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Nucleation and Growth of Structure I Xenon Hydrate
on the Surface of Ice:
Hyperpolarized ^{129}Xe and ^1H NMR Studies.

by

Anivis Ailin Sanchez, B. Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of

Master of Science

Department of Chemistry
Carleton University
Ottawa, Ontario
August, 2000

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Nucleation and Growth of Structure I Xenon Hydrate
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submitted by ANIVIS AILIN SANCHEZ, B. Sc.
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Chair, Department of Chemistry

CARLETON UNIVERSITY
2000

Abstract

^{129}Xe NMR spectroscopy of hyperpolarized xenon has been used to monitor the kinetics of clathrate hydrate formation and decomposition on the surface of ice. The high sensitivity of this relatively new technique allows for detailed studies of these processes. It was found that the kinetics of the hydrate formation depend on the temperature, the xenon pressure and the history of the ice surface treatment. The results obtained herein provide evidence of non-equilibrium behaviour during the hydrate nucleation stage, known as the induction period, suggesting that the small 5^{12} cage plays a special role in the precursor formation. It was found that the decomposition of the clathrate hydrate leaves the surface “pre-organized”, therefore eliminating the induction period for hydrate re-formation.

The so-called Quasi-Liquid Layer (QLL) on the surface of ice has been previously assumed to take part in hydrate formation. In order to test this assumption, a ^1H NMR spectroscopy study of the QLL was performed. The results suggest that impurities and dissolved gases in the ice sample affect the intensity of the QLL signal, indicating that the signal is likely caused by a mobile phase at the ice grain boundaries. Preliminary experiments monitoring the ^1H NMR signal from the QLL during xenon hydrate formation were inconclusive with regards to the involvement of the QLL in the formation process, and further experiments are necessary.

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Chapter I

Description of Clathrate Hydrates

1.1 Introduction

Clathrate hydrates, many of which are also referred to as gas hydrates, are crystalline inclusion compounds formed when small guest molecules come into contact with water near its freezing point. Hydrogen-bonded water molecules form a host network of well-defined cages around the guest molecules. Figure 1.1 depicts the typical structure of a guest-host system formed in clathrate hydrates.

It is believed that the first gas hydrate was reported in 1811 by Sir Humphery Davy, who cooled an aqueous solution saturated with chlorine gas below 9 °C to yield chlorine hydrate.^{1,2} Faraday then determined its approximate composition in 1823.³ Many of the presently-known gas hydrates were prepared and identified by a number of researchers prior to 1900. During the 100 years following the discovery of gas hydrates, the interest was purely academic, and the research involved (a) the identification of hydrate-forming species and (b) the pressure-temperature conditions at which the formation occurs.^{1,2} It was not until 1934, when it was suggested that hydrates could form in natural gas pipelines and effectively block gas flow⁴, that research began to focus on formulating methods to prevent hydrate formation in gas pipelines in cold and deep-sea regions.

1.2 Clathrate Hydrates

1.2.1 Hydrate Crystal Structures

The general formula representing the formation of the hydrate is given by the following:

Figure 1.1 Clathrate Hydrate: guest - host system.

where M is the hydrate forming molecule and n is the number of water molecules per gas molecule required to form solid hydrates.^{5,6} The value of n (commonly known as the hydration number), is variable and depends on the pressure, temperature and composition of the gas phase. The hydrogen-bonded water molecules encase the hydrate former molecule to form the hydrate crystals of different structure. The crystal structures of three principal hydrates have been determined, and are distinguished by different types and numbers of cages. These three structures are identified as: body-centered cubic structure I (sI), diamond lattice cubic structure II (sII)¹⁻³ and the recently discovered hexagonal structure H (sH) hydrate.⁷ Figure 1.2 displays the types of cages and the unit cell formula of the three structures. The crystal structures are given with reference to the water skeleton. All structures contain the basic pentagonal dodecahedron (**D**) 'building block' cavity that has 12 faces with five sides per face denoted as 5^{12} , though the crystal symmetry of this cage for each structure is different. Interstices between the 5^{12} cages are larger cavities, which contain 12 pentagonal faces and either two, four, or eight hexagonal faces (denoted as (**T**) $5^{12}6^2$ in sI, (**H**) $5^{12}6^4$ in sII, or (**E**) $5^{12}6^8$ in sH). In addition, sH has a cavity with square, pentagonal and hexagonal faces denoted as (**D'**) $4^35^66^3$. The small cage of sI and the large cage of sII have cubic symmetry and are thus pseudo-spherical, whereas all the other cages can be described as oblate or prolate spheroids (possessing one unique axis).

Figure 1.3 depicts the stacking of the crystalline lattices of the gas hydrates sI, sII and sH. Structure I hydrate is defined by identifying the vertices of the **T** cages, whereas

Structure Space Group	Small Cages (radius, Å)	Large Cages (radius, Å)	Unit Cell Formula	
sI Pm3n	D 5 ¹² (3.91)	T 5 ¹² 6 ² (4.33)	D₂T₆ • 46H₂O	
sII Fd3m	D 5 ¹² (3.90)	H 5 ¹² 6 ⁴ (5.86)	D₁₆H₈ • 136H₂O	
sH P6/mmm	D 5 ¹² (3.90)	D' 4 ³ 5 ⁶ 6 ³ (3.85)	E 5 ¹² 6 ⁸ (8.31)	D₃D'₂E₁ • 34H₂O

Figure 1.2 Clathrate hydrate polyhedra.

Body-centered
cubic (sI)

Diamond lattice cubic (sII)

Hexagonal
(sH)

Figure 1.3 Crystalline lattices of gas hydrate.

structure II and H are based on different stacking sequences of layers of **D** cages connected by bridging hydrogen bonds. In Figure 1.3, an oxygen atom is located at the vertex of each angle in the cavities; the lines represent hydrogen bonds in which one chemically-bonded hydrogen atom connects to an oxygen atom on a neighboring water molecule.

1.2.2 Guest Size and Structure Relationships

The empty hydrate lattice of gas hydrates is thermodynamically unstable. Guest molecules interact with the cages of the surrounding network of hydrogen-bonded water molecules through weak, non-specific van der Waals interactions.^{1,2} The presence of guest molecules stabilize the hydrate lattice in such a manner that many gas hydrates persist as solids at temperatures above the melting point of ice.¹⁻⁴

Figure 1.4 shows the guest size - hydrate structure relationship along with the hydration number correlation accepted today for hydrates of single guests.¹⁸ This figure illustrates details regarding the guest-cavity size ratio for the hydrates formed of a single component: the sizes of stabilizing guest molecules range between 0.38 and 0.75 nm, and some molecules are too large to fit into the smaller cavities of each structure. Molecules which are close to the separating lines appear to exhibit the most non-stoichiometry due to their inability to fit securely within the cavity.⁸ The largest molecule of a gas mixture usually determines the structure formed and gas molecules falling in the range of 0.58 to 0.70 nm exclusively fill the large **H** cage of sII hydrate. At the upper size limit for sII hydrate, the occupancy of a small ('help gas') molecule in the **D** cage provides extra stability to the lattice in the presence of larger molecules like benzene, butane and cyclohexane.¹⁻⁵ This type of hydrate is known as a double hydrate. Figure 1.5 shows the

		No hydrates		
Largest Guest van der Waals diameter	4Å	Ar Kr N ₂ , O ₂ CO, CH ₄ Xe, H ₂ O	$5^{12} + 5^{12}6^4$, II	5 2/3
	5Å	CO ₂	$5^{12} + 5^{12}6^2$, I	5 3/4
		ethane, ethylene	$5^{12}6^2$, I	7 2/3
	6Å	cyclopropane cyclobutane	$5^{12}6^2$ or $5^{12}6^4$, I or II	17
		cyclopentane propane	$5^{12}6^4$, II	
	7Å	isobutane n-butane(g), neopentane benzene, cyclohexane		
		8Å	adamantane cyclooctane, methyl butanes	
			methylcyclohexane dimethylcyclohexane	

Figure 1.4 Relative sizes of guests, host cavity structure and hydration numbers for single hydrate guest.¹⁸

Figure 1.5 Complexity in guest size-structure correlation for hydrates with two guest species (double hydrates).¹⁸

structure-guest size relationship complexity for double hydrates.¹⁸ Molecules are divided into classifications as to how they would behave as a single guest (i.e. structure II guests come in three size ranges, a, b, c). The following combinations are known, although some of the boundaries may not have been established firmly: Ia + Ib $\rightarrow$ I or II; IIa or Ia + IIb $\rightarrow$ II; Ia or IIa + IIc $\rightarrow$ II; Ia or IIa + Ha $\rightarrow$ H.¹⁸ Structure H hydrates form when larger guest molecules (diameter = 0.72 to 0.86 nm) such as cage compounds like adamantane and many substituted linear and cyclic hydrocarbons are encapsulated in the E cages. So far sH hydrates have been formed only in the form of a double hydrate, with a help gas occupying the smaller **D** and **D'** cages.⁹

1.2.3 Pressure and Temperature Conditions

Pressure-temperature phase diagrams represent the conditions under which hydrates form or dissociate. Figure 1.6 denotes the P-T phase diagram of Xe-water. In the figure, H is used to denote hydrates, I for ice, G for gas phase and L for aqueous phases. The hydrate region is found to the left of the H-I-G.

1.3 Occurrence and Issues of Gas Hydrates

1.3.1 Occurrence

Naturally occurring gas hydrates are mainly methane.¹⁰ Methane hydrate deposits occur under specific conditions of pressure and temperature, where the supply of methane is sufficient to initiate and stabilize the hydrate structure.¹⁰⁻¹² These conditions are met on earth in shallow sediment (< 2000 m), in two regions: (1) continental, including continental shelves at high latitudes where the surface temperatures are very cold (< 0 °C), and (2) submarine continental slopes and rises where water is cold (~ 4 °C) and pressures are very high (> 3 MPa).¹³ Thus in polar regions, gas hydrates are found where

Figure 1.6 Phase diagram of the Xe-H₂O system, values obtained from references 16,17.

temperatures are cold enough for onshore and offshore permafrost to be present. Gas hydrates are found at water depths exceeding 300 to 500m depending on bottom water temperatures in offshore sediment.¹⁰⁻¹³ Figure 1.7 denotes the worldwide locations of known and inferred gas hydrate deposits.

1.3.2 Current Problems

1.3.2.1 Potential Energy Resource

As conventional sources of natural gas supplies are depleted, the need for non-conventional sources will grow, and gas hydrates may become an important source because of both their widespread existence and the concentration of gas. It is estimated that in a fully saturated structure, 1 m³ of methane gas hydrate contains up to 164 m³ of methane at standard pressure and temperature conditions.¹² Gas hydrates will become a viable energy resource when the cost of the energy required to release methane from the hydrate phase is significantly less than the economic value of the methane that can be recovered from the dissociated gas hydrate deposit.

1.3.2.2 Geological Hazard

Since the formation and decomposition of gas hydrates is very sensitive to pressure and temperature conditions any changes in surface temperature and pressure may affect their stability. The lowering of sea level or an increase in bottom-water temperatures can also bring the same dissociation conditions resulting in sea floor failures and gas release.^{11,13} It has been hypothesized that the unexplained disappearance of ships and aircraft in the Bermuda Triangle is due to the venting of gases from beneath gas hydrates in the sea floors.¹⁴

Figure 1.7 World map showing locations of known and inferred gas hydrate deposits.²

Hydrate decomposition may also have an effect on the climate. Methane has a global warming potential 21 times greater than that of carbon dioxide.¹⁵ A continuous increase of methane concentration in the atmosphere from methane hydrate decomposition would enhance global warming and create a continuous greenhouse effect.¹⁰⁻¹⁵ Recent investigations have considered the possibility of disposing industrially produced carbon dioxide as a hydrate in deep ocean to prevent further release into the atmosphere as greenhouse gas.¹⁹

1.3.2.3 Industry

Gas hydrates are a constant nuisance to gas and petroleum companies. Hydrate plugs in offshore oil wells and pipelines for transport of unprocessed fluids present a problem of high economic impact.^{1-3,10-15} The ability to stimulate and inhibit clathrate hydrate formation depends on a detailed understanding of the clathrate formation mechanism.

1.4 Scope of Thesis

In this chapter, the history of gas hydrates is described. Three hydrate structures are known to date: the body-centered cubic structure I (sI), the diamond lattice cubic structure II (sII) and the hexagonal structure H (sH) hydrate, each of which can be formed by numerous different guests. The structure-guest size relationship for double hydrates is quite complex compared to that of hydrates formed from a single guest component.

As previously mentioned, the challenge is to have a detailed understanding of the clathrate hydrate formation mechanism. In this thesis, the kinetics of sI Xe hydrate formation and decomposition are investigated using hyperpolarized (HP) ^{129}Xe NMR, a relatively new technique which gives a sensitivity enhancement of the order of 10^4 over conventional thermally polarized ^{129}Xe NMR spectroscopy. The NMR signal intensity

following a single radio frequency pulse is then sufficient to obtain a spectrum in a single scan. This allows for the monitoring of non-equilibrium behaviour during hydrate formation. A preliminary study into the role of the so-called Quasi-Liquid Layer (QLL) on the surface of ice during hydrate formation is also reported.

This thesis focuses on the application of new experimental NMR techniques to the understanding of the formation of gas hydrate from ice, and the structural behaviour of both ice and hydrates.

1.5 References

1. Sloan, E.D.; Clathrate Hydrates of Natural Gases, 2nd edition, Marcel Dekker Inc., New York, **1998**.
2. Makogon, Y.F.; Hydrates of Hydrocarbons, PenWell Publishing Co., Oklahoma, **1997**.
3. Atwood, J.L., Davies, J.E.D, MacNicol, D.D., Inclusion Compounds, Volume 1, Academic Press, **1994**.
4. Hammerschmidt, E.D.; *Ind. Eng. Chem.*, **1934**, 26, 302.
5. Franks, F.; Water, Volume 2, Plenum Press, New York, **1973**.
6. Hwang, M. J.; Wright, D. A.; Kapur, A.; Holder, G. D.; *J. Inclus. Phen. Mol. Recog. Chem.*, **1990**, 8, 103.
7. Ripmeester, J. A.; Tse, J.S.; Ratcliffe, C.I.; Powell, B. M.; *Nature*, **1987**, 325, 135.
8. Sloan, E. D.; Fleyfel, F.; *AIChE J.*, **1991**, 37, 1281.
9. Ripmeester, J. A.; Ratcliffe, C.I.; *J. Phys. Chem.*, **1990**, 94, 8773.
10. Holder, G. D.; Godbole, S. P.; *Ann. Rev. Energy*, **1984**, 9, 427.
11. Thakur, N. K.; Rao, T.; *Curr. Sci.*, **1997**, 73, 1048.
12. Long, J. P; Sloan, E. D.; *Intern. J. Thermophysics*, **1996**, 17, 1.
13. Kvenvolden, K. A.; *N.Y. Acad. Sci.*, **1994**, 715, 232.
14. Gury, H. J.; *Petr. Eng. Inter.*, **1998**, 71, 71.
15. Englezos, P.; *Ind. Eng. Chem. Res.*, **1993**, 32, 1251.
16. Berez, E., Balla-Achs, M., *Gas Hydrates*, Elsevier, Amsterdam, **1983**.
17. Barrer, R. M., Edge, A.V.J., *Proc. Roy. Soc.*, **1967**, A300, 1.

18. Ripmeester, J. A., 3rd International Gas Hydrate Conference, Salt Lake City, **1999**.
19. Englezos, P., Hatzikiriakos, S., *Ann. N. Y. Acad. Sci.*, **1994**, 715, 27

Chapter II

NMR Methods for Studying Gas Hydrates

Nuclear Magnetic Resonance (NMR) has become a versatile tool for the study of structure and dynamics in solids, and has already been extensively applied to gas hydrates. NMR can be used to measure the relative occupancy of different cages, the dynamic characteristics of hydrates, and to give valuable structural information.¹⁴

2.1 Basic Principles

The fundamental property of the atomic nucleus involved in NMR is the nuclear spin (I), which has values of 0, $\frac{1}{2}$, 1 etc., in units of $\hbar$ (where $\hbar = h/2\pi$ and h is Plank's constant). The value of the spin number of any nucleus depends on the numbers of protons and neutrons it contains. The magnetic moment (μ) is directly proportional to spin

$$\mu = \hbar I \gamma, \quad (2.1)$$

where γ is the magnetogyric ratio and is a constant for each nucleus. When an external magnetic field is applied, the nuclear moments take up certain allowed orientations, with respect to the applied field. A nucleus with spin I has $2I+1$ possible orientations which are given by the value of the magnetic quantum number m_I . The energy of interaction is proportional to the nuclear moment and the applied field (B_0):

$$E = -\gamma m_I \hbar B_0 \quad (2.2)$$

The selection rule for NMR transitions is that m_I can only change by one unit, i.e. $m_I = \pm 1$. Thus the transition energy is given by

$$\Delta E = \gamma \hbar B_0 \quad (2.3)$$

Since the absorption energy must equal the transition energy, then

$$\Delta E = \gamma \hbar B_0 = h\nu, \quad (2.4)$$

where ν is the resonance frequency of the interacting electromagnetic radiation.

NMR spectroscopy involves the absorption of radio-frequency energy by the nuclear spins as they resonate and reorient in the presence of both the external applied magnetic field and the internal magnetic field produced by internal electronic and magnetic interactions.³ The resonance frequency and reorientation times are sensitive to the local environment of the nucleus and to the mobility of the atoms and molecules. The sensitivity to the local environment, together with a natural isotopic selectivity, enables NMR spectroscopy to provide detailed information about the structure and dynamics of many classes of materials.⁴

2.2 Nuclear-Spin Interactions

The interactions experienced by a nuclear spin in an applied magnetic field, can be best described by the total Hamiltonian:

$$\mathcal{H}_T = \mathcal{H}_Z + \mathcal{H}_I \quad (2.5)$$

where $\mathcal{H}_Z$ is the Zeeman interaction of the nuclear magnetic moment with the applied field B_0 . This is by far the strongest interaction and dominates the behaviour of the spin system.⁵ $\mathcal{H}_I$ is the internal Hamiltonian, which consists of the following terms⁴

$$\mathcal{H}_I = \mathcal{H}_{CS} + \mathcal{H}_D + \mathcal{H}_Q + \mathcal{H}_J \quad (2.6)$$

where $\mathcal{H}_{CS}$ is the chemical shift interaction, produced by the shielding of the nucleus by the surrounding electrons; $\mathcal{H}_D$ is the direct dipole-dipole interaction between nuclei; $\mathcal{H}_Q$ is the quadrupolar interactions (existing only for $I > 1/2$); and $\mathcal{H}_J$ is the spin-spin (scalar-coupling) interaction, which is important only for directly connected atoms in molecules.

Since only $\mathcal{H}_{CS}$ and $\mathcal{H}_D$ interactions are applicable to the ^{129}Xe NMR study of this project, only the description of these interactions will follow.

1) *Chemical Shift Interactions*: The electronic screening about the nucleus, which produces a secondary magnetic field, causes the chemical shift interaction. This secondary field is proportional to the applied magnetic field B_0 , but is opposite in direction.¹

The chemical shift Hamiltonian $\mathcal{H}_{CS}$ can be expressed as,⁶

$$\mathcal{H}_{CS} = \gamma \hbar I \sigma B_0 \quad (2.7)$$

where σ is the second rank chemical shift tensor. Second rank tensors describe the three dimensional nature of the nuclear-spin interactions.⁷

In solids, the electronic screening about the nucleus is generally not spherically symmetric, i.e. the distribution of electrons is anisotropic, and the shielding tensor, σ , can be best expressed as⁶

$$\sigma = \sigma_{11} \lambda_{11}^2 + \sigma_{22} \lambda_{22}^2 + \sigma_{33} \lambda_{33}^2 \quad (2.8)$$

The σ_{ii} are the principal values of the chemical shift tensor, that is, the values along a specific set of axes fixed in the molecule, and the λ_{ii} are the directional cosines of the molecule's fixed axes with respect to the external field B_0 .⁵

In solution, the rapid molecular motion results in the averaging of the chemical shift terms over all orientations and only the isotropic chemical shift, σ_{iso} , is observed⁵

$$\sigma_{iso} = 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad (2.9)$$

The position of this averaged line in the spectrum is given by

$$\nu = \frac{\gamma}{2\pi} B_0 (1 - \sigma_{iso}) \quad (2.10)$$

2) *Dipolar Interactions*: The dipolar interaction arises from direct magnetic coupling through space. The dipolar Hamiltonian for the coupling between two unlike nuclei i and j is written as⁵

$$\mathcal{H}_D = \frac{\gamma_i \gamma_j \hbar^2}{r_{ij}^3} \mathbf{I}_i \mathbf{D}_{ij} \mathbf{I}_j \quad (2.11)$$

where γ_i and γ_j are the magnetogyric ratios; r_{ij} is the length of the internuclear vector; $\mathbf{I}_i$ and $\mathbf{I}_j$ are the spin operators of the two nuclei respectively. $\mathbf{D}_{ij}$ is the dipolar coupling second rank tensor. Essential features of this interaction are: (a) it depends on the magnitude of the magnetic moments as reflected in the magnetogyric ratios and hence will be most important for nuclei with large magnetic moments, (b) it is independent of the applied field B_0 , and (c) it decreases very rapidly ($1/r^3$) with increasing internuclear distance, r .⁵ However, rapid molecular reorientation averages the angle that the internuclear vector makes with the external magnetic field such that the dipolar coupling is reduced, and in mobile liquids and molecules in isotropic solutions, dipolar coupling makes no contribution to the line positions in the NMR spectrum.⁸

2.3 The Pulse-Fourier Transform Technique

When nuclear spins are placed in a magnetic field B_0 , the spin magnetization will precess around the direction of the field with a frequency ω_0 , known as the Larmor frequency. Since there is a slight excess of nuclei aligned with the magnetic field, a direct consequence of the Boltzmann distribution, the magnetization vector $\mathbf{M}_0$ results which also lies in the same direction as B_0 , as shown in Figure 2.1.²

This description of the nuclear motions refers to the laboratory reference frame. It is very useful to consider NMR experiments in a rotating reference frame, rather than a fixed laboratory reference frame, since this simplifies the description of the effects

Figure 2.1 Motion of spin $\frac{1}{2}$ nuclei in a magnetic field.²

produced by the application of a radio frequency pulse.¹⁰ The rotating frame is one in which the z' axis is in the fixed field direction but the x' and y' axes rotate about the z' axis at a frequency $\omega_0 = \gamma B_0$, as described by Fig. 2.2.

The displacement of the magnetization from equilibrium is produced by a second magnetic field B_1 , which oscillates at the appropriate radio frequency (rf) and is perpendicular to B_0 . B_1 is used as the reference for the rotating frame and lies in the x' axis.⁸ The effect of applying a constant field along the x' axis, causes M_0 to rotate in a clockwise direction about the x' axis with a frequency, ω_1

$$\omega_1 = \gamma B_1 \quad (2.12)$$

Hence, if the pulse is applied for time t , then M_0 will rotate through an angle θ given by, (see Figure 2.3)

$$\theta = \gamma B_1 t \quad (2.13)$$

Since the spectrometer is designed to determine signals along the y' axis, a tipping of the M_0 through an angle of 90° would give rise to the maximum signal. This pulse is known as the 90° pulse.

Once the rf pulse is removed, the perturbed spin system will relax towards the equilibrium condition, causing the signal induced in the coil by oscillating magnetic fields to decay. This signal is called a free induction decay (FID). The FID is a time domain function and after phase sensitive detection and digitization, the FID is Fourier transformed into a frequency domain function known as the NMR spectrum. The two mechanisms that are involved in the recovery of the original magnetization are the spin-lattice relaxation and the spin-spin relaxation. The spin lattice relaxation is denoted by T_1 and is the time needed to establish longitudinal thermodynamic equilibrium

Figure 2.2 Motion of spin $\frac{1}{2}$ nuclei in a magnetic field rotating at the Larmor frequency ω_0 .²

magnetization after the sample has initially been exposed to the magnetic field or after the manipulation of magnetization by a rf pulse. To obtain equilibrium, energy is exchanged between the nuclear spin and the surrounding molecular lattice. The spin-spin relaxation is denoted by T_2 and is responsible for the loss of phase coherence of magnetization in the x-y plane. These relaxation mechanisms are shown in Figure 2.3.

2.4 ^{129}Xe NMR Spectroscopy

Xenon is an inert gas having a van der Waals radius of 2.2 Å.¹³ The ^{129}Xe nuclear isotope has spin $\frac{1}{2}$, a 26% natural abundance and its relative sensitivity compared to ^1H is 2.12×10^{-2} .¹¹

The high polarizability of the electron cloud of the Xe atom leads to a large chemical shift range and makes the ^{129}Xe chemical shift an especially sensitive measure of local atomic interactions.¹¹ The ^{129}Xe resonance shift has a range of over 7500 ppm, which is enormous when compared to the chemical shift of ^1H (10 ppm) or ^{13}C (250 ppm) and even as a bare atom in different environments, the shift range covers more than 350 ppm.¹¹ The chemical shift is composed of two parts, a diamagnetic shift and a paramagnetic contribution, which produce opposing effects on the nuclear resonance frequency.¹³ Figure 2.4 shows ^{129}Xe chemical shifts of several Xe phases and in different chemical environments.¹¹ The dominant feature of ^{129}Xe NMR of Xe gas is the strong dependence of NMR parameters on gas density due to collisions experienced by Xe atoms.¹²

The gaseous xenon chemical shift can be expressed by a virial expansion of the xenon density ρ over a wide range.¹⁴

$$\delta(T, \rho) = \delta_1(T, \rho) + \delta_2(T)\rho^2 + \delta_3(T)\rho^3 \quad (2.14)$$

Figure 2.3 Relaxation mechanisms.²

Figure 2.4 Representative ^{129}Xe NMR chemical shifts in different environments.¹³

where $\delta(T, \rho)$ is the resonance shift at a temperature T and a density ρ . δ_0 is the position for the isolated atom, which experimentally corresponds to zero pressure and is also temperature independent.²¹ $\delta_i(T)$ are the virial co-efficients of the shift in density.²¹ Jameson et al. obtained the most exact values at 298.15 K.²¹

$$\delta_1 = 0.548 \pm 0.004 \text{ ppm/amagat} \quad (2.15a)$$

$$\delta_2 = (-0.169 \pm 0.02) \times 10^{-3} \text{ ppm/amagat} \quad (2.15b)$$

$$\delta_3 = (+0.163 \pm 0.01) \times 10^{-5} \text{ ppm/amagat} \quad (2.15c)$$

where 1 amagat is the density (2.689×10^{19} atoms cm^{-3}) of an ideal gas at 273.15 K and 1 atm. These results yield a chemical shift of 0.55 ppm per amagat for the linear term.¹¹ Theory and calculations have shown that the density dependence arises from exchange interactions during collisions.¹¹ For densities below 100 amagat, two body collisions are predominant and terms of order higher than one are negligible.¹² These higher order terms contribute at higher pressures when three or more body collisions are the case.¹⁴ The chemical shift is also very sensitive to temperature.¹¹

2.4.1 Relaxation Effects

The dependence of nuclear relaxation times on the temperature and nature of the sample provide information on local xenon structure and dynamics.⁸ An expression for the frequency response of the relaxation rate is given by,¹¹

$$\frac{1}{T_1} = 2\gamma^2 H^2 \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} \right) \quad (2.16)$$

where τ_c is the correlation time (the mean collision time for gas phase relaxation) and H is a random fluctuating magnetic field around the nucleus.

Figure 2.5 displays data for xenon relaxation times under a variety of conditions of temperature and pressure.¹³ The well known features of the plot arise from either slow

Fig 2.5 T_1 and T_2 relaxation times for Xe, plotted schematically as a function of correlation time τ_c .¹³

motions, such as those found in solids or at low temperatures, which lead to long T_1 relaxation times and broad lines (short T_2 values), or fast motions, such as found in the gas or liquid phases, which lead to long T_1 values and narrow lines (long T_2 values). The T_1 minimum occurs where the correlation time is equal to the rate of Larmor precession, $\tau_c \omega_0 = 1$.¹¹ The relaxation time of Xe in the gas phase can be extremely long, in the order of hours.¹² When adsorbed, it usually has significantly shorter T_1 values, on the order of seconds and milliseconds.¹² T_1 values of ^{129}Xe in hydrates are usually long and range between minutes to tens of minutes.¹²

2.4.2 ^{129}Xe NMR Spectroscopy of Clathrate Hydrates

^{129}Xe NMR spectroscopy has been an extremely useful tool for the study of gas hydrates. Xenon is a good model for methane with respect to size and shape, and xenon also forms a clathrate hydrate (see Figure 1.4). Xenon alone forms structure I, but it can also be present as a secondary guest in structures II and H. ^{129}Xe NMR is very sensitive to the size, shape and relative occupancy of the cages. The anisotropy of the ^{129}Xe NMR spectroscopy lineshape reflects the symmetry of the various cages present in different hydrates as can be seen from the ^{129}Xe NMR spectra in Figure 2.6.¹⁴ The large cage of structure I is known to have one unique axis and therefore gives an axially symmetric powder pattern (Figure 2.6). The small pentagonal dodecahedral (5^{12}) cages have different symmetry for all three hydrate types: in sI the cage is pseudospherical and thus gives an isotropic ^{129}Xe NMR line; sII gives an axially symmetric lineshape; and sH gives a nonaxially symmetric lineshape.

The ^{129}Xe lineshape in the two small cages of sH overlap, but have been resolved in a Magic Angle Spinning (MAS) experiment.¹⁵ Table 2.1 displays the ^{129}Xe isotropic

Figure 2.6 ^{129}Xe cross-polarization spectra, obtained at 77K, of Xe in the cages of
 (a) Xe structure I, (b) mixed Xe/*n*-butane structure II and (c) mixed Xe/bicyclo[2.2.2]oct-2-ene structure H. Figure reproduced from reference 14.

Cage	σ_{iso}	$\Delta\sigma$
Structure I small 5^{12}	-242	0
Structure I large $5^{12}6^2$	-152	32
Structure II small 5^{12}	-225	18
Structure II large $5^{12}6^4$	-80	0
Structure H small 5^{12}	-232	<5
Structure H small $4^35^66^3$	-215	~40

Table 2.1 ^{129}Xe isotropic chemical shifts and anisotropies in hydrate cages (ppm).¹⁶

chemical shifts along with the anisotropies in the hydrate cages.¹⁶ Assignments can also be based in the line intensities, for example, the anisotropic line in the Xe hydrate sI has greater intensity because there are three times as many large cages as small. In terms of relative chemical shifts, small cages display a larger downfield shift.¹⁶

The major drawback of this technique is the occurrence of long spin lattice relaxation times, on the order of minutes,¹⁷ for ^{129}Xe in clathrate hydrates. This limits the technique to systems in equilibrium and prohibits studies of non-equilibrium processes, such as kinetics of hydrate formation. This obstacle has recently been overcome by the development of optical pumping techniques to produce hyperpolarized xenon, which increases its sensitivity, by a factor of up to 10^4 .¹⁸⁻²⁰ This technique will be reviewed in the next section.

2.5 Optically Polarized ^{129}Xe

In a normal NMR experiment involving a spin $1/2$ nucleus, the signal strength is mainly determined by the difference of the populations P_i of the two energy states, whose ratio is given by the Boltzmann factor:

$$\frac{P_{-1/2}}{P_{1/2}} = \exp\left(-\frac{(E_2 - E_1)}{kT}\right) = \exp\left(-\frac{\gamma\hbar B_0}{kT}\right) \quad (2.20)$$

This population ratio for ^{129}Xe in a field of 7.05 T is 0.999987046 (which corresponds to a polarization of $6.6 \times 10^{-4} \%$).¹¹ However, an optical pumping technique can be used to generate polarizations of $> 40\%$.²⁰ A 40% polarization represents a sensitivity enhancement of 6×10^4 which is about 340 times greater sensitivity than for a normal ^1H NMR spectrum of H_2O .¹²

The most common technique for the production of hyperpolarized noble gases is by spin-exchange with optically polarized atoms of alkali metals, i.e. rubidium. The optical

pumping of rubidium is displayed schematically in Figure 2.7.¹⁰ Rubidium has an $S_{1/2}$ electron ground state that is split into two levels in a low magnetic field (<100G). The first excited state, $P_{1/2}$, is split into two levels. Only circularly polarized light with right helicity of polarization (σ^+), and a wavelength of 794.7 nm (^{85}Rb D_1 transition²¹) and propagation along the direction of the magnetic field, is absorbed, producing a transition from the ground state to the $P_{1/2}$ excited state according to the selection rule $\Delta m_s = +1$.

This feature has the effect of depopulating the $m_s = -1/2$ ground state. Due to spontaneous emission, the excited states decay within ~ 5 ms back to the two $S_{1/2}$ ground states, but at the gas pressures used (~ 1 atm) collisions cause state mixing before relaxation, with the result that the ground states are repopulated with equal probabilities.^{20,21} Since the relaxation rate restoring equilibrium between the two ground states is about 1 s, the net result of the optical pumping is to leave the $5S_{1/2}$ level (for σ^+) highly polarized.²² The next step relies on the “spin exchange” from the alkali metal to the xenon atom which is accomplished by the formation of a short lived (1×10^{-7} to 1×10^{-9} s) Rb-Xe van der Waals complex, see Figure 2.8.¹¹ The lifetime of these complexes is short at pressures above 1 atmosphere, though spin exchange still occurs at a somewhat reduced efficiency.^{11,22}

Happer and coworkers²⁰ have investigated spin exchange between rubidium and ^{129}Xe and ^{131}Xe and found that xenon polarization rates depend on the rubidium density and its polarization. At high densities, the rubidium polarization can be reduced by radiation trapping, where de-excited rubidium atoms emit photons with the wrong polarization.²⁰ Such photons are subsequently absorbed by other rubidium atoms, causing depolarization.¹¹ The addition of nitrogen or helium as a buffer gas quenches this

Fig. 2.7 Electronic energy levels of rubidium showing optical pumping using right circularly polarized light from the $m_s = -1/2$ ground state to the $m_s = +1/2$ excited state, followed by excited state mixing and emission back to both ground states.¹⁰

Fig. 2.8 A schematic representation of the rubidium-xenon van der Waal complex in a magnetic field B_0 .¹¹

mechanism allowing for large polarizations of xenon (>40%) to be produced at xenon pressures of about 1 atmosphere using high-power (5 watt) narrow band lasers.²¹

Xenon can lose polarization following optical pumping in two main ways. Firstly, the Xe polarization can be lost via reverse spin exchange with the Rb so that the Rb must be quickly condensed out of the gas phase by cooling.¹¹ The second mechanism involves the interaction of Xe atoms with paramagnetic centers on the walls of a container. Silicone or paraffin wall coatings^{21,22} reduce Xe relaxation due to this mechanism.

Although any of the alkali metals are suitable, rubidium is usually chosen. The high vapour pressure of rubidium allows operation at modest temperatures where chemical attack on the glass container is not a problem.²⁰ A simple oven keeps the glass cell at a constant temperature, usually in the range of 80°C to 130°C. This ensures an adequate saturated vapour pressure (typically 10^{11} to 10^{14} cm⁻³) from a few droplets of Rb metal in the cell.²⁰ The pressure of the noble gas is usually in the range of 10 Torr to 10 atmospheres.²² The build-up of the nuclear polarization of the noble gas is most conveniently monitored by NMR. The nuclear polarization is so large that any detection methods using continuous wave or pulsed NMR method will work.²¹

One of the most exciting applications of hyperpolarized xenon lies in its use to study the formation of clathrate gas hydrates. The sensitivity of conventional ¹²⁹Xe NMR is far too low to detect signals on the time scale required to study clathrate hydrate formation. However, the use of hyperpolarized xenon allows for signal detection following a single rf pulse with sufficient sensitivity.¹¹ This work presents a detailed ¹²⁹Xe NMR study on the formation and decomposition of xenon clathrate hydrates using hyperpolarized xenon, which is further explained in the following chapter.

2.6 References

1. Macomber, R. S., NMR Spectroscopy: Essential Theory and Practice, Harcourt Brace Jovanovich, San Diego, **1988**.
2. Abraham, R. J.; Fisher, J.; and Loftus, P., Introduction to NMR Spectroscopy, John Wiley & Sons, New York, **1988**.
3. Slichter, C. P., Principles of Magnetic Resonance, Springer-Verlag, New York, 3rd Ed., **1990**.
4. Haeberlen, U., High Resolution NMR in Solids: Selective Averaging, Academic Press, New York, **1976**.
5. Fyfe, C. A., Solid State NMR for Chemists, CFC Press, Guelph, **1981**.
6. Bruch, M., NMR Spectroscopy Techniques, Marcel Dekker Inc., New York, 2nd Ed., **1996**.
7. Harris, R. K., Nuclear Magnetic Resonance Spectroscopy, Pitman, London, **1983**.
8. Abragam, A., Principles of Nuclear Magnetism, Clarendon Press, Oxford, **1961**.
9. Sanders, J.; and Hunter, B., Modern NMR Spectroscopy: A Guide for Chemists, Oxford University Press, Oxford, 2nd Ed., **1993**.
10. Farrar, T.; and Becker, E., Pulse and Fourier Transform NMR: Introduction to Theory and Methods, Academic Press, New York, **1971**.
11. Raftery, D. and Chmelka, B. F., NMR Basic Principles and Progress: Solid-State NMR I: Methods, Springer-Verlag, New York, **1993**.
12. (a) Ratcliffe, C. I., *Annual Reports on NMR Spectroscopy*, **1998**, 36, 123-221. (b) Hunt, E. R.; Carr, H. Y.; *Physical Review*; **1963**, 130, 6, 2302-2305.
13. Springuel-Huet, M. A., Physical Adsorption Experiment, Theory and Applications, Kluwer Academic Publishers, Netherlands, **1997**.
14. Ripmeester, J. A., Ratcliffe, C. I.; Inclusion Compounds, Oxford University Press, Oxford, England, **1991**, v. 5, 37.
15. Ripmeester, J. A., Tse, J. S., Ratcliffe, C. I., Powell, B. M.; *Nature*, **1987**, 325, 135.
16. Ripmeester, J. A., Ratcliffe, C. I.; Tse, J. S.; *J. Chem. Soc. Faraday Trans.*, **1988**, 84, 3731.

17. Ripmeester, J. A., Davidson, D. W., *J. Mol. Struct.*, **1981**, 75, 67.
18. Pietras, T.; Gaede., H.; Bifone, A.; Pines, A. and Ripmeester, J. A., *J. Am . Chem. Soc.*, **1995**, 117, 7520.
19. Pietras, T. and Gaede., H., *Adv. Mater.*, **1995**, 7, 10, 827.
20. Walker, T and Happer, W., *Rev. Mod. Phys.*, **1997**, 69, 2, 629.
21. Jameson, K.; Jameson, C.; and Gutowsky, H. S., *J. Chem. Phys.*, **1970**, 53, 6, 2310.
22. Augustine, M.; and Zilm, K., *J. Chem. Phys.*, **1996**, 150, 8, 2998.

Chapter III

Towards the Understanding of the Kinetics of Clathrate Hydrate

3.1 Introduction

The industrial interest in gas hydrates began with the discovery that hydrate formation could plug natural gas pipelines.¹ Much of the subsequent research has focused on understanding the conditions of hydrate formation. As a result of extensive thermodynamic studies, considerable hydrate phase equilibrium data and methods to predict hydrate formation conditions are now available.²⁻⁴ In contrast to the advances made in the thermodynamics of hydrates, the kinetics of hydrate formation are less well understood. The kinetics of clathrate formation has been previously studied by a volumetric method,⁵ a technique which does not give information on a molecular scale. It is of interest to search for evidence of precursor structures or other evidence of non-equilibrium behaviour.⁶ As the equilibrium cage occupancy ratios often differ from the stoichiometrical value of three, even after long equilibration times,⁷ it is of particular interest to follow the favourable occupancies of the cages. A good understanding of the hydrate formation kinetics would allow the exploitation of the kinetics mechanism to depress the hydrate formation rate.

3.2 General Understanding of Hydrate Formation and Decomposition

The hydrate formation process is analogous to the crystallization process. As in crystallization, the hydrate formation process can be sub-divided into a nucleation and a growth process. Figure 3.1 displays the typical gas uptake sigmoid curve indicating each process. Hydrate nucleation is the process of forming critically-sized, stable hydrate nuclei, and hydrate growth is the process of growth of these stable nuclei.

Figure 3.1 Typical sigmoid curve of gas-uptake hydrate experiments.

3.2.1 Hydrate Nucleation

The hydrate nucleation process refers to the formation and growth of hydrate nuclei to critical size. The growing clusters of gas and water molecules can be regarded as precursors to hydrate nuclei formation.⁸ Sloan et al.^{1,9} consider these as “labile clusters” and their size depends on the size of the gas molecules.

A growing hydrate nucleus that attains the critical size is a stable nucleus and immediately leads to the formation of a hydrate crystal. The period during which the clusters are formed and grow to critically-sized nuclei is known as the induction period.^{2,5} CO₂ hydrate formation experiments using water from different sources showed that the mean induction period varied with the treatment of water used.¹⁰ In these experiments a shorter induction period was observed when the water had been previously frozen as ice and melted than compared to nontreated water.¹⁰ This phenomenon is known as the “memory effect”, and has been observed in a number of studies concerning the formation of hydrates in aqueous conditions.¹⁰⁻¹³ Melt ice was found to play an important role in hydrate nucleation. After the ice melts, water is thought to retain some of its structure in the liquid phase and this structure serves as a template for hydrate nuclei formation.¹³ Since heating the melt water before hydrate nucleation increases the induction period (a vanishing of the memory effect), it was concluded that the structure present in the liquid phase is metastable; it does not involve either the small cracks in the vessel walls nor dissolved impurities.¹⁰ The mechanism of hydrate nucleation needs to be experimentally studied and understood before any modelling at a molecular level can be accomplished.

3.2.2 Hydrate Growth

The hydrate growth process refers to the growth of stable hydrate nuclei as solid hydrates, and several research groups have studied this process. Barrer and Edge¹⁴ studied the formation of simple hydrates using a shaking steel ball-mill-type apparatus to renew the ice surface that was converted to hydrate. They found that hydrates formed from ice with agitation and an induction period of about one-hour was observed for krypton. During the induction period, the krypton conversion to hydrate was negligible, but induction was followed by a rapid growth of hydrate (crystal growth) before a gradual decline due to the exhaustion of ice. Barrer and Edge did not explain why krypton alone exhibited the induction period.

Falabella¹⁵ used an apparatus similar to the one used by Barrer and Edge, and determined both the equilibrium and kinetic properties of methane, ethane, acetylene, carbon dioxide and krypton. He was not only able to duplicate the results obtained by Barrer and Edge, but also obtained induction periods for krypton and methane. Again, no explanation was given for the induction period of methane or krypton hydrate.

Sloan⁵ proposed a kinetic model in order to understand the induction periods observed for methane and krypton. This model suggests the importance of a nucleation rate and its relation to the guest:cavity size ratio. Since krypton and methane lie close to the lines in Figure 1.4, these molecules exhibit the most non-stoichiometry due to their inability to fit securely within the cavity. Sloan suggests that the observation of the induction for these molecules is due to the oscillation between the 5¹² cavities of sI and sII, before sI achieves the critical nuclei radius stability for simple methane hydrates (or before sII attains critical size for stability of simple krypton hydrates).

Sloan's mechanism of hydrate formation consists of a series of consecutive reactions.⁵ Figure 3.2 presents a schematic of Sloan's hypothesis of the mechanism for hydrate nucleation. In Figure 3.2A, ice is shown together with gas and liquid water. It is assumed that the impingement of the steel balls in the ice/hydrate surface provides sufficient mechanical energy to form a mobile localized water layer, even at low temperatures. This localized liquid water layer is known as the Quasi-Liquid Layer (QLL) on the surface of ice.¹⁶ This QLL on the surface of ice will be explored further in Chapter 4. Sloan explains that this localized liquid water enables the dissolution of gas in the water at the gas surface of the ice/water interface. Since the ice arrangement must undergo considerable relocation to form the pentagonal faces of the hydrate cages, Sloan predicts that this liquid layer must be present on a local scale.

Figure 3.2B represents the formation of the basic 5^{12} cavities as labile species within the liquid film at the ice surface. Sloan suggests that the 5^{12} structure is most favored because it maximizes the number of bonds (30) to molecules (20) along the surface, relative to similar cavities.² Since the 5^{12} cages of both sI and sII differ by 0.5%, Figure 3.2B shows very rapid interconversion between the two structures.

Two parallel paths follow the state in Figure 3.2B. The top path is followed for the construction of sI hydrates while the bottom path is for the formation of sII. The agglomeration of the clusters in Figure 3.2C is a direct consequence of "hydration bonding".⁵ This bond exists when apolar molecules inside clusters of water are attracted to each other.² The sharing of labile cluster "faces" is viewed as a thermodynamic tendency to minimize the negative entropy of solution.⁹ In Figure 3.2C, the unit crystals of either structure are formed. At this point the structures are long-lived but unstable. As

Figure 3.2 Proposed kinetic mechanism for hydrate formation from ice.⁵

long as the unit crystals are not beyond the critical size for growth, some may shrink to the left (Figure 3.2B) or grow to combine with other unit crystals to give the structures of Figure 3.2D. When the species have grown to this state, they have grown beyond the critically-sized crystals, so that they grow monotonically.⁵ This represents the end of the primary nucleation period and the species in Figure 3.2D can grow until either the ice or gas phase is depleted.

Sloan attempted to quantify the physical mechanism in Figure 3.1 by considering the progression from no hydrate (Figure 3.2A = [A]) to a stable growing crystal (Figure 3.2D = [D]). This hypothesis was constructed such that gas and water are in excess. The dependence of each species concentration was then written with first-order chemical kinetics as follows:

$$d[A]/dt = -k_1[A] \quad (3.1)$$

$$d[B]/dt = k_1[A] - k_2[B] \quad (3.2)$$

$$d[C]/dt = k_2[B] - k_3[C] \quad (3.3)$$

$$d[D]/dt = k_3[C] \quad (3.4)$$

where [A], [B], [C], and [D] represent the concentration of each hydrate species, with initial conditions of $[A] = [A_0]$ and $[B_0] = [C_0] = [D_0] = 0$.⁵

The rate constants (k_1 , k_2 , and k_3) were obtained by fitting Falabella's data.¹⁵ An Arrhenius plot of the rate constants versus inverse temperature was plotted indicating a very small activation energy. It was found that longer induction periods go along with smaller rate constants, which confirmed an intuitive view that hydrate formation reactions proceed faster at lower temperatures. Sloan also points out that additional information is still required in order to refine the hypothesized mechanism. One type of information

needed is the nature of precursors, which can be obtained only from spectroscopic data. To date, no other molecular mechanism is available for comparison.

3.2.3 Hydrate Decomposition

Hydrate decomposition has not been studied as extensively as hydrate formation. Bishnoi and co-workers¹⁷ have conducted experiments on methane hydrate decomposition. In their experiments, hydrates were formed at a pressure above the three phase equilibrium region. Decomposition was initiated by a drop in the pressure while maintaining a constant temperature. The data suggest that the hydrate decomposition may be viewed as a two step process: the destruction of the clathrate host lattice at the particle surface followed by the desorption of the guest molecule from the surface.

Makogon¹⁸ suggests that, upon hydrate decomposition effected by lowering the pressure or raising the temperature, the molecules of gas emerge from the fixed cavities formed by water molecules, and the cavities themselves generally remain intact. These cavities, he explains, exist in water as large aggregates. This may come as an explanation for the memory effect phenomena discussed earlier.

3.3 Scope of Study

Conventional ^{129}Xe NMR spectroscopy is a useful tool for monitoring the occupancy of each cage size, but its sensitivity is far too low to detect signals on the time scale required to study clathrate hydrate formation. The use of hyperpolarized (HP) Xe, however, allows for signal detection following a single rf pulse with sufficient sensitivity.²⁹ In the remainder of this chapter, a ^{129}Xe NMR study of the formation and decomposition of xenon clathrate hydrates using HP Xe is presented.

3.4 Experimental Section

3.4.1 Optical Pumping

3.4.1.1 Preparation of Optical Pumping Cells

The optical pumping cell used was a 6 cm long, 35 mm inner diameter Pyrex cylinder ($\sim 50 \text{ cm}^3$ volume) with flat windows and equipped with an Ace 3 mm HV valve. Optical pumping cells were made of Pyrex glass. The cells had a high vacuum valve that allowed the user to release a desirable amount of HP gas. Figure 3.3 displays the reusable cell. Once manufactured, the cells were cleaned with a highly corrosive solution called *Pirhana*, which was made up of a 7:3 volume ratio of concentrated H_2SO_4 (BDH) and 30% H_2O_2 (BDH). Cells were treated with this solution for 30 minutes, rinsed with deionized water (10 times) and air-dried.

The cells were coated with a 10% SurfaSil siliconizing fluid (Pierce Scientific) in an n-pentane solution. Cells were filled with this solution and then set aside for 30 minutes. The cells were emptied and set to drip-dry while inverted for 2½ hours. After rinsing with 5 mL n-pentane, the polarisation cell were air-dried and evacuated overnight in vacuum. Rubidium loading was carried out under dry-box conditions. Rubidium was placed directly in the main body of the cell. Filling the cells with the desired amount of natural abundance ^{129}Xe gas (obtained from Matheson) followed this procedure.

3.4.1.2 Polarization Procedure

Laser-polarized ^{129}Xe was produced by spin-exchange with Rb using a semiconductor diode array laser (Opto Power Corporation, Tucson, AZ) which provided approximately 30W of linearly polarized light centered at 794.7 nm with a line width of 2.8 nm. Circular polarization of the light was provided by 1/4 wave plate, placed between the laser and the cell. The pumping cell was placed in a home-built oven at a temperature of

Figure 3.3 Schematic of optical pumping cell used in hydrate experiments.

approximately 95 °C. The oven sat in a magnetic field of ~15 Gauss provided by a pair of Helmholtz coils. The magnetic field was parallel to the propagation vector of the light. The pumping cell was irradiated and heated for 20-30 minutes. Figure 3.4 displays the optical pumping set up.

3.4.2 NMR Measurements

All NMR measurements were performed on a DSX 400 Bruker NMR Spectrometer, operating at a magnetic field of 9.4 T. The Larmor frequency for ^{129}Xe was 110.3 MHz. A 10 mm double-tuned broad band high-resolution probe was used for all measurements, which had a Xe 90° pulse of 22-25 μs .

3.4.2.1 Preparation of Ice Sample

The ice sample was prepared by dripping D_2O (Aldrich) in a mortar, which sat in liquid nitrogen. The ice droplets were quickly ground up with a pestle and transferred into a NMR sample tube. The specific surface area for ice prepared in this way was consistently $5.1 \pm 0.8 \text{ m}^2\text{g}^{-1}$ as obtained from the modified BET technique. The powdered ice (0.3-0.5 g) was transferred to a cold NMR tube equipped with a high vacuum fitting (Ace Glass Inc.), and inserted into the cold NMR probe. The gas transfer line with attached sample was connected to a high vacuum system, thus allowing exposure of the sample to vacuum or gas as needed. Figure 3.5 shows the NMR experimental set-up. Before adsorption of optically polarized xenon the ice was evacuated for 30-40 minutes to minimize adsorbed oxygen.

The probe and ice sample was cooled to the desired temperature via a flow of cold nitrogen to the dewared sample region. The pumping cell with polarized xenon was also attached to the vacuum line, and the gas was allowed to contact the samples after

Figure 3.4 Optical pumping set-up.

Figure 3.5 Gas transfer line and NMR set-up.

evacuating the line for 5-7 minutes. A VM1500 digital manometer (EBRO Electronic) was used to monitor pressure changes directly in the line (the volume of the line is approximately 25 mL), allowing for an estimation of the quantity of hydrate formed from the pressure difference at the beginning and the end of the experiment.

3.4.2.2 Kinetic Experiments

Kinetic experiments were performed using an automation program for kinetic type measurements, which consisted of small tip angle rf pulses at the ^{129}Xe Larmor frequency, with a pulse length of $2\ \mu\text{s}$ followed by a variable delay list set by the user. This delay list ranged from 0.2 - 10 s. In order to improve accuracy, data acquisition was started before the admission of the gas. These pre-zero points were then eliminated and the time scale was shifted in order to have $t = 0$, corresponding to the initial exposure to HP Xe. Kinetic experiments were performed at temperatures 193 – 243 K and pressures ranging from 400 – 1400 mbar. The kinetics of the following processes were studied:

- a) Test on induction period: Hyperpolarized ^{129}Xe was loaded on a “fresh” ice¹⁹ sample at different temperatures while keeping the initial Xe gas pressure constant, and at different Xe initial gas pressures while keeping the temperature constant.
- b) Hydrate decomposition: The surface hydrates were decomposed via exposure to vacuum.
- c) Test on memory effect: Hyperpolarized ^{129}Xe was loaded on the surface of a “previously exposed” ice¹⁹ sample at different temperatures while keeping the initial Xe gas pressure constant, and at different Xe initial gas pressures while keeping the temperature constant. The “exposed” samples were evacuated continuously for a period 15-120 minutes.

- d) Double hydrate formation: The kinetics of double hydrate formation of Xe/ethane and Xe/propane were followed using different Xe:hydrocarbon ratios at 223K.

3.5 Results and Discussion

3.5.1 Test on Induction Period

Figure 3.6 shows the typical ^{129}Xe NMR single-scan stacked plot spectra obtained at different times t elapsed after the introduction of hyperpolarized Xe to the ice surface. Three distinct peaks are observed. The gas peak is the reference peak at 0 ppm. The signal at ~ 150 ppm is attributed to xenon in the larger $5^{12}6^2$ cages, and the one at ~ 240 ppm is attributed to xenon in the smaller 5^{12} cages.²⁵ It is relevant to emphasize that the three resonances assigned to xenon in the small cage, large cage and gas phase were the only ones observed. The xenon pressure decreased during each experiment once exposed to the surface. Since it is known that xenon forms a clathrate layer on the surface of the ice, which is impenetrable by xenon,²⁰ we assume that excess xenon was available throughout the experiments. The permanent presence of the xenon gas signal in the spectra supports this assumption. It also should be noted that the experiment goes to completion well within the lifetime of the hyperpolarized state of the xenon, the only manifestation of the xenon relaxation being a steady decline in the signal level as time passes. We can conclude that the reaction stops when the thickness of the hydrate layer is enough to become a serious barrier to easy gas transport. Of course, complete conversion to hydrate would take place on a sufficiently long time scale as long as sufficient gas is available at sufficiently high pressure. Since we have estimates of the surface area and know the total gas uptake from the pressure drop, the thickness of the hydrate layer can be estimated. Again, this depends on the exact conditions of the experiment, and varied

Figure 3.6 ^{129}Xe NMR stacked plot spectra of the adsorption of hyperpolarized Xe on D_2O ice at 243K.

between 20 and 100 unit cells (at 12 Å/unit cell this amounts to layer thickness between 500 and 1500 Å).

The spectra were analyzed by integrating the signals and plotting the values as a function of time (Figure 3.7a). It is interesting to note that there is very little intensity in the cage resonance lines at the early stages of the reaction. This induction period is followed by a very rapid increase in intensity, corresponding to a rapid formation of gas hydrate. By looking at the ratio of intensities for the small and large cage resonances, a better understanding of the induction period can be obtained. At equilibrium, the clathrate hydrate lattice has three times as many large cages as small ones. Previous NMR and composition studies have shown that only $\frac{3}{4}$ of the small cages are filled.²¹ Therefore the overall cage occupancy ratio is expected to be 4:1. Figure 3.7b is the representative graph of the integral intensities of xenon in the large to small cages as a function of time after the admission of xenon. This figure shows that during the initial period of exposure, the experimental ratio changes rapidly and does not reach the expected occupancy ratio of 4:1 at the start. During the initial period the experimental ratio changes rapidly with time, but levels off completely at the start of the period of rapid growth. The plot is characteristic of all of the experimental runs, that is the occupancy ratio becomes constant approximately at the time that the rate increases, i.e. at the end of the induction period.

It can then be concluded that this region is the nucleation region, and that the region of constant composition is that of growth of the hydrate crystal, which commences only after the nucleation phase is complete. It can also be noted from Figure 3.7b that the cage occupancy ratio approaches a 1:1 ratio, thus favoring the smaller cages at the shortest times of hydrate formation. The sensitivity still is not enough to reliably follow the ratio

Figure 3.7 Representative graph of integral intensities: (a) as a function of time of Xe absorbed on “fresh ice” sample of D_2O ice at 243K , $P_{\text{start}} = 580\text{ mbar}$, and (b) ratios of xenon on the large to small cages as a function of time after exposure of xenon.

to its earliest values. However, it can be concluded that the early stages of hydrate formation involve the reorganization of water around xenon atoms to give a coordination of water molecules that develops into the 5^{12} cage in the crystal. These findings are consistent with Sloan's nucleation model, in terms of the initial relocation of 20 ice lattice molecules to form the 5^{12} cage.

The occupancy ratio depends on pressure and temperature, increasing with the temperature and decreasing with the pressure as seen on Figures 3.8a,b. Figure 3.9 shows the 3D plot of variation in occupancies with the temperature and pressure.

Since we are dealing with a polycrystalline system, there will be many absorption sites, and therefore, many potential nucleation sites. If nucleation is taken to be a statistical event, the overall sample composition at any time reflects a superposition of all nucleated and pre-nucleated states. Therefore, as explained earlier, rapid growth only occurs after the average composition becomes that of a stable crystal. The time preceding rapid hydrate growth is the induction period. In this study, a molecular interpretation of the induction period as the average time for adsorption of xenon, reorganization of the ice surface around the xenon atom to first form the 5^{12} and nucleation of hydrate crystals is given.

The induction period can also be studied systematically as a function of temperature and pressure. Table 3.1 displays the results from the variable temperature and pressure experiments. Figure 3.10 shows the effect pressure has on the induction period. As the pressure is increased the induction period is decreased. Figure 3.11 also shows the 3D plot of variation in induction period with the temperature and pressure. It was found that as the temperature was decreased the induction period decreased. These findings are in

Figure 3.8 (a) Occupancy ratio as a function of pressure for xenon hydrate on the surface of ice at 223K.

(b) Occupancy ratio as a function of temperature for sI Xe hydrate on the surface of ice at $P_{\text{start}} = 600\text{-}700\text{ mbar}$.

Occupancies ratio vs. Pressure and Temperature

Figure 3.9 3D plot of the occupancy ratios as a function of temperature and pressure of experiment for Xe hydrate on the ice surface.

Temperature (K)	Initial Xe Pressure (mbar)	Induction Period (sec)
193	724	250
193	745	160
203	575	215
203	755	100
213	372	85
213	538	42
213	856	32
223	386	300
223	663	110
223	687	85
223	740	80
223	758	120
223	760	80
223	825	100
223	837	70
223	884	60
223	1358	10
233	425	140
233	1013	28
243	622	200
243	706	428

Table 3.1 Temperature and initial pressures used in adsorption experiments on “fresh” ice surface along with the resulting induction periods.

Figure 3.10 Induction time as a function of pressure for Xe adsorbed on “fresh” ice at 223K.

Figure 3.11 3D plot of the induction time as a function of temperature and pressure of experiment for Xe hydrate on the "fresh" ice surface.

agreement with many hydrate kinetic studies.^{5,13,22,23} It can thus be concluded that the induction period is a complex function of pressure and temperature and represents an average time for the completion of a very large number of statistical events.

3.5.2 Hydrate Decomposition and Testing the Memory Effect

The surface hydrate can be decomposed by its exposure to a vacuum at a constant temperature. This decomposition was followed using HP ^{129}Xe NMR spectroscopy. Figure 3.12 shows the single scan HP ^{129}Xe NMR stacked plot spectra for the decomposition of Xe hydrate. This process is visualized as the destruction of the clathrate host lattice at the surface of the particle followed by the desorption of the guest gas molecule from the surface. The kinetics of decomposition can be fitted as a single-exponent decay (i.e. as first-order kinetics). From the temperature dependence of the decomposition constant the activation energy of $37 \pm 7 \text{ kJ mol}^{-1}$ is estimated (Figure 3.12A). The activation energy for decomposition is somewhat less than the known activation energy for water self-diffusion in the ice lattice, 55 kJ mol^{-1} , which in turn is close to the activation for water self-diffusion in the xenon hydrate, 50 kJ mol^{-1} .²⁴

An important question for further discussion of the nature and kinetics of the surface hydrate formation is how much hydrate has been left on the surface after evacuation. We tested this by measuring the amount of xenon released after melting the samples after evacuation. At 223 K, where most experiments were done, the amount of residual xenon did not exceed 2% of the initial pressure after 20 minutes of evacuation.

Re-exposure of the ice surface (after evacuation) to hyperpolarized xenon yields the absence of the induction period and rapid hydrate growth commences as soon as xenon reaches the surface, as seen in Figure 3.13. Figure 3.13 displays the dependence of the

Figure 3.12 ^{129}Xe NMR stacked plot spectra of the decomposition of surface hydrate in vacuum at 223K. Inset A shows the Arrhenius plot for the hydrate decomposition along with the activation energy of the process.

Figure 3.13 ^{129}Xe NMR stacked plot of hyperpolarized xenon at 243K: sample of (a) “fresh” ice and (b) “pre-exposed” ice sample.

induction period on the history of the surface. These results suggest that the ice surface is left “pre-organized” for hydrate growth after evacuation, and the initial building of the 5¹² cages around xenon as precursor building blocks for the crystalline hydrate is not necessary. As previously discussed, this phenomenon is known as the memory effect. The results obtained thus far in the literature all concern the memory effect on hydrates forming from water. This is the first study in which ice is used to test the memory effect.

If the surface “remembers” its previous state structure, one also should be able to measure the rate at which the surface “forgets” its pre-organized state. This was studied by lengthening the time between desorption and re-adsorption of xenon. Variation of induction time with the evacuation time between consecutive admission of xenon at 223K is shown in Figure 3.14. After 2 hours of continuous pumping about 50% of induction time has returned. Further, an increase in temperature accelerates decomposition of the surface ice/hydrate structures. Thus, if the sample temperature is increased from 223 to 243K, the induction time will be almost completely restored after only 1 hour. With these results, it can be concluded that the ice surface is left in an “pre-organized” state, which virtually eliminates the induction period and allows for faster hydrate growth. This further indicates that the induction period is not only a complex function of temperature and pressure, but also of initial ice surface condition.

3.5.3 Proposed Kinetic Hydrate Formation Model

The mechanism of any heterogeneous reaction is generally considered to include two or more of the following four types of elementary steps: sorption phenomena, reaction at the atomic or molecular scale (homogeneous or interface reactions), nucleation of new phase and transport phenomena (diffusion of reactant and products).

Figure 3.14 Induction time as a function of evacuation time between consecutive admissions of xenon at 223K.

Usually one of these steps is rate determining and thus influences the overall reactivity of the system. The rate-determining step is often reflected in the experimentally observed dependence of the extent of the reaction as a function of time. Commonly the sigmoid shape of the curve, i.e. Figure 3.1, serves as an indication that nucleation as the most important step.

The net equation for the hydrate formation can be written as

As discussed earlier, the induction period observed at the beginning of hydrate formation can be interpreted as arising from the formation and growth of nuclei of the product phase, with overall rate being the product of the rates of formation of the nuclei and of nuclear growth. Beyond the inflection point of the kinetic curves the nuclei are thought to start overlapping, so that the interfacial area between reactant and product decreases and hence so does the reaction rate. Also, if the reaction product (sI hydrate in our case) forms a very compact coating on the outer surface of the reactant, then the gas cannot penetrate into the bulk, and the reaction will eventually cease.

Such type of kinetics can be generally accounted for by the Avrami-Erofeev model,²⁶ where a random nucleation followed by three-dimensional growth of isolated nuclei is assumed. The model supposes that nucleation of a product phase is equally probable on all inner and outer surfaces of the reactant crystal, and that the rate of phase boundary reaction for the growth of the product phase is constant. The rate law for the reaction can then be calculated, provided that the nucleation probability is known as a function of time. In further discussion of the kinetic model ideas developed for the description of kinetics of nucleation and chemical reactions in solid state will be closely followed.²⁶⁻²⁸

It is natural to expect that nucleation occurs only when fluctuations in the local energy are sufficient to provide the necessary activation energy for formation of the nucleus. For the adsorption of xenon and hydrate nucleation on the surface of ice, some kind of structure-sensitivity is expected, such that the nuclei are formed at definite localized spots where the activation energy is least. The number of nuclei formed in a given time will depend upon the number of these potential nucleus-forming sites as well as on the mean activation energy for nucleus formation. Potential nucleus-forming sites are usually associated with some type of lattice imperfection such as cracks, lattice defects or dislocations.

The law governing nucleus formation depends on the number of steps involved in the formation of a nucleus. Nucleation that involves only a single step is commonly associated either with an exponential or linear law.^{26,28} For this case, if there are N_0 potential nucleus forming sites, the rate of nucleus formation is

$$\frac{dN}{dt} = k_I (N_0 - N) \quad \text{or} \quad \frac{dN}{dt} = k_I N_0 \exp(-k_I t), \quad (3.6)$$

where k_I is a constant of nuclei formation (or in another terms, $1/k_I$ is the probability of this event). The number of nuclei increases with time exponentially. A limiting case of equations (3.6) for early stages of the reaction (small t) or for very small k_I (weak interaction) is

$$\frac{dN}{dt} = k_I N_0 \quad (3.7)$$

so that the number of nuclei increases linearly with time. Another possible case is when k_I is very large, so $N = N_0$, i.e. nucleation proceeds instantaneously.

Depending on the shape of the nucleus and character of the processes defining growth/disappearance of nuclei, the following general equation can be used

$$\alpha = 1 - \exp(-kt^n) \quad (3.8)$$

which is known as Avrami-Erofeev equation.^{26,28} The parameter n in this equation is closely related to the type of nucleation and its dimensionality. For spherical nuclei expanding homogeneously in all dimensions, n is equal to 4. For cylindrical nuclei (the centers of formation of the nuclei are edges or surfaces cracks) $n = 3$ and, correspondingly, for flat nuclei, $n = 2$.²⁶ The composite parameter k in the equation is a function of the number of nucleation sites N_0 , the rate constant for nucleation k_i , and the rate of the phase boundary reaction.²⁶ Since k is a combination of several other constants, its interpretation is not straightforward, and normally requires some assumptions about the mechanism of nucleation and the number of sites.

Before applying this equation to our experimental data, the original Avrami-Erofeev equation (3.8) needs to be modified to account for the ^{129}Xe NMR signal intensity decay due to the NMR rf pulses and spin-lattice relaxation. Since not all xenon nuclei are in the detection area of the probe, it is difficult to separate the contributions of each effect in total decay. To characterize this combined effect we will use some effective constant of decay T_1^* . A combination of equation (3.8) and an exponential decay function gives us the fitting function

$$I(t) = I(1 - \exp(-kt^n)) \exp(-t/T_1^*), \quad (3.9)$$

where $I(t)$ is the integrated intensity of the signals, k is the composite nucleation constant as discussed above, and n is effectively the parameter of the nucleation dimensionality. Examples of the fits of Equation 3.9 are shown in Figure 3.15. Parameters for the fits, the intensity of the relative intensity of the small and large cage (A), large to small

Figure 3.15 Examples of fittings of experimental data with equation 3.9.

occupancy ratio (L/S), and the calculated thickness of the hydrate layer (N), are summarized in Table 3.2 for each temperature.

The most important observation from Table 3.2 is the big difference in n and k for fresh and “pre-exposed” samples of ice. For all fresh samples n was consistently above 3, when for “pre-exposed” samples in most cases it is well below 3, suggesting a different nucleation dimensionality. Consideration of this trend and comparison of the corresponding hydrate layer (N) on Table 3.2 indicates that for the pre-exposed samples, the hydrate layer is smaller than for the fresh ice sample. This suggests that the “pre-organized” surface provides faster hydrate formation, but Xe is prevented from penetrating further to continue hydrate formation.

Changes in k are as large as several orders of magnitude. It appears that k also depends on pressure and temperature, certainly increasing with pressure, although less pronounceably with the temperature. Such behavior might be expected since k is a combination of concentration of nucleation sites and the probability of interaction of the sites with xenon.

The constants of effective decay T_1^* can vary by as much as 2-2.5 times for different samples, which can be a result of different concentrations of paramagnetic impurities such as O_2 . Within the same sample, however, the effective constants of decay T_1^* are essentially the same for large and cages, i.e. spin-lattice relaxation times for xenon in different cages are very close.

3.5.4 Double Hydrate Formation

In this study HP ^{129}Xe was used as a tracer of hydrate formation. Different mixture ratios of Xe:propane and Xe:ethane were used in order to test the use of HP ^{129}Xe during hydrate formation in the presence other hydrate formers.

Temperature		Sample	Pstart	Small Cage			Large Cage			N _i layer	L/S		
			(mbar)	A	k(sec ⁻ⁿ)	n	T ₁ [*] (sec)	A	k(sec ⁻ⁿ)	n	T ₁ [*] (sec)		
193K		fresh	724	0.25	9.5E-10	3.17	1341	0.83	5.9E-10	3.28	1790	37	3.40
		pre-exposed	585	0.71	4.0E-05	2.59	1877	2.05	4.0E-05	2.53	1645	45	2.87
		pre-exposed	705	0.82	5.0E-05	2.65	4149	2.42	5.8E-06	3.22	3321	29	2.96
		pre-exposed	745	0.57	3.0E-03	1.96	5000	1.68	2.7E-03	2.00	5000	32	2.96
203K		fresh	574	0.62	2.3E-11	3.85	2757	1.89	1.3E-11	3.93	2463	43	3.07
		fresh	755	0.40	1.7E-09	3.83	2111	1.19	1.4E-09	3.85	1889	27	2.95
		pre-exposed	570	0.52	1.1E-04	2.91	1743	1.52	1.0E-04	2.93	1533	42	2.94
		pre-exposed	675	0.23	1.5E-04	3.01	1553	0.69	1.1E-04	3.08	1447	23	2.96
213K		pre-exposed	835	0.10	5.6E-06	2.71	2661	0.31	4.2E-06	2.79	2492	16	3.17
		fresh	720	0.68	6.8E-08	3.29	1334	2.21	3.5E-08	3.41	1212	30	3.25
		fresh	856	0.37	2.0E-07	3.24	2253	1.23	3.2E-08	3.62	2030	45	3.37
		pre-exposed	538	0.92	2.9E-06	2.49	3383	2.93	5.1E-06	2.38	2555	36	3.20
223K		pre-exposed	770	0.26	3.1E-03	2.60	1671	0.82	2.0E-03	2.76	1503	35	3.11
		pre-exposed	758	0.20	2.0E-13	4.82	4902	0.59	4.5E-13	4.69	4537	63	2.91
		fresh	760	0.57	1.7E-08	3.78	3614	1.96	6.2E-08	3.51	3225	46	3.45
		fresh	190	1.03	1.8E-07	2.95	2367	4.03	7.1E-08	3.11	2031	25	3.92
233K		pre-exposed	333	0.73	2.4E-04	1.89	2286	2.68	1.8E-04	1.94	2022	43	3.68
		pre-exposed	580	1.09	2.0E-05	3.31	2258	3.65	2.0E-05	3.32	1975	53	3.33
		pre-exposed	760	0.38	8.1E-04	2.44	3444	1.40	1.3E-03	2.33	3213	50	3.73
		pre-exposed	942	0.29	4.3E-03	2.10	1986	0.79	2.2E-03	2.31	1595	17	2.74
243K		pre-exposed	555	0.00	2.3E-09	3.53	845	0.00	3.5E-09	3.44	830	80	3.49
		fresh	1013	0.17	7.6E-07	2.87	1881	0.55	4.7E-07	2.96	1708	15	3.32
		pre-exposed	582	0.70	9.0E-05	2.17	1897	2.34	7.0E-05	2.22	1749	29	3.36
		pre-exposed	583	0.72	2.8E-04	2.21	3039	2.85	2.7E-04	2.20	2629	101	3.97
243K		pre-exposed	920	0.17	2.2E-03	1.94	1691	0.53	2.0E-03	1.98	1573	22	3.15
		fresh	622	1.36	1.7E-09	2.82	2500	5.63	6.6E-10	2.94	2500	31	4.13
		fresh	706	0.68	4.7E-10	3.07	5000	2.21	1.4E-11	3.60	5000	58	3.25
		pre-exposed	579	0.56	1.4E-07	2.80	3074	2.26	8.6E-08	2.87	2737	76	4.07
	pre-exposed	615	0.71	3.3E-03	1.18	5225	2.92	2.7E-03	1.20	4624	64	4.09	

Table 3.2 Data on the occupancies of the small and large cages, thickness of the surface hydrate layer and parameters of fitting the experimental data with equation 3.9.

Through the comparison of the induction periods of these Xe/hydrocarbon ratios to the known xenon results, the aim is to get a better understanding of effects of hydrate formation in the presence of a second hydrate former.

3.5.4.1 Xenon/Propane Hydrate Formation

Propane is known to reside solely in the large cage of sII.² The aim was to observe the effect that propane and xenon together have on the induction period. Figure 3.16a displays the stacked ^{129}Xe NMR single-scan stacked plot spectra of a 4:1 hyperpolarized Xe:propane gas ratio on the surface of ice. Two distinct peaks are observed. The gas peak is the reference peak at 0 ppm. The signal at ~ 240 ppm is attributed to xenon entrapped in the smaller 5^{12} cages of sII. No peaks were present for xenon in the large $5^{12}6^4$ cages, and this absence is attributed to propane residing solely in the $5^{12}6^4$ cages. Figure 3.16b shows the integrated signals as a function of time. It is interesting to note that the induction period for the small cage was found to be 20 s. It is impracticable to compare this value to the induction periods obtained in the previous studies since we are dealing with a sII hydrate as opposed to sI hydrate structure.

The propane concentration in the gas mixture was increased in the 3:1 ratio experiment for which stacked plot spectra are shown in Figure 3.17a. The ^{129}Xe NMR spectra reveals the two previously mentioned peaks along with an extra peak at 160 ppm. This relatively narrow isotropic peak at 160 ppm has no induction period (Figure 3.17b) whereas the small cage peak has an induction period of 50 s. At first the 160 ppm peak was thought to be xenon entrapped in another hydrate cage, but additional blank experiments showed that this was not the case. The blank experiment was performed exactly as all other experiments, except an empty NMR tube was used. The peak at ~ 160 ppm was seen with no induction period, suggesting that the signal is from Xe dissolved in

Figure 3.16 (a) ^{129}Xe NMR stacked plot of hyperpolarized xenon and propane (4:1) at 223K.

(b) Relative integral intensity as a function of time for (a).

Figure 3.17 (a) ^{129}Xe NMR stacked plot of hyperpolarized xenon and propane (3:1) at 223K.

(b) Relative integral intensity as a function of time for (a).

propane, which liquifies under these temperature and pressure conditions.

It is hypothesized that the difference in induction periods between the 4:1 and 3:1 ratio experiments is due to lack of nucleation sites in the lower xenon concentration experiment. As the propane concentration in the gas mixture increases, liquid propane is produced. This liquid propane film coats the ice surface and prevents xenon from nucleating the small cages. This is also apparent from the relative intensities of the spectra. It can be seen that in the 4:1 mixture (Figure 3.16a), the intensity of the small cages is significantly higher than in the 3:1 ratio experiment (Figure 3.17a). It is important to note the lower signal-to-noise ratio of the gas mixture spectra compared to the pure xenon hydrate spectra (Figure 3.6). This difference is most likely due to the cross-relaxation between HP Xe and the protons of the second guest.

From these experiments it can be concluded that xenon solely prefers the small cage of sII and that more reliable information is obtained when a smaller propane gas composition percentage is used in the gas ratio due to the tendency of propane to liquify and to dissolve xenon.

3.5.4.2 Xenon/Ethane Hydrate Formation

It is known that ethane alone forms structure I hydrate in which ethane solely resides in the $5^{12}6^4$ cage.² Figure 3.18a displays the ^{129}Xe NMR stacked plot spectra obtained during the adsorption of 4:1 Xe:ethane mixture at 223K. The gas peak is referenced to 0 ppm. The signal at 155 ppm is attributed to xenon entrapped in the $5^{12}6^2$ cages, and the one at 244 ppm is due to xenon in the smaller 5^{12} cages of structure I hydrate.

Figure 3.18b shows the relative intensities of the large and small cages, and, as indicated, the induction period was 17 s. The shorter induction period, compared to the

Figure 3.18 (a) ^{129}Xe NMR stacked plot of hyperpolarized xenon and ethane (4:1) at 223K.

(b) Relative integral intensities as a function of time for a.

pure xenon hydrate experiment, indicates that the presence of a second sI hydrate former aids in the formation of the hydrate and serves as a “help gas”. One needs to note the presence of the xenon resonance at 155 ppm, which indicates that even in the mixture with ethane, xenon resides in the large cage.

The gas composition ratio was increased to 3:1 Xe:ethane. No hydrate formation could be followed using NMR spectroscopy since no ^{129}Xe peaks were observed. A pressure drop was noted, indicating that a hydrate did form, but no peaks were observed in the ^{129}Xe NMR spectrum. It was concluded that ethane effectively depolarizes hyperpolarized xenon through cross relaxation effects. The signal-to-noise ratio in the Xe:ethane hydrate spectrum is considerably less intensive compared to that of the Xe hydrate spectrum (Figure 3.18, 3.6). At higher concentration of ethane, depolarization of xenon becomes more significant.

The results of these experiments indicate that there are certain limitations where HP ^{129}Xe NMR can be used to follow the formation of double hydrates. The presence of a second gas can produce a significant depolarization of HP ^{129}Xe , with the consequence that no hydrate formation can be followed by this technique.

3.6 Conclusion

Using HP ^{129}Xe NMR spectroscopy, the formation of Xe clathrate hydrate was monitored. Under different conditions it was found that the kinetics of the hydrate formation depends on the temperature, xenon pressure and the history of the surface treatment. The concentration of occupied small cages relative to large cages was found to be higher at the initial moments after adsorption, which could indicate a special role of the 5¹² cage in Xe hydrate precursor formation. The equilibrium is reached within 20-100 s, depending on the experimental pressure and temperature. The decomposition of

the clathrate hydrate leaves the surface “pre-organized”, therefore eliminating the induction period for hydrate re-formation.

HP ^{129}Xe NMR spectra were used to monitor the formation of ethane sI and propane sII hydrates. Xenon was found to reside in both small and large cages of sI in the presence of ethane. Ethane and propane both effectively depolarize xenon through cross relaxation. In the presence of propane, only sII hydrate was formed, and xenon was found to reside solely in the small cages. At higher propane:Xe ratios, propane was found to liquify, dissolving Xe, thus increasing the induction period of hydrate formation.

3.7 Future Work

It is important to note that the hydrate formation kinetic conclusions apply only to single sI hydrate formers, which can occupy both small and large cages. It is suggested that for these hydrate formers, the smaller hydrate cage must first be formed for the hydrate to grow. An extension to this study would be to investigate those sI hydrate formers that can only reside in the large cage without the use of HP Xe, e.g. ethane. It is expected that a different type of kinetics would be encountered since in the absence of xenon, there is no guest that would occupy the small cages to initiate hydrate growth.

A similar type of kinetic hydrate formation study is also needed to understand the behaviour of sII hydrate. In this case the smaller cage is more predominant than the larger cage, and therefore it will be of great interest to further study those sII hydrate formers that solely reside in the large cage, e.g. propane, without xenon.

As seen from the Xe/ethane and Xe/propane experiments, HP ^{129}Xe depolarizes much more rapidly in the presence of these other hydrate formers. A further study is needed to determine the depolarization mechanism, as it was only hypothesized to be due to the cross relaxation between the two guests.

3.8 References

1. Hammerschmidt, E. G., *Ind. Eng. Chem.*, **1934**, 24, 851.
2. Sloan, E.D., Clathrate Hydrates of Natural Gases, 2nd edition, Marcel Dekker Inc., New York, **1998**.
3. Holder, G. D., Corbin, G., Papadopoulos, K. D. *Ind. Eng. Chem.*, **1980**, 19, 282.
4. Englezos, P., Bishnoi, P. R., *Ind. Eng. Chem. Res.*, **1991**, 30, 1655.
5. Sloan, E. D., Fleyfel, F., *AIChE J.*, **1991**, 37, 1281.
6. Ripmeester, J. A., Ratcliffe, C. I., Klug, D. D., Tse, J. S., *N.Y. Acad. Sci.*, **1994**, 715, 161.
7. Ripmeester, J. A., Davidson, D. W., *J. Mol. Struct.*, **1981**, 75, 67.
8. Englezos, P., Bishnoi, P. R., *Fluid Phase Equilibria*, **1988**, 42, 129.
9. Christiansen, R. L., Sloan, E. D., *N.Y. Acad. Sci.*, **1994**, 715, 283.
10. Takeya, S., Hori, A., Hondoh, T., Uchida, T., *J. Phys. Chem. B*, **2000**, 104, 4164.
11. Monfort, J. P., Nzihou, A., *N.Y. Acad. Sci.*, **1994**, 715, 555.
12. Baez, A. L., Clancy, P., *N.Y. Acad. Sci.*, **1994**, 715, 177.
13. Hwang, M. J., Wright, D. A., Kapur, A., Holder, G. D., *J. Incl. Phenon. Mol. Rec. Chem.*, **1990**, 8, 103.
14. Barrer, R.M., Edge, A. V., *Proc. Roy. Soc.*, **1967**, A300, 1.
15. Falabella, B. J., Ph. D. Dissertation, U. of Mass., Amherst, MA, **1975**.
16. Wettlaufer, J. S., Dash, J. G., *Scientific American*, **2000**, 282, 50.
17. Kim, H. C., Bishnoi, P. R., Heidenmann, R. A., Rizvi, S. S. H., *Chem. Eng. Sci.*, **1987**, 42, 1645.
18. Makogon, Y.F., Hydrates of Hydrocarbons, PenWell Publishing Co., Oklahoma, **1997**.

19. Ice samples quoted "fresh" samples are those that have had no xenon absorbed on the sample before, samples quoted "previously exposed" are those samples that have been previously exposed to xenon once or even more times, and before the next exposition it was evacuated for a certain amount of time.
20. Barrer, R. M., Ruzicka, D. J., *Trans. Faraday. Soc.*, **1962**, 58, 2262.
21. Davidson, D. W., Handa, Y. P., Ripmeester, J. A., *J. Phys. Chem.*, **1986**, 90, 6549.
22. Vysnisauskas, A., Bishnoi, P. R., *Chem. Eng. Sci.*, **1983**, 38, 1061.
23. Vysnisauskas, A., Bishnoi, P. R., *Chem. Eng. Sci.*, **1985**, 40, 299.
24. Davidson, D. W., Ripmeester, J. A., *Inclusion Compounds*, vol. 3, edited by J.L. Atwood, J. E. D. Davies and D.D. MacNicol, Academic Press, New York, 1984.
25. Ripmeester, J. A., Tse, J. S., Ratcliffe, C. I., Powell, B. M.; *Nature*, **1987**, 325, 135.
26. B.V. Erofeev, *Comptes Rendus de l'Academmmie des Sciences de l'URSS*, **1946**, 52, 511.
27. (a) M. Avrami, *J. Chem. Phys.*, **1939**, 7, 1103; (b) M. Avrami, *J. Chem. Phys.*, **1940**, 8, 212; (c) M. Avrami, *J. Chem. Phys.*, **1941**, 9, 177.
28. P.W.M. Jacobs, F.C. Tompkins in *Chemistry of the Solid State*, ed. W.E. Gardner, Academic Press, London 1955, p. 184.
29. Raftery, D., Long, H., Meersmann, T., Pines, L., *J. Phys. Rev. Lett.*, **1991**, 66, 584.

Chapter IV

Quasi-Liquid Layer on ice: a ^1H NMR Study

4.1 Introduction

The properties of the ice surface have attracted scientific interest since Faraday's proposal on the existence of a thin water layer on the surface of ice in equilibrium with the bulk at temperatures below the bulk melting point.¹ This mobile phase, the so-called quasi-liquid layer (QLL), is known to play an important role in phenomena such as regelation, adhesion, snow metamorphism, the abnormally low coefficient of friction of ice and crystal growth.² These all occur at temperatures below the melting point of ice. The widely-held theory of the existence of QLL is based on the same phenomenon seen with surfaces: that the free energy of the solid surface is lowered when a liquid layer exists.²⁻⁵

The QLL on the surface of ice has been incorporated in some gas hydrate formation models and is presumed to take part in hydrate growth.⁶ In this study, the presence of QLL on the surface of ice and its possible role in hydrate formation is investigated by ^1H NMR spectroscopy.

4.2 QLL: Perspectives on Previous Experiments

Many theoretical and experimental studies have been carried out ever since Faraday's proposal. Fletcher³ discussed theoretically the stability of the QLL on the basis of the interaction energy between water molecules at the ice crystal surface, and indicated that the layer is energetically favored at temperatures above -5 ± 3 °C. Furthermore, the thickness of the QLL (1 to 4 nm) increases as the temperature approaches 0 °C.

In order to investigate the existence of this transition layer, experiments have been carried out using various spectroscopic techniques including NMR spectroscopy. Proton NMR spectra^{7,8} of ice between -20 °C and the melting point are composed of a narrow component centered on top of a broad line. The narrow component was attributed to mobile water trapped between growing crystals or, possibly to non-hydrogen-bonded water molecules in spaces in the ice lattice.⁸

Bell and co-workers⁹ observed the narrow component at temperatures well below -50 °C. They postulated that impurities, such as dissolved gases, present in the ice could not be the direct cause of the apparent presence of the liquid water in “pure” ice. However, attempts to observe the narrow component in a relatively pure ice sample were unsuccessful. Although a narrow component was observed in some of their vapour deposited ice samples, neither the preparation of such samples nor the subsequent temporal behaviour of the line was reproducible. Barer and coworkers found that an increase in temperature is accompanied not only by an increase in the thickness of the liquid layer, but also by a decrease in its viscosity.¹⁰

Mizuno and Hanafusa¹¹ used ^1H NMR spectroscopy to investigate the dynamical properties of the QLL, along with the correlation time for rotational molecular motion in the QLL. They obtained variable temperature ^1H NMR spectra for the surface mobile phase of ice particles of less than 150 μm in diameter made by freezing supercooled water, and were unable to detect the narrow signal at any temperature when only bulk ice was used. The measurements were made with increasing the temperature from -100 °C to -5 °C and the ^1H NMR spectrum was obtained after 200 scans. The ^1H NMR signal revealed a broad signal which was attributed to the crystalline ice, and a narrow signal

component was attributed to a mobile phase at an interface between air and crystalline ice and/or at grain boundaries.¹¹ The relative intensity (normalized to the intensity at $-5\text{ }^\circ\text{C}$) of QLL signal and line width variation was plotted against temperature. Greater intensity was expected at $-5\text{ }^\circ\text{C}$, but was not obtained due to the reduction of surface area by ice grain sintering. The molecules at the surface were found to rotate at a frequency of about five orders of magnitude larger than that of crystalline ice, but only about $1/25$ of that of a molecule in liquid water.¹¹

In this chapter, attempts are described to investigate the role of the QLL in gas hydrate formation, as seen in many gas hydrate formation studies.^{6,12,13} In Chapter 3, it was shown that the kinetics of hydrate formation can be followed by HP ^{129}Xe NMR spectroscopy. The ^{129}Xe NMR results indicate that rapid growth of hydrate crystals takes place only after an induction period. The induction period is a complex function of temperature, pressure and initial conditions, namely the ice surface. In order to understand the behaviour of the QLL under conditions such as sintering and evacuation, various ^1H NMR experiments on ice have been conducted. It is anticipated that these ^1H NMR experiments might help answer a key question concerning the QLL: does the QLL reside on the ice surface and/or at grain boundaries?

4.3 Experimental Section

4.3.1 Ice Sample Preparation

In order to test the effect of sample preparation on the behaviour of the QLL, several different techniques for making the ice sample were used throughout this work, and are described below:

1. Ice cube tray technique: Water was placed in a regular ice cube tray and frozen at -15°C in a freezer. The ice cubes were placed in liquid nitrogen, and finely ground up with a mortar and pestle. For this method several sources of water were used as described below:
 - a) *Distilled and Tap Water*. Both regular untreated distilled and tap water were used for these samples
 - b) *Aerated Distilled and Tap Water*. Air bubbles were introduced into the ice volume by saturating distilled water with air before freezing. Air saturation was carried out for a period of 5 minutes and/or 60 minutes prior to freezing.
 - c) *Degassed Distilled Water*. The amount of dissolved air was reduced by boiling distilled water for 1 hour prior to freezing.
2. Aluminum cell technique: To ensure even freezing of water samples, an aluminum cell was constructed. The cell (Figure 4.1) consisted of two aluminum plates ($10 \times 1.25 \times 8$ cm), each containing two semi-circular cavities with a radius of 7 mm and 5 cm in length. When bolted together, the plates create two cavities. Ice samples were prepared by filling the cavities with the desired water samples (below) and frozen at -15°C . This technique also used several different types of water as described below.
 - a) *Distilled, Tap and HPLC (HP) Grade Water*. Regular untreated distilled, tap and HPLC Grade (EM Science) water were used for these samples.
 - b) *Degassed Distilled Water*. Reduction of air bubbles in the ice volume was achieved by evacuating the water sample prior to freezing.
3. Vapour deposited ice technique: Ice was prepared by the slow vapor deposition of HP grade water (EM Science) at very low pressures on a cryoplate kept at 14 K.

Figure 4.1 Schematic of aluminum cell used in ice preparation.

4.3.2 NMR Experimental Procedure

4.3.2.1 NMR

Once all the water samples were prepared and frozen, the resultant ice was transferred to a 10 mm test tube for NMR spectroscopy. NMR measurements were conducted on an AMX 300 Bruker NMR Spectrometer, operating at a magnetic field 7.1 T and Larmor frequency for ^1H of 300 MHz. The decoupling channel of a double tuned broad band high-resolution probe was used for all measurements. The 90° pulse for ^1H was 17 μs . The temperature of the sample was controlled with a temperature-controlling unit with an accuracy of $\pm 0.3^\circ\text{C}$. To achieve temperature equilibrium throughout the sample, measurements were started after holding the sample temperature for 20 minutes.

4.3.2.2 Temperature Dependent Experiments

The temperature dependence of the intensity of the QLL signal was obtained by raising the temperature from 253 to 272 K. The temperature hysteresis of the QLL signal was tested by cooling these samples down to 264 K, and then rewarming them again to 272 K. The ^1H NMR spectrum for the mobile phase was an average of 128 accumulations.

4.3.2.3 Evacuation Experiments

Evacuating the atmosphere above the ice sample also tested the presence of the QLL on the surface of ice. Evacuation measurements were conducted at 271 K using a distilled-water ice rod sample. The atmosphere above the sample was evacuated with a vacuum pump connected to a gas transfer line. Figure 4.2 shows the evacuation set up.

Evacuation was conducted for a period of 20 minutes, during which ^1H NMR spectra were obtained every 5 minutes. Once evacuation was terminated, the system was opened

Figure 4.2 NMR Set-up for evacuation and gas hydrate experiments

to air and a spectrum was obtained every 10 minutes for a period of 60 minutes. This procedure was further modified by a second step. After evacuation, the system was closed to vacuum, and also to the atmosphere for a period of 20 minutes to test the recovery of the QLL under vacuum. After this, the system was opened to air and the QLL signal recovery was further followed.

4.3.2.4 ^{129}Xe Hydrate Formation and the QLL

The role of the QLL in hydrate formation was tested by exposing the surface of an ice rod to Xe at pressure above the triple point on the phase diagram. ^1H NMR temperature-dependent spectra were obtained prior to and during Xe exposure at 271K. Figure 4.2 displays the NMR experimental set-up for this type of experiment.

4.4 Results and Discussion

A common theme in the literature concerning the QLL is the lack of signal reproducibility and/or sample preparation.^{7-9,11} We also observed this with technique 1 of ice preparation. Temperature-dependent ^1H NMR spectra for this technique were not reproducible. The uneven freezing of the ice cube was suspected to be the reason this irreproducibility. As the ice cube freezes in the tray, the cube freezes from the outside inwards, and this may provide an uneven distribution of temperature, resulting in a broad distribution of the grain sizes and air bubbles.

To overcome this problem, the second ice preparation technique was used. The aluminum cell (section 4.3.1) gives a more even distribution of temperature during ice freezing and this technique provided very reproducible results for the bulk ice. Figure 4.3 shows the variation of the 300 MHz ^1H NMR spectra as a function of temperature for tap, distilled, HP grade and degassed distilled water. All signals are composed of a narrow

Figure 4.3 ^1H NMR stacked plot spectra of the QLL in Tap, Distilled, HP grade and Degassed distilled water using technique 2.

line superimposed on a broad line. The broad component of the signal is attributed to the ^1H signal from the bulk solid ice and the narrow component is attributed to the ^1H signal from the mobile phase, the QLL. The intensity of the NMR signal of the QLL peak depends largely on the type of water used (Figure 4.4).

Each point on the graph is an average of three different experimental readings and is normalized with the intensity of tap water ice sample at 272K. The highest intensity was obtained for tap water ice, followed by distilled, HP grade and finally by degassed distilled water ice. The difference in water origin provides evidence on where the QLL signal is coming from. In this series, tap water is considered to have the greatest amount of impurities, such as dissolved gases, compared to the other water types. The concentration of impurities decreases from distilled, HP grade water to degassed distilled being the “pure” ice sample. As the tap water freezes, the impurities present in the sample provide a great number of nucleation sites yielding not only a faster crystallization process, but also smaller ice grain crystals. The degassed distilled water sample has the smallest amount of dissolved gas, and thus freezes at a rate slower than the tap water sample and providing a longer crystallization time for larger grains to develop. Therefore, the QLL ^1H NMR signal arises mainly from the grain boundaries present in each sample, as evident from the highest relative intensity QLL signal obtained from the tap water ice signal. It is interesting to note that even at 253 K, the QLL signal is observed in the tap, distilled and HP grade ice water samples, but for degassed distilled ice water sample, the QLL signal does not appear until 270 K. This observation may indicate that dissolved gases in the sample affect the ice grain size.

Figure 4.4 Relative intensity of QLL signal of all waters tested as a function of temperature using technique 2. Error estimated to be $\pm 10\%$.

As previously mentioned, the narrow component was observed in ice prepared by vapour deposition but the results were not reproducible.⁹ In this study, attempts were made to observe the QLL narrow component in the ^1H NMR spectrum of vapour-deposited ice. The narrow component was not observed in any of our vapour-deposited ice samples. This result may indicate that dissolved gases, lacking in this sample, must be present in order for the QLL to exist.

The surface area between ice particles decreases during the sintering process, thus decreasing the number of grain boundaries.^{8,9,11} The effect of this process is seen when the narrow signal disappears upon warming of the ice samples.^{7-9,11} In this study, the disappearance of the narrow component due to the ice grain sintering effect was tested during the annealing, cooling and re-annealing of the ice rod. Figure 4.5a shows the ^1H NMR spectra of a distilled water ice rod during the first and second annealing. Figure 4.5b shows the relative intensity as a function of temperature for the first and second annealing. Similar results were obtained for the other types of water samples. Since the narrow signal does not disappear during both annealings, we conclude that no sintering effect occurs at these temperatures or that perhaps sintering already has occurred at temperatures lower than temperatures used in this study.

Evacuating the atmosphere above the ice rod tests the accessibility of the mobile phase to the atmosphere. Figure 4.6 shows the ^1H NMR spectra obtained during evacuation and exposure to air at 271 K. Figure 4.7 shows the relative intensities during evacuation and exposure to air as a function of time. The intensity of the QLL signal decreases to zero after 5 minutes of evacuation and is restored quantitatively upon re-opening the system to the atmosphere.

Figure 4.5 (a) ^1H NMR spectra for the QLL during 1st and 2nd annealing
(b) Relative intensity as a function of time for (a). Error $\pm 10\%$.

Figure 4.6 ^1H NMR spectra of the QLL obtained during the evacuation and exposure to air at 271K.

Figure 4.7 Relative intensity as a function of time for evacuation experiments.

The accessibility test was further studied by allowing the system to restore when still under vacuum. Figure 4.8a,b shows the restoration of the QLL signal under vacuum and after exposure to the atmosphere. It was found that the restoration of QLL signal is slower while under vacuum. This phenomenon may be partly due to the reduced thermal conductivity of the sample under these conditions and/or that during evacuation the sample is cooled, thus no QLL signal is observed. Further studies are needed to better understand this process. As the sample is opened to the atmosphere, the signal restoration is much faster and returns quantitatively. These findings indicate that the QLL is accessible to the atmosphere.

As previously stated, the QLL is used in some gas hydrate formation models and is presumed to take part in hydrate growth.⁶ A preliminary study into the QLL role in hydrate formation was conducted. Xe hydrate formation was followed by the drop of Xe pressure while simultaneously monitoring the ^1H NMR QLL signal for any changes in a distilled ice rod sample prepared using technique 2. The system was placed under dynamic vacuum for 20 minutes, then under static vacuum for 20 minutes followed by the introduction of Xe at 271K. Figure 4.9 shows the ^1H NMR spectra of the QLL prior to and after Xe exposure, and shows that no changes are observed in the QLL signal during hydrate formation. The results obtained in this initial study may suggest that the QLL does not interact with Xe during hydrate formation at these conditions. Interactions between Xe and the QLL may be restricted by the slow Xe diffusion in the bulk ice. At this point, this result is inconclusive since it cannot be stated definitely that the QLL does not take part in hydrate formation. More experiments are needed for a better understanding of this phenomenon. Two parameters that are very important are both the pressure and

Figure 4.8 (a) ^1H NMR spectra of the loss and recovery of the QLL. (b) Relative intensity as a function of time for (a).

Figure 4.9 ^1H NMR spectra of QLL before and during Xe exposure.

temperature of the experiments. The pressure and temperature used in this experiment were outside the range for which the hyperpolarized Xe experiments in Chapter 3 were conducted. Perhaps conducting a similar QLL-Xe hydrate study at lower temperatures and higher pressures may give different results.

4.5 Conclusion

A new ice preparation technique was developed, which provided reproducible results and allowed for the investigation of the properties of the quasi-liquid layer using ^1H NMR spectroscopy.

Dissolved gases in the ice sample were found to affect the intensity of the QLL ^1H NMR signal, indicating that the signal is likely caused by a mobile phase at the ice grain boundaries.

The behavior of the QLL ^1H NMR signal during annealing of the ice sample due to the sintering effect was investigated. The QLL ^1H NMR signal does not change during repeated annealings, indicating that no sintering effect occurs over the experimental temperature range, or that perhaps sintering had finished at even lower temperatures.

The QLL was found to be accessible to the external atmosphere. Preliminary results into the role of the QLL during hydrate formation were inconclusive and further experiments are necessary.

4.6 Future Work

The experiments described in this chapter have led to a number of new questions. Firstly, during the evacuation of the ice sample, the QLL ^1H NMR signal disappears. Further experimental work is needed to explain this observation. One mechanism might be worth exploring in detail, namely: does the QLL evaporate or freeze when evacuated?

Secondly, preliminary studies into the interaction between the QLL and Xe during hydrate formation were found to be inconclusive. More complete studies of this type are necessary for the understanding of the role of the QLL during hydrate formation. Higher Xe pressure and lower temperature hydrate formation experiments should be conducted to see if the ^1H NMR QLL signal changes during the induction period at these conditions. This study could also be extended to different hydrate formers, like CH_4 or CO_2 to see if any changes occur.

4.7 Thesis: Overall Conclusions

In this thesis, the kinetics of hydrate formation and decomposition were investigated using a relatively new technique known as HP ^{129}Xe NMR. Using this technique, information about the kinetics of hydrate formation was obtained on the molecular level with time resolution 0.1 s. The results obtained provided evidence of non-equilibrium behaviour during the hydrate nucleation stage, known as the induction period, suggesting that the small 5^{12} cage plays a special role in the precursor formation. It was also found that the decomposition of the clathrate hydrate leaves the surface “pre-organized”, therefore eliminating the induction period for hydrate re-formation.

A ^1H NMR spectroscopy study of the so-called Quasi-Liquid Layer (QLL) on the surface of ice was performed in order to understand its role during hydrate formation. The results suggest that dissolved gases in the ice sample affect the intensity of the QLL signal, indicating that the signal is likely caused by a mobile phase at the ice grain boundaries. Preliminary experiments monitoring the ^1H NMR signal from the QLL during xenon hydrate formation were inconclusive with regards to the involvement of the QLL in the formation process, and further experiments are necessary.

4.8 References

1. Faraday, M., *Phil. Mag.* **1859**, 17, 162.
2. Fletcher, N. M. *Phil. Mag.* **1962**, 7, 255, **1968**, 18, 1287.
3. Kuroda, T., Lacmann, R. *J. Cryst. Growth.* **1982**, 56, 1898.
4. Dash, J. G. *Science.* **1989**, 246, 1591.
5. Baker, M.; Dash, J. G. *J. Cryst. Growth.* **1989**, 97, 770.
6. Sloan, E. D., Fleyfel, F., *AIChE J.*, **1991**, 37, 1281.
7. Akitt, J. W., Lilley, T. H., *Chem. Commun.* **1967**, 323.
8. Clifford, J. H., *Chem. Commun.* **1967**, 880.
9. Bell, J. D., Myatt, R. W., Richards, *Nature Phys. Sci.*: **1971**, 230, 91.
10. Barer, S. S; Kvividze, V. I.; Kurzaev, A. B.; Sobolev, V. D.; Churaev, N. V.; *Dokl. Akad. Nauk. SSSR*, **1977**, 235, 601.
11. Mizuno, Y; Hanafusa, N.; *J. Phys.*, **1987**, 48, C1-511.
12. Barrer, R. M.; Edge, A. V. J.; *Proc. Roy. Soc., London*, **1967**, 1, A300.
13. Falabella, B. J.; "A Study of Natural Gas Hydrates", Ph.D. Dissertation, U. of Massachusetts, MA, **1975**.
14. Davidson, D. W.; Handa, Y. P.; Ripmeester, J. A.; *J. Phys. Chem.*, **1986**, 90, 6549.