires rather good spectral resolution, but in most situations the signals can be separated reasonably well. Chemical shifts of methane in the large $5^{12} 6^2$ and $5^{12} 6^4$ cages of Str.I and Str.II are better separated at -6.5 to -6.7 and -8.1 to -8.2 ppm, respectively.

As was already mentioned, NMR offers a possibility to perform quantitative measurements of hydrate composition. Two spectroscopic techniques are commonly used for acquiring the ^{13}C MAS spectra: direct excitation and Cross-Polarization (CP). The first method consists in excitation of the nuclei by applying a short radiofrequency (RF) pulse on their Larmor frequency (most often it is ^{13}C, but can be any other nucleus), followed by a detection of the free induction decay accompanied by simultaneous irradiation at the proton frequency to remove (decouple) the line broadening interaction with protons. The detection scheme is commonly called Bloch Decay (BD) or Single Pulse (SP).

The restoration of nuclear magnetization after the RF pulse is an exponential process with the rate defined by the spin-lattice relaxation time T_1:

$$I = I_0 \cdot \exp[\, -t / T_1\,] \qquad (1)$$

The BD signal is linearly proportional to the number of nuclei in the probe's coil only if the time between consecutive accumulations is long comparing to the spin-lattice relaxation time of the

detected nucleus. If several sites are present, the acquisition delay for quantitative measurements has to be at least $3*T_1$ for the site with the longest T_1. Since the values of the ^{13}C T_1's are often between several seconds and some tens of seconds, the time required for a good quality quantitative ^{13}C HPDEC MAS spectrum can be between just 30 minutes and 5-6 hours.

A few examples of quantitative ^{13}C {^{1}H} HPDEC MAS spectra of synthetic and natural gas hydrates are shown on Figure1. The signals from methane in small and large cages are very well separated and one can easily see that only Str. I hydrate is present in all the samples.
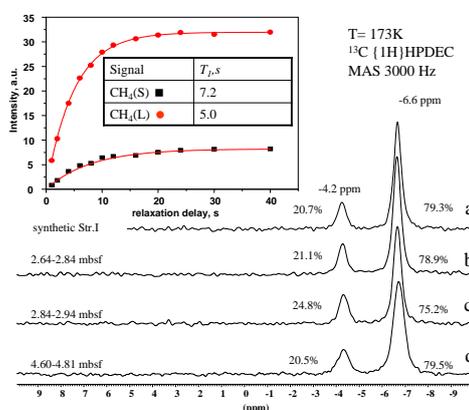

Figure 1. ^{13}C {^{1}H} DEC MAS of synthetic Str.I methane hydrate (a) and natural gas hydrates from Cascadia range (b-d). The inset shows experimental saturation-recovery curves for ^{13}C of methane in small and large cages and the T_1's evaluated with Equation 1.

Integration of the signals gives the relative occupancies of the small and large cages and provides the means of calculating the hydration numbers. From NMR and Raman measurements the hydration numbers were estimated to be on average 6.1 ± 0.2. Differences in methane content and lattice parameters for synthetic and natural samples are relatively minor. The fact that only Str.I is observed could be an indication on biogenic nature of the methane gas present in these samples of natural hydrates.

A more complicated case of ^{13}C HPDEC MAS in natural gas hydrate from Barkley Canyon, Northern Cascadia Margin is shown on Figure 2. The complete assignment of the signals is given in

the figure caption, and it illustrates the systematics of encagement on the ^{13}C NMR chemical shifts of hydrocarbon guests.
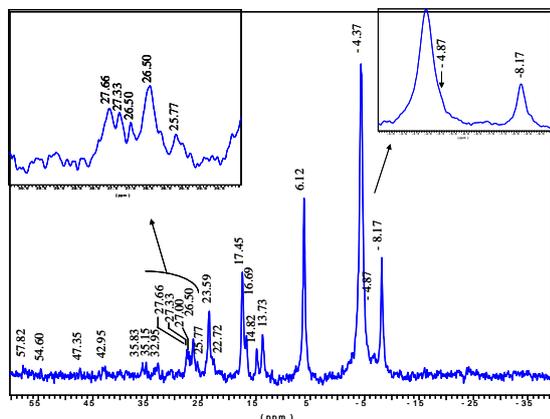
Figure 2. ^{13}C HPDEC MAS NMR spectra of gas hydrate from Barkley Canyon, offshore Vancouver Island. Among the signals: -8.17 ppm for methane in $5^{12}6^4$ of sII hydrate; -4.87ppm of methane in $4^35^66^3$ of sH hydrate; -4.37 ppm for methane in of 5^{12} sII and sH hydrates; 6.12 ppm for ethane in $5^{12}6^4$ of sII hydrate; 16.69 ppm and 17.45 ppm for propane in $5^{12}6^4$ of sII hydrate; 13.73 ppm and 25.77 ppm for n-butane in $5^{12}6^4$ of sII hydrate; 23.59 ppm and 26.50 ppm for i-butane in $5^{12}6^4$ of sII hydrate; 27.66 ppm for cyclohexane in $5^{12}6^4$ of sII hydrate; 25.77 ppm, 35.15 ppm and 35.83 ppm for methylcyclopentane in $5^{12}6^8$ of sH hydrate; 23.59 ppm and 27.33 ppm for methylcyclohexane in $5^{12}6^8$ of sH hydrate; 22.72 ppm, and 32.95 ppm for iso-pentane $5^{12}6^8$ in of sH hydrate.

Two important points need to be emphasized in relation to this spectrum. First, the spectrum gives a definitive confirmation of the existence of natural sH gas hydrate. Secondly, it reports n-pentane and n-hexane as new sH gas hydrate formers, with both of them present in the natural hydrate (but only in conjunction with other sH guests suitable for the large cage).

The main problem of the BD type of experiment such as ^{13}C HPDEC MAS is the long ^{13}C relaxation times resulting in lengthy experiments. In a Cross-Polarization (CP) type of experiment [ ], which is another commonly used SS NMR technique in hydrate research, the detectable nuclear magnetization of ^{13}C nuclei is produced indirectly by transferring nuclear polarization during a contact time τ from more abundant protons to observed nuclei (i.e., ^{13}C). The delay

between consecutive accumulations in a CP experiment is thus defined not by a slow relaxation of ^{13}C, but typically much faster relaxation of protons. The techniques, however, has serious problems with quantification.

The dependence of the intensity in the CP experiment with contact time τ is described by equation (2)

$$ I = \frac{I_0}{1 - \frac{T_{CP}}{T_{1\rho}}} \left[\exp(-\frac{\tau}{T_{1\rho}}) - \exp(-\frac{\tau}{T_{CH}}) \right] \quad , \quad (2) $$

where the signal build-up is controlled by the cross-polarization constant T_{CH}, and the proton spin-lattice relaxation in rotating frame $T_{1\rho}$ controls the signal decay[34]. The distance between protons and carbons and motion of the molecules will have a dramatic effect on T_{CP} and $T_{1\rho}$, causing vast variation of the intensities in the CP spectra for different molecules in different environment. Understandably this makes any reliable intensity measurements using CP very complicated.

Figure 3 shows an example of the CP signals dependence in iso-C_4H_{10}/CH_4 and neo-C_5H_{12}/CH_4 mixed Str. II hydrates. In-spite of the structural type and similarity of the guests, the dynamics of cross-polarization in these two hydrates are quite different and illustrates difficulties of quantification in CP spectra.
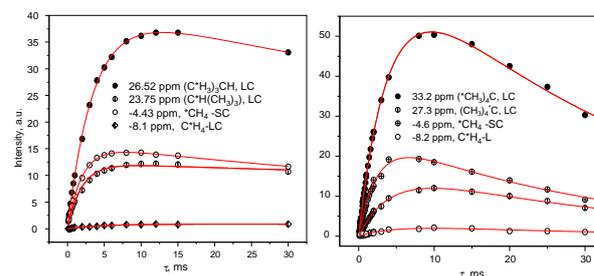

Figure 3. Intensities of the signals in the CP spectra of hydrates as a function of contact time in selected hydrates.

In the first case reasonably accurate relative intensities can be obtained by measuring the spectra with τ about 10-15 msec, when the

intensities of all the signals change synchronously and vary only a little with τ. In the second case, however, finding a region with a weak or similar dependence for *all signals* is very difficult. When CP is used, the best approach to obtaining quantitative (or, perhaps, nearly quantitative) data would be to acquire complete τ dependences for all the signals followed by a simultaneous fit of all the curves with the equation 2.

For not very complex systems such as Str.I methane hydrate the results obtained from the CP experiments are usually quite similar to the quantitative data of the BD experiments, but they certainly required more effort. One should note that the accuracy can be significantly improved if $T_{1\rho}$'s are measured independently. To sum up, shortening of the accumulation time because of a shorter repetition time in CP experiment can turn into a fairly time consuming relaxation time measurement, saving little if any time, if quantitative data are required.

The CP experiment, however, has some other advantages. Because of the CP sensitivity to the mobility of the molecules, it can be used for the purpose of spectral editing. At short contact times only signals originated from carbon atoms in immobile molecules and in close proximity to the protons (i.e. encaged) are observed. The signals from mobile species such as free non-caged molecules will be completely filtered out. Such a spectral editing is demonstrated in Figure 4 for Str.II mixed i-Butane/CH_4 hydrate.
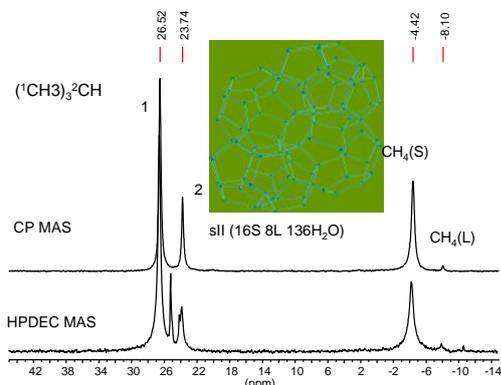
**Figure 4**. ^{13}C CP MAS and ^{13}C HPDEC spectra of Str.II mixed i-Butane/CH_4 hydrate.

Three sharp signals at 25.1, 24.1 and -10.8 ppm found in the ^{13}C HPDEC MAS are completely absent in the CP MAS spectrum, and assigned to free i-Butane and CH_4 molecules adsorbed on the surface of hydrates.

The variations in the guest and structural type of hydrate can have a very profound effect on the dynamics in the lattice of hydrates, causing dramatic changes in the spectra. A certain degree of caution needs to be exercised when the CP is used in characterization of hydrates. Figure 5 shows ^{13}C HPDEC and CP MAS spectra of a synthetic mixed hydrate prepared from TBME and methane. The HPDEC and CP spectra recorded at different conditions show some significant differences.
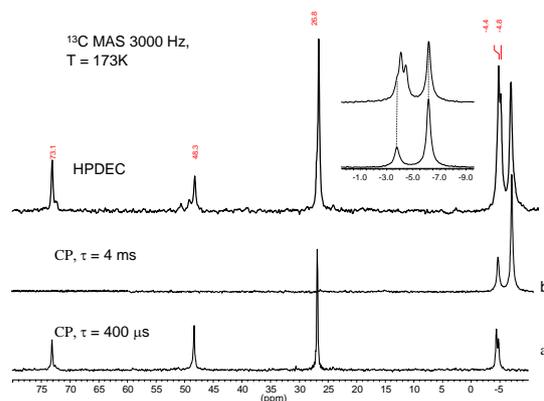
Figure 5. Cross-polarization (*a* – contact time 400 μs, *b* - contact time 4 ms) and HPDEC (*c*) ^{13}C MAS spectra of synthetic mixed hydrate prepared with TBME and methane. Inset shows expanded region of CH_4 signals in spectrum *b* and *c*.

The cross-polarization spectrum recorded with a very short mixing time suggests that the sample is entirely Str.H mixed TBME/CH_4 hydrate (trace a). The spectrum recorded at a moderate mixing time of 4 ms, however, shows absolutely no signs of Str. H. Instead, the spectrum demonstrates two signals at -4.2 and -6.6 ppm with a relative intensities ratio close to 1:3, a clear sign of Str.I methane hydrate. The observed HPDEC spectrum is in essence a superposition of two previous situations plus some minor signals from free TBME. Evidently we have here a mixture of Str.I methane hydrate and Str.H mixed TBME/CH_4 hydrate.
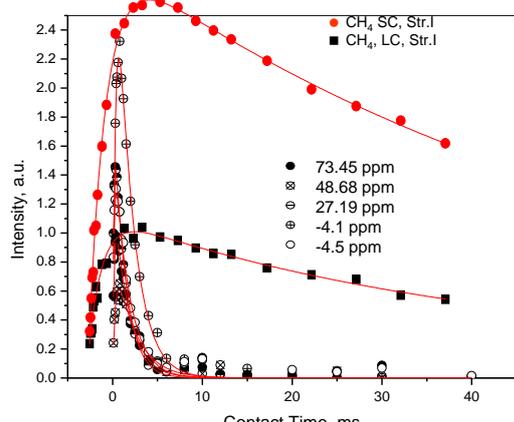
Figure 6. Signals' dependencies on the contact time for this Str. H mixed hydrate. The curves are fitted based on equation 2 with the parameters reported in Table 1.

Signal, ppm	73.45	48.7	27.2	-4.1	-4.4	-4.8	-6.6
T_{1IS}, ms	0.16	0.31	0.12	1.5	0.34	0.13	1.9
$T_{1\rho}$, ms	1.68	2.26	1.32	41.3	1.73	1.67	59.9
T_1, s	3.1	1.8	0.4	7.2	6.1	6.5	5.0
Assign-ment	C2 LC StrH	C3 LC StrH	C1LC StrH	CH$_4$ SC StrI	CH$_4$ SC StrH	CH$_4$ MC StrH	CH$_4$ LC Str.I
$(^1CH_3)_3$-^{2}C-O-^{3}CH$_3$							

Table 2. T_1 an $T_{CH}/T_{1\rho}$ relaxation data at 173 K for Str.H TBME/CH$_4$ and Str.I CH$_4$ hydrates.

Variations in the lattice dynamics in these two different hydrates produce a situation when under certain experimental conditions only one hydrate is observed with the total suppression of the signals from the second hydrate. Figure 6 illustrates the dependence of the signals in the cross-polarization spectra of the discussed sample. One can see that in Str.H hydrate the build up and decay of the signals are much faster than those in Str.I, resulting in a complete loss of the signals from Str.H at longer mixing times that are favorable in detection of Str.I. All in all, this example shows how easily the experimental results can be misinterpreted if an incomplete set of data is acquired.

Requirement of a very fast spinning limits the experiments to structural and compositional studies in equilibrated samples. Most of the NMR studies pertinent to hydrate research were performed with spinners open to atmospheric pressure and representing open systems, although there were some recent attempts to use SS NMR to follow decomposition of hydrates in sealed tubes by increasing the temperature [8]. Inability to provide a constant supply of gas at elevated pressure to a fast spinning sample effectively limits applications of the SS NMR in studies of hydrate formation to a "stopped flow" type of experiment. Here, the reaction is allowed to progress for a certain period of time, after which it is abruptly stopped (i.e. by a very fast freezing) followed by the analysis of the products.

We attempted this type of experiment studying the partitioning of the higher hydrocarbons during the formation of mixed hydrates of methane with the isomers of butane. In this experiment a small amount of ice (3g) was pressurized to 23 bar at -3°C with the mixture of 2% isobutene, 2% n-butane, and 96% methane in a 300 ml stainless steel reactor for a measured period of time followed by cooling in liquid nitrogen. The time development of hydrate composition was analyzed by ^{13}C HPDEC MAS NMR.
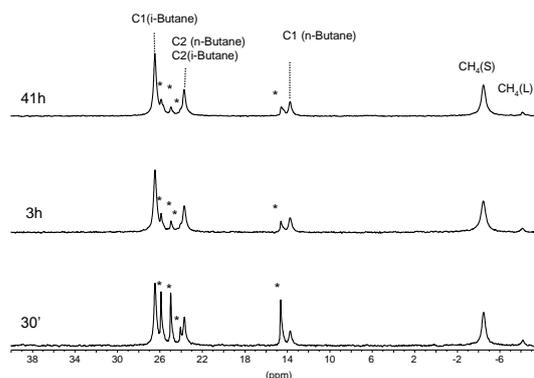
Figure 7. ^{13}C HPDEC MAS spectra (T=173K, 2500 Hz) of hydrates formed from interaction between ice and the mixture of 2% isobutene, 2% n-butane, and 96% methane at -3°C for indicated periods of time. The asterisks above the spectra indicate the signals from free (un-reacted) butanes. The assignment of other signals is as shown.

Some selected spectra taken at different reaction times are shown on Figure 7. The development of composition is summarized in Figure 8. NMR data indicate that only Str. II hydrate is formed under the given experimental conditions from the gas mixture used. A substantial amount of un-reacted butanes can be found at short times of exposure, which gradually disappear with increased reaction time. Both i-butane and n-butane occupy only large cages. Methane occupies mainly small 5^{12} cages, nevertheless some small amount of methane also resides in the large cages of the hydrate.
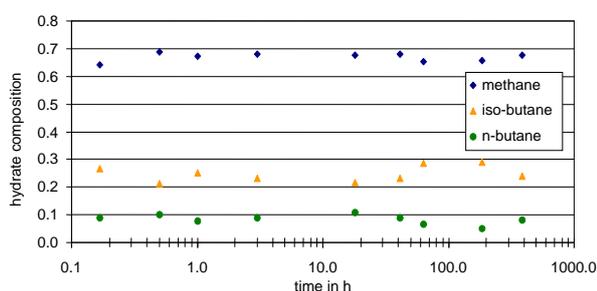
Figure 8. Time development in composition of Str.II hydrate prepared from the mixture of 2% isobutene, 2% n-butane, and 96% methane (23 bar, -3°C) .

Although the concentrations of butane isomers in the gas are the same, the concentration of n-butane comparing to i-butane in the hydrate is about half. Integration of the signals in the spectra demonstrates clearly that the composition of the hydrate at reaction times above 10 minutes is practically constant. This may be considered an indication of the relatively homogeneous formation of hydrate although this would need to be checked by localized measurements of the Raman spectrum.

¹H and 13C MAS in mixed hydrogen hydrates. ¹H MAS NMR studies of gas hydrates represent several specific challenges of different degrees of difficulty. First, due to a limited choice of material suitable for building the MAS stators, most of the probes have very strong proton background signals which in general will change with the temperature. The intensity of background signal can be so strong that it makes the BD spectra completely unusable. To a significant extent this problem can

be alleviated by acquiring instead the spin-echo signals synchronized with the rotation of the sample. Acquiring of the echoes adds some extra difficulties in the spectral quantification. The intensity of the spin-echo signal decays with the echo delay τ as

$$I = I_0 \exp[\ -\tau / T_2\ ]. \qquad (3)$$

Any delay $\tau > 0.05 * T_2$ will result in appreciable (though accountable) attenuation of the signal. In MAS spin-echo experiments τ is to be set as a multiple of the inverse spinning speed n/ν_{MAS}. With the large sizes of MAS spinners (6-8 mm ID) commonly used in the hydrate measurements, only relatively slow spinning speed of 2 - 5 kHz are usually achievable in low temperature measurements. Thus the shortest commonly achievable echo delay in MAS experiment is around 200-500 μs. The T_2's on the order of magnitude of 1 ms and shorter, however, are quite common for protons in molecules involved in gas hydrates. The result is a notable attenuation of the signal.

This signal loss is not so important for the overall intensity of the signals since the sensitivity of ¹H NMR is very high, but is critical for relative intensity measurements. Different protons in a molecule will often have different T_2's, and for a quantitative intensity measurement this will require very accurate T_2's for each site. The limited spinning speed also results in incompletely averaged CSA and dipole-dipole interactions, thus broadening and only partially resolving the signals. While accounting for one dominating interaction such as the CSA in ¹³C can be done relatively well using simulation software, several interactions together can be very difficult to deal with.

A situation requiring an account of the effect of a short T_2 on signal intensity was encountered while studying the composition of mixed H_2/CO_2 hydrate. Figure 9 shows a ¹H MAS spectrum of such a hydrate recorded as a spinner-synchronized spin-echo. Three signals can be seen in the spectrum. The broader line at 6.59 ppm, based on its position and its presence in the spectrum of pure CO_2/D_2O hydrate, can be assigned to the residual protons in the D_2O that was used in the hydrate preparation to reduce the total proton signal.
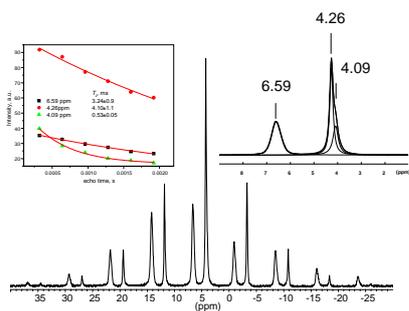
Figure 9. Spin-echo rotor synchronized ^1H MAS (T=173K, 3000 Hz) of $H_2/CO_2/D_2O$ hydrate prepared from H_2-CO_2 mixture (3:2, 80 bar). Insets show the expanded region of the central signals and dependence of the signal intensities on the echo delay time.

A prominent signal at 4.26 and a shoulder at 4.09 ppm are from H_2 molecules trapped in the hydrate cages. In addition to the chemical shift of the signals, which is close to the shift of molecular hydrogen, the assignment is also supported by a slow decrease of the signals with the time. The later is likely due to decomposition of hydrate at 173K. In the course of three hours the combined intensity of the two signals reduces by about 30%. Because the T_2's of the protons in the sample are only 2 to 10 times longer than the shortest echo delay used, there is a notable attenuation of all the signals which has to be corrected. While the direct integration of the spectrum gives the relative intensities of the H_2 signals as 2:1, the adjusted for T_2 ratio is closer to 3:1. The absolute amount of hydrogen in the sample can be estimated by comparing the intensity with the spectrum of a reference with known concentration of protons and obtained in identical conditions. We found that THF/D_2O hydrate is a convenient quantitative reference with sufficiently long T_2's for both ^{13}C and ^1H. In the H_2/CO_2 mixed hydrate studied, the total detected proton intensity corresponds to 1.24 wt.%. In order to separate the contribution of residual protons in D_2O, the experimental spectrum has to be simulated taking into account all of the spinning sidebands. Such a procedure results in a fraction of residual protons of 0.476, with 0.392 and 0.132 taken to be the fractions of the total intensity of the signals at 4.26 and 4.09 ppm, respectively. If it were certain that all

protons in the system contribute to the ^1H NMR spectrum, the total of the two signals would correspond to 0.65 wt.%. The uncertainty comes from the fact that the hydrogen molecule exist in the form of two spin isomers – ortho- and para-hydrogen. These isomers result from parallel (spin 1) or anti-parallel (spin 0), coupling of the nuclear spins, with only the ortho-isomer being observable by proton NMR.

At room temperature different spin states have the same probability, but the spontaneous transitions between them are very slow. As a consequence, normal hydrogen behaves as a mixture of three volumes of ortho-hydrogen (parallel spins) with one volume of para-hydrogen (antiparallel spins). In the gas phase this ratio does not change much down to 150K. There have been very few studies regarding orto-/para–hydrogen in hydrates [29], and it is not entirely certain whether the ratio between orto- and para-states will be constant for hydrogen molecules entrapped in hydrate cages. If, however, the ratio is maintained, the total amount of hydrogen in the hydrate studied will be close to 1 wt.%. Considering that this amount is preserved at ambient pressure, the result indicates a rather high stability of this mixed hydrate. We note that similar results were obtained for THF-H_2 and CO_2-C_3H_8-H_2 hydrates. At this time it is not possible to say whether the signals at 4.09 and 4.26 ppm originate from H_2 molecules in single and double occupied small (or even large cages of hydrate).

From the PXRD the discussed hydrate is found to be Str.I, which has been confirmed by ^{13}C MAS NMR (Figure 10).
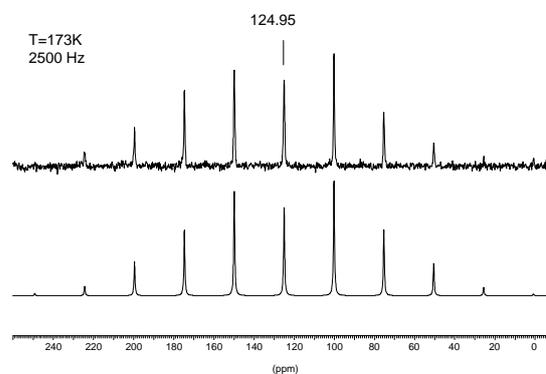
Figure 10. ^{13}C HPDEC MAS of $H_2/CO_2/D_2O$ hydrate prepared from H_2-CO_2 mixture (H_2:CO_2 = 3:2, 80 bar). T=173K, spinning speed of 2500 Hz.

The observed spectral pattern is characteristic of the CSA, as one may expect for CO_2 molecules encaged in the $5^{12}6^2$ cages of Str.I . Although only one signal can be resolved in the MAS spectrum, the observed pattern is likely not from a single site but a result of averaging over many possible orientations of CO_2 molecules inside the cage, that are frozen at this low temperature. The total integral of the signal (again, THF hydrate has been used as an external quantitative reference) corresponds to $2.74 \pm 0.35 \cdot 10^{21}$ CO_2/g, which is very close to a complete occupancy of the large cages. This leaves a large number of vacant small cages that can be filled with hydrogen.

Conclusions.

Applications of Solid State NMR have been demonstrated to a broad range of problem encountered in studies of gas hydrates. The technique can be a big help in solving many problems in gas hydrate research. This includes the analysis of the composition and structure of multi-component mixed gas hydrates, characterization of the natural gas hydrates, and evaluation of the formation conditions and properties of mixed hydrogen hydrates. The potential pitfalls of the method have been highlighted and sensible choices of experimental conditions and techniques that ensure accurate results are discussed. We expect that all these recent experimental developments will prompt wider application of Solid State NMR in hydrates research.

REFERENCES

[1] Davidson DW, Garg SK, Gough SR, Handa YP, Ratcliffe CI, Ripmeester JA, Tse JS, Lawson WF. *Laboratory analysis of a naturally oocurring gas hydrate from sediment of the Gulph of Mexico*, Geochim. Et Cosmochim. Acta 1986; 50:619-623.

[2] Fyfe CA, *Solid State NMR for Chemists*, Guelph: C.F.C. Press, 1983.

[3] Stejskal EO, Memory JD. *High Resolution NMRin the Solid State, Fundamentals of CP/MAS,* New York: Oxford University Press, 1994.

[4] Lu HL, Seo YT, Lee JW, Moudrakovski I, Ripmeester JA, Chapman NR, Coffin RB, Gardner G, Pohlman J. *Complex gas hydrate from the Cascadia margin.* Nature 2007; 445: 303-306.

[5] Subramanian S, Kini A, Dec SF, Sloan ED, *Evidence of structure II hydrate formation from methane plus ethane mixtures*, Chem. Eng. Sci. 2000; 55 (11) : 1981-1999.

[6] Kida M, Sakagami H, Takahashi N, Hachikubo A, Shoji H, Kamata Y, Ebinuma T, Narita H, Takeya S. *Estimation of gas composition and cage occupancies in CH_4-C_2H_6 hydrates by CP MAS C-13 NMR technique J.* Japan Petr. Inst. 2007; 50 : 132-138.

[7] Rovetto LJ, Bowler KE, Stadterman LL, Dec SF, Koh CA, Sloan ED. *Dissociation studies of CH_4-C_2H_6 and CH_4-CO_2 binary gas hydrates.* Fluid Phase Equil. 2007; 261: 407-413.

[8] Gupta A, Dec SF, Koh CA, Sloan ED. *NMR investigation of methane hydrate dissociation.* J. Phys. Chem. C 2007; 111: 2341-2346.

[9] Okuchi T, Moudrakovski IL, Ripmeester JA. *Efficient storage of hydrogen fuel into leaky cages of clathrate hydrate.* Appl. Phys. Lett. 2007; 91: 76-78.

[10] Susilo R, Ripmeester JA, Englezos P. *Characterization of gas hydrates with PXRD, DSC, NMR, and Raman spectroscopy.* Chem. Eng. Sci. 2007; 62: 3930-3939.

[11] Zeng H, Moudrakovski IL, Ripmeester JA, Walker VK. *Effect of antifreeze protein on nucleation, growth and memory of gas hydrates.* AICHE Journ. 2006; 52: 3304-3309.

[12] Park Y, Kim DY, Lee JW, Huh DG, Park KP, Lee J, Lee H. *Sequestering carbon dioxide into complex structures of naturally occurring gas hydrates.* Proc. Natl. Acad. Sci. 2006; 103: 12690-12694.

[13] Park J, Seo YT, Lee JW, Lee H. *Spectroscopic analysis of carbon dioxide and nitrogen mixed gas hydrates in silica gel for CO_2 separation.* Catal. Today 2006; 115: 279-282.

[14] Avakian R, Mao YG, Chagolla D, Ba Y. *Temperature-gradient assisted gas-dissolved liquid-phase synthesis of clathrate hydrates.* Energy & Fuels 2006; 20 (3) : 1197-1200.

[15] Lee J, Lu HL, Moudrakovski IL, Ratcliffe CI, Ripmeester JA. *n-pentane and n-hexane as coguests in structure-H hydrates in mixtures of 2,2-dimethylbutane and methane.* Angew. Chemie Int. Ed. 2006; 45 (15) : 2456-2459

[16] Lee JW, Kim DY, Lee H. *Phase behavior and structure transition of the mixed methane and nitrogen hydrates.* Korean J. Chem Eng. 2006; 23 : 299-302

[17] Lu HL, Moudrakovski I, Riedel M, Spence G, Dutrisac R, Ripmeester J, Wright F, Dallimore S. *Occurrence and structural characterization of gas hydrates associated with a cold vent field, offshore Vancouver Island.* J. Geophys. Res. Solid Earth. 2005; 110 : 10-18.

[18] Kim DY, Uhm TW, Lee H, Lee YJ, Ryu BJ, Kim JH. *Compositional and structural identification of natural gas hydrates collected at Site 1249 on Ocean Drilling Program Leg 204.* Korean J. Chem. Eng. 2005; 22: 569-572.

[19] Seo YT, Moudrakovski IL, Ripmeester JA, Lee JW, Lee H. *Efficient recovery of CO_2 from flue gas by*

clathrate hydrate formation in porous silica gels. Env. Sci. Techn. 2005; 39: 2315-2319.

[20] Seo YT, Lee H. *Structure and guest distribution of the mixed carbon dioxide and nitrogen hydrates as revealed by X-ray diffraction and C-13 NMR spectroscopy*. J. Phys. Chem. B 2004; 108: 530-534.

[21] Seo YT, Lee H. *C-13 NMR analysis and gas uptake measurements of pure and mixed gas hydrates: Development of natural gas transport and storage method using gas hydrate*. Korean J. Chem. Eng. 2003; 20: 1085-1091.

[22] Uchida T, Takeya S, Wilson LD, Tulk CA, Ripmeester JA, Nagao J, Ebinuma T, Narita H. *Measurements of physical properties of gas hydrates and in situ observations of formation and decomposition processes via Raman spectroscopy and X-ray diffraction*. Can J. Phys. 2003; 81: 351-357.

[23] Seo Y, Lee H. *Hydrate phase equilibria of the ternary CH4+NaCl plus water, CO_2+NaCl plus water and CH4+CO2 plus water mixtures in silica gel pores*. J. Phys. Chem. B 2003; 107 (3) : 889-894.

[24] Seo Y, Lee H, Uchida T. *Methane and carbon dioxide hydrate phase behavior in small porous silica gels: Three-phase equilibrium determination and thermodynamic modeling*. Langmuir 2002; 18 (24) : 9164-9170.

[25] Seo Y, Lee H, Ryu BJ. *Hydration number and two-phase equilibria of CH_4 hydrate in the deep ocean sediments.* Geophys. Res. Lett. 2002; 29 (8) : 670-673.

[26] Seo Y, Lee H. *Phase behavior and structure identification of the mixed chlorinated hydrocarbon clathrate hydrates*. J. Phys. Chem B. 2002; 106: 9668-9673.

[27] Moudrakovski IL, Sanchez AA, Ratcliffe CI, Ripmeester JA. *Nucleation and growth of hydrates on ice surfaces: New insights from Xe-129 NMR experiments with hyperpolarized xenon.* J. Phys. Chem. B. 2001, 105: 12338-12347.

[28] Subramanian S, Ballard AL, Kini RA, Dec SF, Sloan ED. *Structural transitions in methane plus ethane gas hydrates - Part I: upper transition point and applications.* Chem.Eng. Sci. 2000, 55: 5763-5771.

[29] Senadheera L, Conradi MS. *Rotation and diffusion of H_2 in hydrogen - Ice clathrate by H-1 NMR*. J. Phys. Chem. B 2007, 111: 12097-12102.

[30] Bennett AE, Rienstra CM, Auger M, Lakshmi KV, Griffin RG. *Heteronuclear decoupling in rotating solids.* J. Chem. Phys. 1995; 103: 6951- 6958.

[31] Massiot D, Fayon F, Capron M, King I, Le Calvé S, Alonso B, Durand J O, Bujoli B, Gan, Hoatson G, *Modelling one- and two-dimensional Solid State NMR spectra.* Magn. Res. Chem. 2002; 40: 70-76.

[32] Eichele K, Wasylishen RE. *WSOLIDS NMR Simulation Package,* Version 1.17.26; 2000.

[33] Buess M. *NMR Tools for Origin. http: www.nmrtools.com*

[34] Mehring M. *Principles of High Resolution NMR in Solids.* Berlin: Springer-Verlag, 1983.