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AN NMR STUDY OF THE ORIENTATIONAL PHASE TRANSITION IN SOLID HYDROGEN AND DEUTERIUM

The Ohio State University

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AN NMR STUDY OF THE ORIENTATIONAL PHASE TRANSITION IN
SOLID H₂ AND D₂

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Cheol Eui Lee, B.Sc.

* * * * *

The Ohio State University

1986

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Advisor
Department of Physics
To My Parents
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FIELD OF STUDY

Major Field: Physics
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CHAPTER I

INTRODUCTION

At low temperatures, the hydrogen molecules (H₂, D₂, etc.) form the simplest of all molecular solids. These solids provide a fascinating low temperature behavior that can be understood to a large extent from first principles. This behavior is due to their light mass, small moment of inertia, weak molecular interactions and the quasi-metastable ortho-para species¹. Especially, H₂ solid is called a quantum solid due to the large zero point motion at T=0. The molecules rotate freely even in the solid due to the very weak intermolecular interactions and the large rotation energy (small moment of inertia).

Hydrogen molecules in their ground state consist of two protons and two electrons. The electron spins form a spin single state (zero spin) and the vibrational quantum number is zero. Since the hydrogen (H₂) nuclei are two fermions, the H₂ molecules must satisfy the Fermi statistics and the symmetric nuclear spin state I=1 is paired with the antisymmetric rotational states with odd quantum number J. This state is called "ortho hydrogen (oH₂)". Likewise, the antisymmetric nuclear spin state I=0 is
paired with the symmetric rotational states with even J’s. This state is called "para hydrogen (pH₂)". On the contrary, in the case of deuterium (D₂), where the nuclei are two bosons and must obey Bose-Einstein statistics, the antisymmetric nuclear spin state J=1 must be paired with the antisymmetric rotational states with odd J’s. In D₂, the state with J=1 and odd J is called para D₂ (pD₂). The symmetric nuclear spin states J=0, 2 are paired with the symmetric rotational states that have even J’s. This state is called ortho D₂ (oD₂) in D₂.

When the temperature is lower than the difference in energy, expressed as a temperature, between the lowest two states, only the states with J=0 and J=1 have any appreciable probability of being populated. Thus at low temperatures, only the states having J=0 and J=1 are thermally populated so that "even J" reduces to J=0 and "odd" J reduces to J=1.

The J=1 molecules form a meta-stable species because of the difficulty in satisfying the conservation conditions simultaneously to decay to the ground state J=0 molecules. The rate equation governing conversion in the solid or liquid H₂ is second order²:

\[
\frac{dc}{dt} = -KC^2 \quad \ldots \ldots \ (I.1)
\]

with the solution
where $K$ is the rate constant. Conversion requires a simultaneous change of rotational angular momentum by $\Delta J = 1$ and the nuclear spin state must change between the triplet and the singlet state. An isolated molecule is stable and will not convert; the perturbation that causes the transition arises from interactions with neighboring ortho molecules that have nuclear spin magnetic moment and the rotational magnetic moment.

In $D_2$, the rate equation is given by

$$\frac{dc}{dt} = -Kc^2 - K'c(1-c) \quad \ldots \quad (I.3)$$

where the term in $K'$ arises from the interaction of the $pD_2$ ($J=1, I=1$) molecules with the dipolar magnetic field of the $I=2$ state of an $oD_2$ ($J=0, I=2$) molecule.

At low temperatures hydrogens have a disorder-order phase transition in which the molecules align along certain crystalline directions. This orientationally ordered state has been studied by x-ray$^4$ and neutron diffraction$^6$, NMR (nuclear magnetic resonance), Raman$^6$ and infrared absorption$^7$, specific heat measurements$^8,9$, etc. From these measurements, it is known that the phase transition is accompanied by a crystal structure change from the hcp to the fcc lattice (the lowest energy is obtained for the
Pa3 structure). An NMR anomaly in nH₂ (normal hydrogen, J=1 concentration x_j = 0.75) was first observed by Hatton and Rollin in 1949 and correctly interpreted. Then, Reif and Purcell studied it in more detail and gave it a complete description in 1953. This was interpreted as an orientational ordering of the J = 1 molecules. Now, a large body of theoretical work exist on the orientational order-disorder phase transition. However, there has been no successful treatment of the complete double phase transition, i.e., hcp to fcc and orientational ordering, although James and Raich came close to it.

It has been shown that the transition from disordered fcc to ordered fcc should to be first order. For a quadrupolar system (J = 1), two normalized local order parameters can be defined,

\[ \sigma = \frac{-1}{2} \langle 3J^2 z_i - 2 \rangle_T \]  \hspace{1cm} (1.4)

and \[ \eta = \langle J^2 x_i - J^2 y_i \rangle_T \]  \hspace{1cm} (1.5)

In the configuration of axial symmetry that occur for the Pa3 structure, \( \eta \) is zero. A number of equivalent definitions of the long-range order parameter have been used in the literature:

\[ \sigma(T) = -(1/2N x_j) \Sigma_i \langle 3J^2 z_i - 2 \rangle_T \]  \hspace{1cm} (1.6)

\[ = (4\pi/5)^{1/2}/(N x_j) \Sigma_i \langle Y_20(\omega_i) \rangle_T \]  \hspace{1cm} (1.7)
where \( x_J \) includes the possibility of dilution for generality. \( N \) is the number of molecules, \( \langle \rangle_T \) is a thermal average, and \( \omega_i=(\theta_i, \phi_i) \), where \( \theta_i \) is the deviation of the molecular axis from the ordering direction. With this definition \( \sigma \) is normalized to be 1 with full order \((J^2_z=0, \cos^2\theta=1)\) and 0 when completely disordered \((J^2_z=2/3, \cos^2\theta=1/3)\).

The temperature dependence of the order parameter was first measured by Meyer et al.\(^{13}\) (1972) in D\(_2\) by using NMR. By defining the "splitting" \( \delta \nu \) as the frequency difference between the flattened peaks in the absorption spectrum, they showed that

\[
\delta \nu = 3d\langle 1-(3/2)J^2_z \rangle_T \quad \text{........... (1.9)}
\]

\[
= (15d/4)\langle 3\cos^2\theta \rangle_T = (15d/4)\sigma \quad \text{............. (1.10)}
\]

by relating \( J^2_z \) to \( \cos^2\theta \), where \( d \) is the intramolecular splitting constant. Thus they showed that the quantity \( \delta \nu \) is proportional to the long range order parameter \( \sigma \).

With a new and powerful NMR method, namely quadrature signal detection, we have attempted to reexamine this long range ordered phase transition to verify that NMR is a sensitive way of probing a phase transition. To this end, measurements of the conventional
long range order parameter $\sigma$ (actually, the quantity $\delta \nu$ was measured instead of $\sigma$) and a new order parameter $Q$ have been made. The order parameter $Q$ is defined as the ratio of the average frequency in the absorption spectrum to that in an ideal Pake doublet. These order parameters were monitored as a function of temperature through the phase transition. Although the measurement of the order parameter $\sigma$ has been made in $D_2$ by several workers, few experiments have been available in $H_2$, basically because of technical problems arising from the more rapid J=1 to J=0 conversion in $H_2$. Rapid measurements on $H_2$ contained in this dissertation were made possible thanks to the batch file programs written for taking data without interruption between different pulse sequences. Thus, the changes in both the order parameters and the lineshape for both $H_2$ and $D_2$ were monitored through the phase transition and compared.

According to the theory of Metzger and Gaines\textsuperscript{14}, neglecting the fluctuating terms and considering only the static terms in the Hamiltonian of a pair of protons in an external magnetic field, the echo sequence $90^\circ - \tau - \beta \phi$ ($\beta$ is the length of the second pulse and $\phi$ is its phase shift with respect to the first pulse) will duplicate the shape of the FID (Free Induction Decay) when the time origin is shifted to $t = 2\tau$. Powles and Strange\textsuperscript{15} have also shown this for echo sequences $90^\circ - \tau - 90^\circ$ and $90^\circ - \tau - 90^\circ \ 90^\circ$. To test these theories systematically and see if they are still valid in the vicinity of the phase transition, the three echo sequences $90^\circ - \tau$
- 90°, 90° - \tau - 90°_{90°}, and 90° - \tau - 180° were used and their echo shapes were compared with that of the FID. The motivation for this study comes from the increasing use of chemists to use pulsed NMR techniques as an analytical tool in solids. The NMR lineshape is extracted from the pulsed responses without regard for proximity to a phase transition.

In 1972, Sullivan and Pound\textsuperscript{16,17} proposed the existence of a new phase named the "Quadrupole Glass" in the intermediate range (x_j \leq 0.55). The name Quadrupole Glass implies a randomly distributed orientationally ordered quadrupoles. In 1981, Sokol\textsuperscript{18} did an experiment in D_2 in that same concentration range and reported cusplike behavior in the spin-lattice relaxation time T_1 and obtained a lineshape resembling a Pake doublet, characteristic of an ordered state with a well defined order parameter. However, the existence of the Quadrupole Glass phase has been recently challenged and is not acceptable to some workers. In this dissertation, it is suggested that this phase is really something similar to the higher concentration long range ordered phase. Thus systematic measurements of T_1 and the same order parameter Q defined in Sokol's work on the high J = 1 concentration give some clues to this problem. This is one of the motivations for the work done in this dissertation.

This dissertation is organized in the following way: Chapter II contains a review of pertinent theories; Chapter III is a
description of the experimental apparatus used for the work in this dissertation; Chapter IV is a systematic collection of data taken from the experiments; finally, Chapter V is for discussions and conclusions from the data in this dissertation.
CHAPTER II

THEORIES

1. The λ Anomaly in Heat Capacity in Hydrogen Isotopes

The existence of the anomaly in the heat capacity of ortho-para mixtures of solid hydrogen was first observed in 1931\textsuperscript{19}. This provided some of the initial indications that interesting phenomena occurred in the hydrogens at low temperatures due to the quenching of the molecular rotation. For ortho concentrations less than 60\%, a broad anomaly was detected with a flat maximum. However, at higher concentrations, a sharp transition occurred in the solid, with the transition temperature increasing almost linearly with increasing ortho concentration. This transition was classified as a λ anomaly. Comparable effects were observed by NMR experiments on high J=1 concentrations in solid H\textsubscript{2}\textsuperscript{10,11}. The splitting of the broad resonance line into a resolved doublet at a temperature nearly identical to the calorimetric transition temperature, was interpreted as the onset of a cooperative quenching of the rotational motion of the ortho molecules. These anomalies in solid H\textsubscript{2} are also seen in D\textsubscript{2} and in both cases are interpreted as a removal of the rotational degeneracy of the J=1
molecules in the solid mixture. Grenier and White\textsuperscript{20} measured heat capacities of solid deuterium (33.1\%-87.2\% para) from 1.5K to the triple point. The measurements in D\textsubscript{2} had a significant advantage over the ones in H\textsubscript{2} because of the much slower conversion of J=1 to J=0 molecules and thus much smaller heat of conversion in D\textsubscript{2}. Thus, the exact shape of the heat capacity anomaly in D\textsubscript{2} was determined in the neighborhood of the transition temperature. All the heat capacities of the solid showed anomalies due to the quenching of the molecular rotation of the J=1 species present in the mixtures. For para compositions above 60\% pD\textsubscript{2}, a sharp \textlambda transition was observed as well as a linear dependence of the transition temperature upon para content. A calculation of the entropy from the data showed that the threefold degeneracy of the J=1 species is completely removed at the absolute zero. They also showed that the quenching of the molecular rotation is principally a result of quadrupolar interactions. The anomalous heat capacities of the solid, at sufficiently high temperatures, were expressed by the relation

\[
\frac{C_T^2}{R} = \alpha x_j + \beta x_j^2 \quad \ldots \ldots \quad (\text{II.1})
\]

where $x_j$ is the J=1 concentration in D\textsubscript{2} or H\textsubscript{2}. 
2. Theory of NMR Lineshapes

In the continuous-wave (cw) experiments, the NMR signal is obtained in the form of the energy absorption in the frequency domain. In other words, a continuous RF wave with a constant frequency is fed into the sample cell and a change in the transmitted energy is monitored as the magnetic field is swept. In the pulse NMR, the signal is obtained in the form of a decay of the magnetization in the xy plane. By Fourier transforming the pulsed NMR signal, the lineshape or the energy absorption spectrum in the frequency domain is obtained. Thus, cw NMR and pulse NMR are related to each other by the Fourier transformation, so long as the high temperature approximation (valid usually above 100 mK) can be made.

In a paper on an NMR experiment on \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) (gypsum), Pake calculated a proton absorption spectrum in powdered (polycrystalline) gypsum sample shown as the broken line in Fig. 1. This was later named "Pake doublet". This would be the shape of the spectrum if the elementary spectrum of each crystal were composed of two discrete lines. In fact, each of these lines is broadened by the interaction of the protons. The continuous line in Fig. 1 takes this into account. In his single crystal sample, he observed an angle dependence of the spectrum, resembling the Pake doublet at some angles.
Fig. 1

Pake Doublet

Dashed line: unbroadened lineshape

Solid line: dipolar broadened lineshape
The Pake doublet lineshape is obtained when a system under study is a powder with a single order parameter. However, this is not the only case where the Pake doublet is obtained. In general, the Pake doublet lineshape is obtained only if the sample has a well defined, nonzero value for the order parameters.

In the solid hydrogens, the long range order parameter

\[ \sigma = (\frac{-1}{2})<3J_z^2 - 2>^\tau \]  \hspace{1cm} \text{(II.2)}

is defined. In the completely orientationally ordered state, \( J_z = 0 \) is the only occupied state. This gives the order parameter \( \sigma = 1 \).

The lineshape corresponding to this case is broadened in frequency and resembles the "Pake doublet". In other words, the appearance of a Pake doublet is an indication of the orientationally ordered state in our phase transition.

Above the phase transition temperature, there is no long range order and the motional narrowing theory takes over. Suppose the absorption spectrum initially consists of two sharp absorption lines separated by a frequency \( 2\delta \). This is the case when \( \delta \gg \Omega \), where \( \Omega \) is the probability of jumping from one frequency to another. As \( \Omega \) becomes greater, the two lines are broadened by an interaction of the two frequencies and when \( \delta \ll \Omega \), the two lines coalesce to form a single line at the center of the two original
lines (Fig. 2). This is the theory originally proposed by P. W. Anderson. 

3. Theory of $T_1$ Through the Phase Transition

In NMR, the Hamiltonian of a system of interest in the rotating frame can be broken into two parts, i.e., one of which commutes with $I_z$ ($I_z$ = z component of the spin observed in NMR) and one of which does not. Thus we can write the Hamiltonian $H$ as

$$H = H_C + H_{NC} \quad \ldots \ldots \ldots (II.3)$$

The commuting part leads to frequency shift or determines the NMR lineshape. This part is static in the rotating frame. The noncommuting part, $H_{NC}$ is time dependent in the rotating frame and thus is responsible for the nuclear relaxation. According to the Golden Rule of time dependent perturbation theory, the relaxation rate $1/T_1$ ($T_1$ = spin-lattice relaxation time) is given by

$$1/T_1 = 2\pi/\hbar |\langle i|H_{NC}|f\rangle|^2 \rho(E_f) \quad \ldots \ldots (II.4)$$

where $i$ and $f$ denote the initial and final states respectively and $\rho(E_f)$ is the density of states for the Zeeman energy of the final state. According to the Debye model, in the solid, the phonon
Motional Narrowing

The theoretical lineshape of a system with two frequencies $\pm \delta$, jumping from one to the other with an average frequency $1/\tau=\omega$. 
density of states is proportional to the square of phonon frequency. In typical solids, the cutoff temperature is \(10^2-10^3\)K and the Zeeman energy is typically of the order \(10^{-3}\)K. Thus the phonon density of states at the Zeeman energy is extremely small at low temperatures and so is the relaxation rate. This in turn makes \(T_1\) extremely long and NMR would be impossible to detect if the direct spin-lattice relaxation mechanism was the only nuclear relaxation mechanism. In fact, in every case where NMR is observable at low temperatures, there is some intermediate system that "matches" the nuclear spin levels to the lattice. In the case of solid hydrogens, the rotational spin-phonon coupling is strong. The rotational bath energy levels are nearly continuous due to the randomness of configurations and they match the lattice modes well in magnitude. Both direct and Raman like processes are able to contribute. Thus \(T_1\) in solid hydrogens is really due to the spin-rotation coupling and since the rotational spin-phonon coupling is strong, \(T_1\) in some sense probes the density of states at the Larmor frequency \(\omega_0\).

From the above discussion, it is clear that if the bond between the nuclear spin system and the "lattice" (as the phonons are collectively called) gets weaker, then the relaxation rate will decrease accordingly, resulting in a longer \(T_1\). This is what happens when the solid hydrogens undergo the transition into the rotationally ordered phase. In the rotationally ordered state, much smaller density of rotational spin states is available. This
would result in a much smaller nuclear relaxation rate and thus much longer relaxation time $T_1$.

The above argument can be amplified as follows. Suppose the density of states (spectral density) $J(\omega)$ is normalized. $J(\omega)$ is shaped in such a way that it is flat until it approaches the cutoff frequency and falls off rapidly around $\omega_c$ ($\omega_c$ is the "linewidth"). Then the relaxation rate $1/T_1 \propto J(\omega_0) \propto 1/\omega_c$. Thus, $1/T_1 \propto J(\omega_0)$ is maximum when $\omega_0 = \omega_c$ or $T_1$ has a minimum when $\omega_0 \approx \omega_c$. Near a phase transition, the width collapses (with increasing correlation time $\tau=1/\omega$) so the amplitude at $\omega_0$ increases increasing the rate (decreasing $T_1$) since the area under $J(\omega)$ remains 1. However, as the cutoff frequency passes through $\omega_0$, the rate decreases (increasing $T_1$) since less density of states is available at $\omega_0$.

4. Change of Crystal Structure Through the Phase Transition

The path to understanding the crystal structure and/or the phase diagram of solid hydrogen has been long, difficult, and full of pitfalls\textsuperscript{1}. However, it was found that the crystal structure depends on the ortho concentration and the temperature even in early measurements\textsuperscript{23}. 
The change in crystal structure is known to take place as a result of the electric quadrupole-quadrupole (EQQ) interaction. The first nonzero multipole moment of H₂ is the electric quadrupole (EQ) moment which is defined by

\[ Q(R) = (1/2)R^2 - \langle 3z^2 - r^2 \rangle \quad \cdots \quad (II.5) \]

for fixed nuclei of separation R, in a coordinate system with z along the intermolecular axis. Q(R) can be evaluated as a function of R. Then, Q(R) in a given nuclear state is determined by evaluating the matrix elements of the vibrational and rotational states:

\[ Q^{(2)}_{vJ,v'J'} = \int Q(R) \psi^*_{vJ}(R) \psi_{v'J'}(R) R^2 dR \quad \cdots \quad (II.6) \]

which is the radial matrix element of Q(R), where \( \psi_{vJ}(R) \) represents the radial part of the molecular wave function in the \( vJ \) vibrational-rotational state. To obtain the quadrupolar moment in a given rotational state, \( |Jm\rangle \), represented by the spherical harmonic \( Y_{Jm}(\theta,\phi) \), the quadrupole moment must be expressed in a laboratory frame. Since Q(R) has axial symmetry and is a second rank tensor, one has \(^{24}\)

\[ Q^{(2)}_{vJ,v'J'} = Q^{(2)}_{vJ,v'J'} Y_{20}(\theta,\phi) \quad \cdots \quad (II.7) \]
which is the rotational matrix element of $Q(R)$, where $\theta, \phi$ are the polar angles of the symmetry axis of the molecules with respect to the $z$-axis of the laboratory frame. We shall collectively define $\theta, \phi = \Omega$. The rotationally averaged moment is

$$Q_{vJm, v'J'm'}^{20} = \langle Jm | Q_{vJ, v'J, J'm'}^{20} | J'm' \rangle. \quad \ldots \quad (\text{II.8})$$

At low temperatures, the most important matrix elements are the diagonal $v=0, J=0, 1$. In the spherically symmetric ground state, $Q_{20000, 0000}=0$; in the $J=1$ state $Q_{2001m, 01m} = (2/5)Q_{2001, 01} = Q$. At long ranges, when the molecules are sufficiently far apart so that the overlap of their charge distribution may be considered to be negligible, the potential of the intermolecular interaction arises from the interaction of electronic multipole moments and may be expanded in powers of the interatomic separation

$$\phi (R, \Omega_i, \Omega_j) = \sum_k C_k^k (\Omega_i, \Omega_j)/R^k, \quad \ldots \quad (\text{II.9})$$

where we set $\phi (\omega, \Omega_i, \Omega_j) = 0$. This can be separated into an isotropic and an anisotropic part. The most important term is for $k=5$ and it arises from the interaction of the permanent electric quadrupoles of the two molecules (EQQ interaction). This anisotropic EQQ interaction is responsible for the lifting of the degeneracy of the $J=1$ states and its coupling constant when $R$ is the nearest neighbor separation is about $1K$. The lowest energy configuration is the one
in which the molecules have the principal axes of the quadrupole moments perpendicular to each other ("T" configuration, as \( \rightarrow \uparrow \)).

It has been shown that an array of ordered EQ moments would have a lower lattice energy on an fcc lattice than on an hcp lattice. The phase transition from a disordered hcp lattice to the fcc lattice is evidently driven by the EQQ interaction since the difference in energy of the hcp and fcc lattice for isotropic interactions (~10\(^{-3}\)K/molecule) is much smaller than the EQ energy (~5K/molecule). It has also been determined that the structural transition from disordered hcp to fcc takes place only for \( J=1 \) concentrations above 0.56\(^{25,26,27} \). The critical temperature for the structural phase transition depends on the concentration, the higher the concentration, the higher \( T_c \). The critical temperatures \( T_c \) for the structure change and for the long range order transition determined by NMR are observed to be nearly identical.

Fig. 3 shows the phase diagram of \( D_2 \) as a function of \( J=1 \) concentration and the temperature determined by the lineshape measurements (the solid line)\(^{28} \). The dashed line is the phase boundary between the disordered hcp phase and the ordered hcp phase at the intermediate concentrations as determined by Sokol\(^{18} \) according to the equation

\[
T_c(x) = 1.12K \sqrt{(x - 0.287)} \quad \text{......... (II.10).}
\]
Fig. 3

Phase Diagram
In the intermediate concentrations, the solid line is determined from the lineshape, and the dashed line from the $T_1$. 
Sokol determined the transition temperatures from the cusp in the relaxation rate. The phase diagram for H\textsubscript{2} is the same as that for D\textsubscript{2} except for the lower transition temperatures for the same concentrations in the case of H\textsubscript{2}.

5. Theory of Spin Echos

Spin echos in solid hydrogen were first observed and theoretically explained by Metzger and Gaines\textsuperscript{14}. The Hamiltonian for an isolated molecule in a reference frame rotating at an angular frequency $\omega$ is given by

$$H = -\hbar(\Delta \omega)I_z + \alpha \hbar I_z^2 \quad \ldots \ldots \quad (11.11)$$

where $\Delta \omega = \omega - \omega_0$ and $\alpha = (3d/4)(1-3\cos^2\theta)$. The $I_z^2$ term comes from the intramolecular interaction and the $I_z$ term comes from the spin rotation interaction and possibly an "off-resonance" contribution from the Zeeman interaction.

Using the density matrix approach, the signal following a 90° pulse is given by

$$S(t) = 2\int f(\alpha) \cos(a\Delta \omega) \cos(\Delta \omega t) d\Delta \omega \quad \ldots \ldots \quad (11.12)$$
where $F(t)$ and $G(t)$ are the Fourier transforms of the distribution functions for $\alpha$ and $\Delta \omega$ respectively. Using the same approach, Metzger and Gaines\textsuperscript{14} found the response for a 90° pulse followed by a pulse of rotation $\beta$ and phase shift $\phi$,

$$S(t) = A(t)\exp(-i\phi) + B(t)\exp(i\phi) \quad \ldots \quad (11.14)$$

where

$$A(t) = G(t-2\tau)[\cos\beta(1-\cos\beta)F(t)-\sin^2\beta F(t-2\tau)] \quad \ldots \quad (11.15)$$

$$B(t) = G(t)[\cos\beta(1+\cos\beta)F(t)+\sin^2\beta F(t-2\tau)] \quad \ldots \quad (11.16)$$

Considering the case when $G(t)=G(0)=1$ (no damping due to the $\Delta \omega$ distribution) as a special case, the signal takes the form

$$S(t) = 2\cos\phi \cos\beta F(t) + 2i[\sin\phi \sin^2\beta + \cos\phi \cos^2\beta F(t)] \quad \ldots \quad (11.17)$$

No echo is predicted by (II.11) for $\phi=0$ (no phase shift). If, however, when $\phi=90^\circ$ ($90^\circ$ phase shift between the 90° pulses), one has an echo. The above case (no damping due to the $\Delta \omega$ distribution) is not physically plausible because the magnetic field seen by each molecule will always be different from site to site, giving rise to different $\Delta \omega$ for each molecule.
Assuming that the main contribution to the lineshape comes from the \( \alpha \) distribution, then at \( t=2\tau \), \( F(t) \ll F(t-2\tau) \). Furthermore, if the term \( G(t) \) is small at \( t=2\tau \) (finite damping due to the \( \Delta \omega \) distribution), then

\[
S(t) = -\sin^2 \beta G(t-2\tau) F(t-2\tau) \exp(-i\phi) \quad \ldots \quad (11.18)
\]

This duplicates the FID in shape. Especially, a \( 90^\circ - \tau - 90^\circ \) and a \( 90^\circ - \tau - 90^\circ,90^\circ \) pulse sequence will give an echo equal in size to the FID but with opposite signs. For a \( 90^\circ - \tau - 180^\circ \) sequence, a very small echo response is predicted.

In the above theory, the \( 90^\circ - \tau - 90^\circ \) and \( 90^\circ - \tau - 90^\circ,90^\circ \) sequences duplicate the FID shape. However, the fluctuations of the order parameters were neglected there and this is unacceptable in the vicinity of a phase transition where the motional correlation times are of the same order as the reciprocal anisotropic spin interactions. The theory comparing NMR lineshapes obtained by Fourier transform of the solid echo (\( 90^\circ - \tau - 90^\circ,90^\circ \)) with that of the free induction decay (FID) has been worked out by Spiess and Sillescu\(^{29}\) for the example of two-site exchange in an I-1 spin system. They found large differences in the region where the time between the two \( 90^\circ \) pulses of the solid echo sequence is comparable with the motional correlation time. They showed the solid echo is distorted and reduced by a factor over 0.5.
6. The Theory of Power Emission in the Long Range Ordered State

As discussed earlier, the NMR lineshapes give the power absorption spectrum. Thus, positive values in the spectrum come from the absorption of power whereas negative values arise from the emission of power instead of absorption. In an experiment on the ordered state of solid hydrogen, Hardy and Berlinsky\textsuperscript{30} found an anomalous negative part in their lineshape corresponding to emission of power. This was ascribed to a pumping process resulting from J=1 to J=0 conversion. In the ordered state, conversion takes place from only one of the J=1 substates since the excited states, the librons, are not thermally populated. Thus the nuclear-spin populations are driven far away from their equilibrium values. From an examination of the theory of Motizuki and Nagamiya\textsuperscript{22}, they concluded that when conversion takes place from a single m\textsubscript{J} state (m\textsubscript{J}=0 is the only occupied state in the ordered state of hydrogens) in the low temperature solid, then the conversion rate is not necessarily the same for the various initial nuclear-spin states. If one assumes, for example, that J=1 molecules having m\textsubscript{I}=0 convert faster than those with m\textsubscript{I}=\pm 1, then one would be left with an excess of molecules having m\textsubscript{I}=\pm 1, and the m\textsubscript{I}=1-0 transition will be enhanced positively and the m\textsubscript{I}=0\rightarrow 1 enhanced negatively. The latter case results in the emission of power.
Since emission of power seems to come from the long range order, i.e., emission of power seems to be a characteristic of the long range ordered state, we could say that when we have emission of power, we have a long range ordered state. Thus, this can be used as a test if the so-called Quadrupole Glass phase is really something like the long range ordered state. In other words, if emission of power is found in the intermediate J-1 concentration range (x_J \leq 0.55), then the above suggestion can be said to hold true.
CHAPTER III

EXPERIMENTAL APPARATUS

1. The Cryostat, The Probe, and Thermometry

A set of glass dewars was used for storage of liquid nitrogen and liquid helium. The probe (Fig. 4) was put into the liquid helium dewar and the vacuum can on the probe provided thermal insulation between the helium bath and the helium subpot inside the vacuum can. The sample cell located in the helium subpot was in direct contact with the helium liquid in the subpot. Especially in the case of nH₂, where the heat of conversion is large, this provided a good thermal contact for the sample. The temperature range of 4.2K to 1.1K was obtained by pumping the helium subpot with a Stokes pump and using a temperature controller which provided temperature stability within 10 mK. The temperature was read by a calibrated Germanium sensor and a potentiometric conductance bridge (S.H.E. Model PCB). The sample cell was centered in the gap between the poles of a Varian magnet (Model VFR-2503).
Fig. 4

The Probe
sample bulb

needle valve

Stokes pumping line

flange

vacuum can pumping line

subpot pumping line

sample fill line

subpot fill line
2. The Sample Cells and The Sample Coils

In an effort to make the field homogeneity in the sample as good as possible, very small sample volumes were used (about 0.1 cc). The sample was put into the sample coil which had a larger volume than that of the sample. In the nH$_2$ and D$_2$ experiments, the sample cell (Fig. 5) was made of Kel-F (a kind of plastic containing the elements carbon and fluorine) threaded on the outside in order to hold the sample coil. The sample coil was made of bare copper wire (0.017 mm in diameter). In the 1 % H$_2$ in D$_2$ experiment, a glass sample cell was used to avoid any spurious fluorine signal from the sample cell because the signal to noise ratio was small. A platinum wire (0.018 mm in diameter) was potted in sulfur and used for the sample coil. The tuning for the sample coil was done externally, with the tuning components outside the cryostat. For the two experiments at 30 MHz, nH$_2$ and H$_2$ in D$_2$ two inductors were used for the tuning, however two capacitors were necessary for the 6 MHz D$_2$ experiment. The tuning was monitored by using a vector impedance meter. The coil plus transmission line was tuned to be pure resistive with an impedance of 50 Ω. This is required by the NOVEX spectrometer employed in the experiments. An ARENBERG transmitter modified for use as a pulse amplifier was used to generate 90° pulse of length 1 μs for proton NMR and 4μs for the D$_2$ NMR.
Fig. 5

Kel-F Sample Cell
Threaded for sample coil

0.2''

0.9''

0.312''

Kel-F plug

Hole for sample admission

Sample space

3/8-24 "Q" drill

0.5''
3. The NOVEX Spectrometer

A spectrometer manufactured by NOVEX Inc. was used for the experiments. The spectrometer includes a pulse programmer, a digitizer, a preamplifier, a transceiver, and a power amplifier. A signal at twice the Larmor frequency was fed into the transceiver which generates a small pulse modulated at the Larmor frequency. This gated RF signal is then amplified by the pulse amplifier. The transmitted power from the Arenberg transmitter was fed into the transmission line through a connection on the preamplifier. The NMR signal received by the preamplifier is sent to the transceiver to be further amplified before it is digitized by the digitizer. The averager board in an IBM PC computer then receives the digitized NMR signal and converts it into a data file which is written to a floppy diskette. The pulse programmer is also operated from the IBM PC. The data file consists of two parts, i.e., the real and imaginary part. A file can contain up to 8 K of data. However, since the resolution of the data points is limited to 0.5 μs regardless of the data size, the choice of the data size depends on the $T_2$ of the NMR signal. For the proton experiments, a data size of 1 K was used but 4 K was necessary for the $D_2$ experiment. The signal averaging is done by an averager program on the IBM PC so that as many scans as necessary can be made and accumulated.
Data files were analyzed after converting them first into a binary file and then into a file form to be analyzed by a commercial analysis software called ASYST. Using ASYST, all the NMR signals, which had been phase corrected by the NOVEX AVERAGER program, were corrected for zero baseline. Since the NOVEX data files were nonzero from \( t=2 \mu s \), the data files were shifted by \( 1\mu s \). The deadtime in the FID signals, typically \( 7 \mu s \), was replaced by a Gaussian fit to the channels 1 to 13 using ASYST. This was not necessary for the echo signals because the data files contained no deadtime. To obtain the lineshape, the FID files were Fourier transformed by ASYST. In addition, where appropriate, the lineshape was differentiated to obtain the order parameter \( \delta \nu \) using ASYST. An HP 7470A plotter was used to plot the graphs.

4. The \( \text{pD}_2 \) Enrichment Apparatus

The high \( J=1 \) concentration \( \text{D}_2 \) sample was made by an apparatus set up in our laboratory. The working principle of the apparatus is described in a paper by Depatie and Mills\(^{32} \). It makes use of the preferential adsorption of the \( J=1 \) molecules on the surface of aluminum oxide at the temperature of liquid hydrogen (20K). Since the adsorbed \( J=1 \) species forms a layer on the aluminum oxide (Alcoa
Chemicals, activated alumina grade F-1, mesh 8-14), the two species of J-1 and J-0 can be separated by pumping out the J-0 species. A flow of nD₂ is admitted into a space filled with aluminum oxide at about 20K until the vapor pressure is saturated. Then the temperature is slowly raised by the heater wire while pumping out the space. The concentration of the exhaust gas is continuously monitored until it indicates a high enough concentration. The concentration is determined by a thermal conductivity cell described by Devoret et al.³³. It makes use of the difference in thermal conductivities of the J-1 and J-0 species at liquid nitrogen temperatures. The thermal conductivity of a binary gas consisting of both J-1 and J-0 species depends on the molar fractions of the two (the J-0 species has the higher thermal conductivity). When a high J-1 concentration is reached, the pumping is stopped and the high concentration gas is retrieved by heating the sample space. Depatie and Mills³² reported that a D₂ sample with 99 % J-1 concentration could be obtained by this method. The enrichment cell was attached to a conversion apparatus in the laboratory which ordinarily is used to convert the J-1 species into the J-0 species. (of course, the conversion part is not used when it is used for enrichment) in order to use the same gas handling system.
CHAPTER IV

DATA AND ANALYSIS

The data presented in this dissertation can be divided into three categories: (1) proton NMR data on normal H\textsubscript{2}; (2) deuteron NMR data on enriched D\textsubscript{2} where the J=1 concentration is above 70%; and (3) proton NMR on the previous enriched D\textsubscript{2} sample where 1% nH\textsubscript{2} has been added as a probe.

1. Proton NMR Data on Normal Hydrogen (nH\textsubscript{2})

In this section, we present the $T_1$'s, the FID's and echos at various pulse intervals at different temperatures above and below the rotational transition for the normal hydrogen sample. In addition, the lineshapes and an order parameter

$$Q = \int_0^\infty \omega I(\omega) d\omega / \int_0^\infty \omega I_{pd}(\omega) d\omega \quad \ldots \ldots (IV.1)$$

will be presented as a function of temperature and discussed.

In Fig. 6, $T_1$ was measured as the sample was cooled down from 4K through the transition to the lowest obtainable temperature,
Fig. 6

$T_1$ versus Temperature
T1's for N-H2

+ as cooling down
X as warming up

Temperature (K)
1.1K, and then as it was warmed back to 4K. The sample exhibits a sharp cusp-like behavior which is characteristic of the transition. We note that there is a thermal hysteresis in the value of $T_1$ which means that the value of the $T_1$ is not reproduced when the sample is warmed back up and the minimum in $T_1$ is shifted to a little lower temperature although this may be an effect due to the change of ortho concentration in time.

In Fig. 7, both the real part and the imaginary part of the FID at 4K are shown. All the NMR measurements on nH$_2$ were taken at the Larmor frequency of 30 MHz. The 4K FID was phase corrected so that the imaginary part vanishes at time $t = 0$. The oscillation on the FID is an example of a "Lowe beat" and is discussed in Metzger and Gaines$^{14}$. Figs. 8 to 10 show the echo responses at pulse separations $\tau = 5$, 20 and 50 $\mu$s. Fig. 8 shows the response to the solid echo sequence $90^\circ - \tau - 90^\circ 90^\circ$, a $90^\circ$ pulse applied at $t = 0$ followed time $\tau$ later by another $90^\circ$ pulse with a phase shift of $90^\circ$. We will call this echo sequence "echo 1". In Fig. 9, we have the $90^\circ - \tau - 90^\circ$, a pulse sequence consisting of a $90^\circ$ pulse with no phase shift applied time $\tau$ after the initial $90^\circ$ pulse. We will call this "echo 2". Fig. 10 is the response to the "Hahn echo", a $90^\circ - \tau - 180^\circ$ pulse sequence, which we call "echo 3". In all of the NMR responses of echo sequences, the time origin was shifted to twice the pulse separation which is supposed to be the center of the responses. The sign difference between echo 1 and echo 3 is real (and in agreement with calculations).
Fig. 7

4K FID of nH$_2$

(a) real part

(b) imaginary part
Fig. 8

4K Echo 1 of nH₂

(a) real part

(b) imaginary part
Fig. 9

4K Echo 2 of nH$_2$

(a) real part

(b) imaginary part
4K N-K2 ECHO 2 REAL

- 5US
- - 20US
- - - 30US

TIME (US)

4K N-K2 ECHO 2 IMAGINARY

- 5US
- - 20US
- - - 30US

TIME (US)
Fig. 10

4K Echo 3 of nH₂
(a) real part
(b) imaginary part
Comparing Fig. 8 - 10 at r-5μs with Fig. 7, we note that the shape of the real parts of the echo sequences closely resemble that of the 4K FID, with the real part of echo 3 being inverted. In the figures, we see the time shift in the center of the echo responses. This has been pointed out in Cho's dissertation\(^{34}\). However, we see that the imaginary parts of the echos do not look like the imaginary part of the FID. Rather, they resemble the real parts of the echos. This is not a real surprise considering that the imaginary part of the NMR response is 90° phase shifted with respect to the real part in the xy plane and the spins rotate or precess in that plane. Because of the pulse separation, 5 μs in this case, the contributions of the spins to the FID and to the echos have different time spans for rotation. In other words, since the individual spins see different magnetic fields, they have their own characteristic Larmor frequency\(^{35}\). After the spins are rotated 90° by a 90° pulse, the individual spins rotate in the xy plane with their own speed. When the second pulse of the echo sequences is applied, the spins as a whole have dephased to a certain degree depending on the pulse separation, giving rise to the finite imaginary part due to the second pulse. Also we note the dips near the origins of the imaginary parts of echos 1 and 2, supporting the above picture because this shows the time lag for rephasing of the imaginary part for of the spins compared to the real part when the pulse separation is short.
In Figs 8 to 10, we also present the echos with separations of 20 $\mu$s and 50 $\mu$s. Echo 1 displays little change in shape as a function of pulse separation except for the disappearance of the dip in the imaginary part. However, the real part of echo 2 becomes inverted around $r=20$ $\mu$s and the dip disappears as well. We notice the significant decay of echo 3 due to increased separations.

After taking the data at 4K the sample was cooled down rapidly over a time of the order of 5 minutes to the lowest temperature, 1.1K. Figs. 11 through 14 show the data taken at 1.1K. Again the real part of echo 1 resembles that of the FID. However the imaginary part of echo 1 becomes inverted as the separation increases. The real part of echo 2 at $r = 5$ $\mu$s displays an extreme departure from the shape of the oscillation of the FID. Echo 3 closely resembles the oscillation of the FID, again displaying the rapid decay as the separation increases.

The data taken at 1.3K and 1.5K, temperatures below the transition temperature, show little departure from those at 1.1K except for the decrease of signal amplitude expected from Curie's law as we warm up gradually to the transition temperature of 1.6K. The FID and the echos with $r=5$, 20, 50$\mu$s for $T=1.6$K are shown in the Figs. 15 to 18. This is the temperature at which the largest deviations of the echos from the FID are expected. In taking the $nH_2$ data, speed was an essential factor because the conversion from the ortho to para molecules is fast enough to move the transition
Fig. 11

1.1K FID of nH₂

(a) real part

(b) imaginary part
Fig. 12

1.1K Echo 1 of nH₂
(a) real part
(b) imaginary part
Fig. 13

1.1K Echo 2 of nH$_2$

(a) real part
(b) imaginary part
Fig. 14

1.1K Echo 3 of nH₂

(a) real part
(b) imaginary part
Fig. 15

1.6K FID of $n\text{H}_2$

(a) real part

(b) imaginary part
62 K N-42 FID REAL

TIME (US)

62 K N-42 FID IMAGINARY

TIME (US)
Fig. 16

1.6K Echo 1 of nH₂

(a) real part

(b) imaginary part
Fig. 17

1.6K Echo 2 of $\text{NH}_2$

(a) real part

(b) imaginary part
Fig. 18

1.6K Echo 3 of nH₂

(a) real part

(b) imaginary part
temperature in a noticeably short time. In fact, the accepted conversion rate is 1.9% per hour. Since the data taking sequences are initiated by a computer, there was a need to write batch files in order to minimize the time between the different pulse sequences. As it is, the comparison between the FID and the echos reveals very peculiar features at 1.6K. First, it is noteworthy that the imaginary part of the FID does not vanish at t=0 indicating that some kind of phase shift has taken place through the transition. Since the FID at 1.6K looks like a superposition of the high temperature FID and the low temperature oscillatory behavior, the oscillatory component in the NMR signals appears to be a good criterion for comparison. As τ is lengthened, the oscillatory behavior in the real part of the echo 1 diminishes while its imaginary part undergoes no particular change. In contrast, the real part of echo 2 has stronger oscillatory component as τ gets longer. It is pointed out that for τ=5 μs, the real part of echo 2 shows no oscillatory behavior at all while its imaginary part has a strong indication of the oscillation around the origin. It is astounding to compare the imaginary part for τ=5 μs (Fig. 17) and the real part for τ=20 μs (Fig. 17). They look almost identical except for the fact that they are inverted with respect to each other. Echo 3 shows little difference over different τ’s but the real part for τ=20 μs (Fig. 14) shows an apparent junction of the oscillation of low temperature FID and the motionally narrowed FID at around t=10 μs.
Figs. 19 through 22 show the 1.7K data where the sample has gone through the transition to the motionally narrowed phase. Fig. 19 shows the FID which generally looks like the 4K FID. However, the imaginary part shows the nonzero value at the origin. The real part of echo 1 looks like the real part of the Gaussian 4K FID while its imaginary part looks like the real part of 1.7K FID. The real part of echo 2 at $t=5 \mu s$ resembles that of echo 1, again being inverted at around $t=20 \mu s$. The imaginary part of echo 2 for $t=5 \mu s$ looks like that of the FID, while echo 2 at $t=20 \mu s$ looks similar to echo 3. It is also noted that for $t=50 \mu s$, echo 1 and echo 2 look alike although they are inverted with respect to each other. Also, the imaginary part of echo 3 at $t = 50 \mu s$ looks like that of echo 2 at $t=5 \mu s$ but with opposite sign. This behavior of the echo responses is believed to be a consequence of the different time spans for spin precessions (i.e., different dephasing) for each of the pulse sequences as discussed previously. However, up to date, no comprehensive theory exists to explain these echo responses qualitatively. Data were also taken at 2K, 2.5K, 3K. However, data at those temperatures display no significant departure from those at 1.7K, except for the amplitudes, so it is not worthwhile to include that data.

Fourier transforms of the FID's at all the temperatures were performed to get the lineshape. While the FID gives the decay of the magnetization in the time domain, its Fourier transform gives the behavior of the spins in the frequency domain. Since our data
Fig. 19

1.7K FID of nH₂

(a) real part

(b) imaginary part
Fig. 20

1.7K Echo 1 of nH₂

(a) real part

(b) imaginary part
Fig. 21

1.7K Echo 2 of $n\text{H}_2$

(a) real part

(b) imaginary part
Fig. 22

1.7K Echo 3 of nH$_2$

(a) real part

(b) imaginary part
are taken with quadrature detection (the time domain signal contains both the real part and the imaginary part which are Fourier transformed together), it is believed that our lineshapes should be superior to those published in the past by various workers who used the conventional one-component detection. The real part of the Fourier transform is the conventional lineshape which gives the energy absorption spectrum of the Hamiltonian while its Kramers-Kronig relation counterpart, the imaginary part, has no immediate physical significance.

Figs. 23 to 26 give the lineshapes, obtained by Fourier transforms, in the order of the data taken. Again, the lineshapes at 1.3K and 1.5K look like the one at 1.1K and those at 2K, 2.5K and 3K do not look much different from the 1.7K case. At 4K, the motionally narrowed lineshape is shown in Fig. 23. As the sample was cooled to the ordered state at 1.1K, the lineshape became similar to the Pake doublet shaped absorption spectrum (see Fig. 24). In Fig. 27 (a), the lineshape obtained by Hardy and Berlinsky\(^0\) for the 96% ortho hydrogen at 1.1K is shown for comparison. Unlike our data, which is obtained by the Fourier transform of the pulse NMR, their lineshape was directly taken from the continuous-wave (cw) NMR. Up to about 150 kHz, we see that two lineshapes look like each other including the negative absorption part. The sharp negative absorption in the measurements is attributed to the population inversion of the \(m_I\) states as in the low temperature ordered solid, conversion takes place from a
Fig. 23

4K Lineshape of nH₂

(a) real part

(b) imaginary part
Fig. 24

1.1K Lineshape of $nH_2$

(a) real part

(b) imaginary part
Fig. 25

1.6K Lineshape of nH₂

(a) real part

(b) imaginary part
Fig. 26

1.7K Lineshape of nH$_2$
(a) real part
(b) imaginary part
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1.7K N-H2 LINESHAPE REAL

FREQUENCY (KHZ)

1.7K N-H2 LINESHAPE IMAGINARY

FREQUENCY (KHZ)
Fig. 27

Lineshape from Hardy and Berlinsky

(a) without folding

(b) with folding
INTEGRAL OF EXPERIMENTAL DERIVATIVE SIGNAL

$\Delta v \text{ (kHz)}$

$x_J = 0.96$
single $m_j$ state ($m_j=0$), causing emission of energy instead of absorption in some cases. In one-component pulsed NMR, any signal or noise on one side of the carrier at $\nu_0$ is indistinguishable from the same signal or noise on the other side of the carrier. So, a single spectral feature can be detected at two different frequencies symmetrically located about $\nu_0$ and the process of reflecting the feature at, say, $\nu_0 + \Delta \nu$ to $\nu_0 - \Delta \nu$ is called "folding". Fig. 27 (b) is the folded spectrum for the lineshape from Hardy and Berlinsky, Fig. 27 (a). In Fig. 27 (b), the emissive part around 100 kHz disappears, implying no detection of power emission for the folded spectrum. Thus, the detection of power emission was made possible by the use of the quadrature signal detection. At 1.6K, where the transition takes place, we have a motionally narrowed lineshape around 0 kHz, as well as the negative absorption part around 90 kHz, characteristic of the ordered state. As seen in the Fig. 26, the emissive part disappears above the transition temperature.

Following the work of Sokol, an order parameter is defined by

$$Q = \frac{\int_0^\infty \omega I(\omega) d\omega}{\int_0^\infty \omega I_{pd}(\omega) d\omega}, \quad \cdots \cdots \text{(IV.2)}$$

where $I(\omega)$ is the normalized intensity of the absorption spectrum and $I_{pd}(\omega)$ is the normalized intensity for an ideal Pake doublet. Sokol gives the value for the integral involving the Pake doublet.
as 66.63 kHz. As can be seen from the definition of the parameter Q, Q is the ratio of the average value of $\omega$ for the lineshape of interest to that of the Pake doublet that represents complete order. In Fig. 28, Q values of normal hydrogen (75% ortho) and for Sokol's 1% nH2 in 52% pD2 are plotted as a function of the reduced temperature $T/T_c$, where $T_c$ is the transition temperature. In Sokol's case, the transition temperature was defined to be 0.5K. As can be seen in the graph, the Q values are higher in the case of nH2 and they undergo a much sharper change through the transition temperature. For nH2, there is no doubt regarding a phase transition but the lower concentration sample may not be undergoing the same type of transition. Also, in the nH2 case, the remanant effect is seen by comparing the values at 4K and 3K.

As well as the order parameter Q, the conventional long range order parameter $\sigma$ was obtained as a function of temperature. In their work on high J=1 concentration D2, Meyer et al.\textsuperscript{5} showed that the separation $6\nu$ between the flattened peaks in the derivative of the absorption spectrum is proportional to $\sigma$. Thus, we took the derivative of our lineshape and it gave the quantity $6\nu$. Fig. 29 shows the derivatives thereby obtained at various temperatures and Fig. 30 shows the plot of the order parameter normalized to 1 for perfect order together with the other parameter Q and the inverse of $T_1$ as a function of the temperature for comparison. Either order parameter shows a sharp change through the transition and $1/T_1$ shows a cusp mentioned earlier.
Fig. 28

$Q$ vs. $T/T_c$ for $n\text{H}_2$ and for Sokol's Sample
Q'S VS. REDUCED TEMPERATURE

+ : Sokol's H2 in 52% P-02

+ : Lee's N-H2 sample

REDUCED TEMPERATURE
Fig. 29

Derivatives of Linshapes of $nH_2$

(a) at 4K   (b) at 1.1K
(c) at 1.6K  (d) at 1.7K
Fig. 30

$\sigma, Q, 1/T_1 \text{ vs. } T/T_c \text{ of } nH_2$
TI, DELTA NU, Q VS T/Tc

+ : I/T1 IN UNITS OF 10/MSEC
• : ORDER PARAMETER DELTA NU
x : ORDER PARAMETER Q

REDUCED TEMPERATURE T/Tc
To study the decay of echos in solid hydrogen, the three echo sequences were applied with various values of \( r \). The decay of echos in solid hydrogen was first discussed by Metzger and Gaines\(^{14}\) and they attributed it to the intramolecular terms in the Hamiltonian neglected in echo formation. The data taken show that while the decays of echo 1 and echo 2 fit the Gaussian form very well, the decay of echo 3 is not well defined, showing an oscillation of the amplitude for different \( r \)'s and fits the form of an exponential decay better than that of a Gaussian decay. Fig. 31 shows an example of decay of echo 1 at 1.1K fitted to a Gaussian function. The echo decay constants as a function of reduced temperature is shown in Fig. 32. As in the order parameters, changes at the transition temperature, especially an abrupt one in the case of echo 2, are noticed.
Fig. 31

Decay of Echo 1 at 1.1K in nH₂
Fig. 32

Echo Decay Constants vs. $T/T_c$ in nH$_2$
ECHO DECAY TIMES VS $T/T_c$ IN MICRO SECONDS

+ : ECHO 1
× : ECHO 2

REDUCED TEMPERATURE $T/T_c$
2. Deuteron NMR Data on High Concentration para Deuterium (pD$_2$)

We have seen that the J=1 ortho molecules cooperate in the ordered state to cause the oscillation in the FID signal in the case of nH$_2$. Fig. 33 shows the 4K FID of high concentration pD$_2$ at the Larmor frequency of 6 MHz. In the FID, we see the superposition of a Gaussian signal from the ortho molecules and an oscillation coming from the para molecules (note, the ortho molecules for D$_2$ have J = 0 while the para molecules have J = 1). In the 4K FID we notice the particularly long T$_2$ which is about 20 times longer than the nH$_2$ case. To understand this longer T$_2$, we must consider the intermolecular dipolar interactions.

According to Abragam$^{36}$, in a rigid lattice, the second moment $M_2$ due to "like" spins is given by

$$M_2 = (3/5)\gamma^4\hbar^2 I(I+1)\sum \frac{1}{r_{jk}^6}, \quad \ldots \quad \text{(IV.3)}$$

where the summation is over occupied sites. If only a fraction $f$ of sites is occupied,

$$\sum_{\text{occ}} \frac{1}{r_{jk}^6} = f \sum_{\text{all}} \frac{1}{r_{jk}^6}, \quad \ldots \quad \text{(IV.4)}$$

In the hcp lattice appropriate to the 4K disordered D$_2$ case,

$$\sum \frac{1}{r_{jk}^6} = 14.45/a^6, \quad \ldots \quad \text{(IV.5)}$$
Fig. 33

4K FID of $D_2$

(a) real part

(b) imaginary part
where a is the lattice constant. Note the factor 14.45 as compared to the 12 nearest neighbors in the hcp lattice. Applying the above formulae to the D$_2$ lattice with a para concentration $x_J$,

$$M_2 = \frac{3}{5} \gamma^4 \hbar^2 [2xJ + (5/6)6(1-x_J)] \sum (1/r_{jk}^6)$$

$$= \frac{3}{5} \gamma^4 \hbar^2 \sum (1/r_{jk}^6)(5 - 3x_J) \quad \text{......(IV.6)}$$

$$\propto 5 - 3x_J$$

Since $M_2$ is related to $T_2$ by

$$M_2 = 1/T_2^2, \quad \text{......(IV.7)}$$

by calculating the $T_2$'s from the nD$_2$ (33% para) FID and the high concentration pD$_2$ FID and comparing them, we estimate the value of $x_J$ for the high concentration samples to be at least 80%.

The pD$_2$ NMR experiments are hampered by the long $T_1$'s, especially in the ordered state. Hardy and Berlinsky$^{14}$ list the theoretical values of $T_1$. They estimate that $T_1$ is $4.72 \times 10^6$ seconds at 1K for pure pD$_2$. For lower J = 1 concentrations, $T_1$ will be shorter but it is still inconveniently long to do much signal averaging.
Figs. 34 to 36 show the echo sequences with $\tau = 500 \mu s$
triggered at $t = 400 \mu s$ after the second pulse. The trace of the pD$_2$
is manifest in the real parts of echo 1 and echo 2 but in echo 3 it
does not show up at all indicating the degree of decay constant, or
$T_{2E}$, of the pD$_2$ signals in each case. To be specific, since the
trace of the pD$_2$ signal is the most pronounced in echo 2 and is less
visible in echo 1 and is unnoticeable in echo 3 for the pulse
separation of 500 $\mu s$ (recall that the pulse separation has to do
with the spin precession time in the xy plane.), it turns out that
echo 3 has the greatest decay constant followed by echo 1. Echo 2
has the smallest decay constant. We also note that the imaginary
parts do not show any sign of the pD$_2$ component.

In an attempt to see if there was any angular dependence in
the lineshape of the pD$_2$ crystal, FID's were taken at various
angles between 0 and 90° in the 1.1K ordered state. These
measurements are shown in Fig. 37 with angles 0, 30, 60 and 90°. We
see an obvious dependence on the angle indicating that the
sample is not a powder. It is possible that our sample is a single
crystal but we cannot say for sure. Washburn et al. reported an
angular dependence of the lineshape and the order parameter $\sigma = <1
- (3/2)J_z^2>_T$ for the H$_2$ solids with ortho contents less than 55% in
which there is no transition to the ordered state. In their paper
they represent $M_2$ in the form

$$M_2 = \Phi(x_T, T) f(\cos \theta_{HC}) \quad \ldots \quad (IV.8)$$
Fig. 34

4K Echo 1 of D₂

(a) real part

(b) imaginary part
Fig. 35

4K Echo 2 of D₄
(a) real part
(b) imaginary part
Fig. 36

4K Echo 3 of $D_2$
(a) real part
(b) imaginary part
Fig. 37

Angle Dependence of $D_2$ at 1.1K

(a) $0^\circ$  (b) $30^\circ$

(c) $60^\circ$  (d) $90^\circ$
where $\theta_{Hc}$ is the angle between the applied magnetic field and the crystal axis. In the ordered state in our sample, the angular dependence is expected to be more pronounced than in their sample because our sample displays a Pake doublet lineshape characteristic of the long range orientational order.

As was done in the case of $\text{H}_2$, a lineshape was obtained by Fourier transforming the FID at 1.1K to test for emission of power. This is shown in Fig. 38. A very sharp negative absorption part (emission of power) at 40 kHz is noticed. A broad and less sharp negative part in the absorption spectrum of the $J=0$ molecules in $D_2$ was observed earlier by Hardy and Berlinsky\textsuperscript{30}. However, the negative absorption accompanying the line splitting in our lineshape is the first one directly observed from the pulsed NMR of $J=1$ molecules although partial contribution from the $J=0$ molecules ($I=2$) is included in our lineshape.
1.1K Lineshape of \( \text{D}_2 \)

(a) real part

(b) imaginary part
As stated in the previous section, the deuteron NMR poses a serious problem because of the long $T_1$ making it difficult to take an extensive set of data within a reasonably short time. The low Larmor frequency due to the limited magnetic field strength gives a longer deadtime after the first pulse. This deadtime is inversely proportional to the frequency so, to first order, the higher the frequency, the lower the deadtime. Also a poorer signal to noise ratio ($S/N$), proportional to the square of frequency results for deuterium NMR. If we put 1% $nH_2$ in the $pD_2$ sample and use the protons, with their much shorter $T_1$ and much higher Larmor frequency as a probe for the $pD_2$ crystal, we can conduct extensive measurements of FID and echos at the Larmor frequency of 30 MHz. In this case, it is to our advantage to lose signal to noise ratio by magnetic dilution as we recover it by signal averaging. The ortho $H_2$ molecules share many properties with the para $D_2$ molecules (both have $I=1$, $J=1$) like the same quadrupole moment which is independent of their mass difference. Thus the $oH_2$ molecules act as mass defects in the $pD_2$ lattice and they should show the properties of the $D_2$ lattice.

This section presents data obtained in the same fashion as in section 1. Because of the longer $T_1$ and poorer signal to noise ratio (1/100 of the number of $oH_2$ molecules), echo sequences of $\tau=50 \mu s$ only were taken. As Sokol also reported in his
dissertation, the 90° - τ - 180° sequence gave too small an amplitude to give any useful information, especially in the ordered state, so we do not present signals from this sequence in this dissertation.

Figs. 39 to 41 show the 4K FID, echo 1 (90° - 50 μs - 90°90°) and echo 2 (90° - 50 μs -90°). The real and imaginary parts of the echos resemble the real part of the FID with the real part of echo 2 inverted. In contrast to the nH₂ case, we do not see the Lowe beat in this case (nor is it expected due to the magnetic dilution of the oH₂ spectrum).

Figs. 42 to 44 show the 1.1K signals which give us much the same comparison as the 4K case. At both temperatures echo 1 gives a much larger real part than echo 2 but their imaginary parts are almost identical.

Figs. 45 to 47 present the 3.1K data where the transition occurs. Comparing the real parts of the FID, echo 1 and echo 2, we see a noticeable difference among them, mainly in the mixture of contributions from the oscillatory component and from the motionally narrowed structure.

Figs. 48 to 50 present the 3.3K data which generally resembles the 4K behavior, with the change of ratio of the real part and the
Fig. 39

4K FID of H₂ in D₂

(a) real part

(b) imaginary part
Fig. 40

4K Eche 1 of H₂ in D₂
(a) real part
(b) imaginary part
Fig. 41

4K Echo 2 of $H_2$ in $D_2$

(a) real part

(b) imaginary part
Fig. 42

1.1K FID of $H_2$ in $D_2$

(a) real part

(b) imaginary part
1.1K Echo 1 of H₂ in D₂
(a) real part
(b) imaginary part
Fig. 44

1.1K Echo 2 of H₂ in D₂
(a) real part
(b) imaginary part
3.1K FID of H$_2$ in D$_2$

(a) real part
(b) imaginary part
Fig. 46

3.1K Echo 1 of H$_2$ in D$_2$

(a) real part

(b) imaginary part
Fig. 47

3.1K Echo 2 of H₂ in D₂

(a) real part

(b) imaginary part
Fig. 48

3.3K PID of H\textsubscript{2} in D\textsubscript{2}

(a) real part

(b) imaginary part
Fig. 49

3.3K Echo 1 of H₂ in D₂
(a) real part
(b) imaginary part
Fig. 50

3.3K Echo 2 of H$_2$ in D$_2$

(a) real part

(b) imaginary part
imaginary part of each signal to be noticed, again indicative of some phase shift through the transition.

As in the nH₂ case, lineshapes were obtained by Fourier transforming the FID signals. Fig. 51 shows the motionally narrowed lineshape with an unidentified negative absorption around 40 kHz. This leaves its trace in the 1.1K lineshape in Fig. 52 and up to the transition temperature in Fig. 53, disappearing above the transition, in Fig. 54.

The 1.1K lineshape, Fig. 52, displays a line splitting, to be compared with Fig. 24 from the nH₂ case. We again have the negative absorption, i.e. emission of power, right after 80 kHz. Fig. 53 shows the characteristic of Fig. 25, the line splitting getting weaker, still showing the emission of power. Fig. 54 shows a simple motionally narrowed lineshape with no emission of power.

In the same manner as the nH₂ case, the order parameter Q as a function of the reduced temperature T/Tc is plotted in Fig. 55, again demonstrating a much more drastic change in Q than the 52% sample of Sokol¹⁰ through the transition temperature.

The derivative of the lineshape was taken for all the temperatures. Fig. 56 shows the derivative of the absorption spectra at various temperatures. δν, the frequency difference between the flattened peaks in the absorption spectra was measured
Fig. 51

4K Lineshape of H₂ in D₂

(a) real part

(b) imaginary part
Fig. 52

1.1K Lineshape of H\textsubscript{2} in D\textsubscript{2}

(a) real part

(b) imaginary part
Fig. 53

3.1K Lineshape of H$_2$ in D$_2$

(a) real part

(b) imaginary part
Fig. 54

3.3K Lineshape of H₂ in D₂

(a) real part

(b) imaginary part
3.3A NO IN P=02 - FINE SHAPE ABSORPTION

3.3A NO IN P=02 - FINE SHAPE DISPERSION
Fig. 55

Q vs. $T/T_C$ for H$_2$ in D$_2$ and for Sokol's Sample
Q'S VS. REDUCED TEMPERATURE

♦ : SOKOL'S 52% SAMPLE

♦ : LEE'S SAMPLE

REDUCED TEMPERATURE T/TC
Fig. 56

Derivatives of Lineshape $H_2$ in $D_2$

(a) at 4K          (b) at 1.1K
(c) at 3.1K        (d) at 3.3K
and it is plotted as a function of the reduced temperatures in Fig. 57, normalized to 1 for complete order. A sharp change of the order parameter is again noticed. However, unlike Q, it is zero above the transition temperature.

Sokol used the conventional one-component detection with no phase correction for his 52% sample. He also saw no indication of emission of power on the lineshape below the transition temperature. It is possible that had Sokol used the quadrature detection with a constant phase correction, he would have seen the negative absorption. To test this possibility, we introduced different phase corrections in an attempt to artificially remove the emissive part. However, this resulted in a significant distortion of the lineshape and it still showed a visible structure from the position of the emission on. In contrast, Sokol's lineshape showed no structure at all after the line splitting, decaying smoothly in the frequency domain. This leads to the conclusion that for the 52% sample of Sokol, probably there is no emission of power.

To test the theory of Metzger and Gaines\textsuperscript{14} that the decay of echos arises from the intramolecular interactions, data for echo 1 and for echo 2 were taken with various pulse separations. Unlike the case of nH\textsubscript{2}, echo 1 gave the only well defined decay in time. Following a Gaussian fit, the decay times of echo 1 are plotted as a function of the reduced temperatures in Fig. 58.
Fig. 57

$\sigma$ vs. $T/T_c$ of $H_2$ in $D_2$
X H2 IN D2 SIGMA(T)/SIGMA(0) VS. T/Tc

REDUCED TEMPERATURE T/Tc
Fig. 58

Decay Time of Echo 1 vs. $T/T_c$ of $H_2$ in $D_2$
H2 IN D2 ECHO 1 DECAY TIME VS. T/Tc

REDUCED TEMPERATURE T/Tc
CHAPTER V

DISCUSSION AND CONCLUSIONS

The work covered in this dissertation is related to four scientific issues: (1) the usefulness of NMR as a probe of phase transitions; (2) the detection of power emission in the orientationally ordered state of hydrogen isotopes; (3) qualitative comparisons of lineshapes from FID's and echos to indicate when echo responses can be used for lineshape analysis; (4) the cause of the decay time of echos in a simple solid such as H₂ and D₂. Some of the above questions have been investigated before by other workers. However, in this study, a superior experimental approach was possible due to the use of quadrature detection so that even the previously investigated areas yielded some new results. I will comment on each of the above issues below.

(1) In a series of experiments done on H₂ and D₂ with high J=1 concentrations, we have verified the results of others concerning the existence of a phase transition. This transition is due to a cooperative quenching of the free rotation of J=1 molecules in the solid that leads to an orientationally ordered state below some specific temperature. This is a \( \lambda \) transition in nature. In the case
of n-H$_2$, the transition temperature, $T_c$, was 1.6K and for the p-D$_2$ sample made in our laboratory, $T_c$ was 3.1K. In terms of the MNR measurements, this phase transition is characterized by sudden changes in both the lineshape and the spin-lattice relaxation time. This means that above $T_c$, the lineshape is motionally narrowed, while below $T_c$, we have a resolved doublet line resembling a Pake doublet. In time domain, as observed by the FID signal, the split lineshape is observed as a damped oscillation with the period of oscillation determined by the width of the line splitting.

This phase transition in the hydrogen isotopes is sharp, drastically changing the lineshape over a temperature range of less than ±3 % in the reduced temperature $T/T_c$. This observation demonstrates that NMR is a sensitive indicator of the orientational order in hydrogen isotopes. For this phase transition, the conventional order parameter $\delta \nu$, which is a measure of the line splitting, appears to be a good order parameter for the long range order that accompanies the transition. On the other hand, the quantity $Q$, defined to be the ratio of the average frequency in the lineshape to that of an ideal Pake doublet, better characterizes short range (or local) order. In other words, while $\delta \nu$ vanishes above the transition, $Q$ is non-zero above $T_c$ although it does change at $T_c$, reflecting local order in clusters and possibly also long range order. The phase transition is marked by an abrupt change in all of the quantities $T_1$, $\delta \nu$ and $Q$. 
In the experiment on 1% n-H$_2$ in D$_2$, we have shown that n-H$_2$ in D$_2$ is an acceptable probe of the orientational ordering transition in D$_2$. In other words, an NMR experiment on n-H$_2$ in D$_2$ reflects the properties of D$_2$. The change in the lineshape (e.g. line splitting) and the order parameters $\delta\nu$ and Q as well as the relaxation rate occurs at $T_c$ for D$_2$. Although some experiments on H$_2$ in D$_2$ have been done by previous workers in our laboratory$^{29}$, the author has verified the above points by a direct comparison between direct D$_2$ NMR and proton NMR in the samples with high concentration J-1 D$_2$.

(2) By means of proton NMR in n-H$_2$ and high concentration J-1 D$_2$, we have observed a special feature of NMR in the ordered state, namely power emission resulting from selective J-1 to J=0 conversion (in the orientationally ordered state, $m_J$-0 is the only occupied state) that depends on the particular $m_J^1$ state. This emission had only been observed in H$_2$ before this study. While Hardy and Berlinsky$^{21}$ theoretically predicted and also reported an observation of power emission in the ordered state of H$_2$, the observation in D$_2$ reported in this dissertation is the first one ever. The reason it was difficult to observe the power emission in continuous-wave (cw) NMR is that in cw NMR, the delicate adjustment between the absorption and dispersion mode can easily lead to an incorrect absorption part (lineshape) due to the mixing of the two parts. In contrast, in our quadrature detection pulse NMR, all the
adjustments including the phase correction were done once, well above the phase transition, and were not changed after that, eliminating any ambiguity. This is one of the reasons our quadrature detection NMR is superior to any conventional methods of NMR employed to investigate the hydrogen isotopes previously.

Power emission in D₂, which comes from the conversion of J=1 molecules to J=0 molecules is of special interest because the conversion rate in D₂ is much smaller (.06 % per hour) than in H₂ (1.9 % per hour). In our lineshapes, the emission part in D₂ was as visible as in H₂ in spite of the much smaller conversion rate. This would seem to require some additional theoretical exploration or some improved physical insight.

The observed power emission in D₂ also casts a new light onto the characterization of the "Quadrupole Glass" (where a cusp in 1/T₁ was also observed) range of concentrations. It suggests a new set of experiments to probe that range because the observation of the power emission effect seems to be a characteristic of the long range ordered state. In the intermediate J=1 concentrations for the "Quadrupole Glass" with the same experimental setup as in the work in this dissertation, by testing for power emission in those concentrations, we can test if the so called Quadrupole Glass is the same long range ordered phase as the high concentration phase studied here. In this case, the use of the word "glass" would be incorrect. In our work, the order parameter Q displayed a much
sharper change, with respect to the reduced temperature, than it did in Sokol's work on the Quadrupole Glass phase. It is possible that in the intermediate concentrations, the order shown in $1/T_1$ and the lineshape is short range (or local) order rather than the long range order seen for the higher J-1 concentrations.

(3) The third aspect of the work done in this dissertation is the comparison of the FID and the echo shape of three echo sequences, i.e., "echo 1" ($90^\circ - \tau - 90^\circ$) (with a $90^\circ$ phase shift), "echo 2" ($90^\circ - \tau - 90^\circ$) and "echo 3" ($90^\circ - \tau - 180^\circ$). A theory due to Powles and Strange predicts that the echo 1 and echo 2 should each duplicate the FID. On the other hand, Spiess and Sillescu showed that the lineshape of echo 1 in the slow-motion region where the motional correlation times are the same order as the reciprocal anisotropic spin interactions (this is in the vicinity of our phase transition) is not the same as that of the FID. To test these theories, we have done systematic measurements on the FID and the echo sequences through the phase transition. As a result of qualitative comparisons, we conclude that above and below the transition, echo 1 duplicates the FID very accurately. However, the shape of echo 1 shows a considerable deviation from the shape of the FID near $T_c$. Thus, when one wants to get the lineshape well away from a phase transition and avoid the problem of the instrumental deadtime, it is possible to use echo 1 instead of the FID itself. In fact, this is an excellent
way of getting the lineshape although it should not be used for that purpose in the vicinity of a phase transition. By comparison, echo 2 does not produce a shape resembling the FID closely enough even away from the phase transition. Especially, unlike echo 1, the shape of echo 2 depends on pulse separation $r$, and becomes inverted at around $r=20 \mu s$.

Finally, echo 3, or the Hahn echo, has a large decay constant compared to either echo 1 and echo 2 and it is distorted in shape compared to the FID even more than echo 2. As is in the case of echo 1, echo 2 and echo 3 have the same overall features of the FID above and below the phase transition. While echo 1 deviates considerably from the FID in the vicinity of the phase transition, echo 2 and echo 3 show even more of a deviation in that region.

(4) As far as we know, the work on the echo decay in the hydrogen isotopes presented in this dissertation is the most systematic one in that area to be reported. This has something to do with a problem arising from conventional one-component detection because it gives only one component of the echo signal vector in the xy-plane. Since the echo signal vector precesses in that plane, its vector amplitude can be obtained only if the projections along the x-axis and the y-axis are available. The quadrature detection employed for this dissertation solves this problem and makes it possible to obtain the echo amplitudes as a function of $r$. 

This is another example for the superiority of the quadrature detection.

The decays of echo 1 and echo 2 in \( nH_2 \) are well defined and fit the Gaussian form of a decay very well. However, the decay of echo 3 is not well defined, showing an oscillation of the amplitude. Furthermore, it fits an exponential decay better than the Gaussian decay. This is thought to be because echo 3 is very sensitive to even a very slight mistuning (or a fluctuation in the applied field).

Plotted on the reduced temperature scale, the decay times of echo 1 and echo 2 show different slopes above and below the transition temperature. Namely, the slopes are steeper below the transition than above the transition. The decay time of echo 1 on the reduced temperature scale is a continuous quantity with different slopes above and below the transition. However, the decay time of echo 2 is a discontinuous quantity, consisting of two completely separated segments of lines. Thus, the echo 2 decay time displays a more dramatic change characteristic of the \( \lambda \) transition (with a discontinuous feature) than that of echo 1.

Comparing the decay constants of echo 1 in \( nH_2 \) directly observed by signals from the \( oH_2 \) molecules (Fig. 31) and in \( D_2 \) with the \( oH_2 \) molecules as a probe (Fig. 57), we find that around the phase transition temperature, they are very close with the same
order of magnitude and the general trend is the same (they are decreasing with increasing temperature) although in the case of H\textsubscript{2} in D\textsubscript{2}, there is a slight sudden increase in the decay constant at the transition temperature. This implies that the decay of echos comes from the intramolecular interactions as Metzger and Gaines\textsuperscript{14} suggested. Their theory is supported in that if the decay of echos comes from the intermolecular interactions, the decay constant for H\textsubscript{2} in D\textsubscript{2} would be 7 times longer than the nH\textsubscript{2} case because the intermolecular interactions for D\textsubscript{2} molecules are 7 times weaker. Obviously, this is not the case.

To conclude this dissertation, a systematic study has been done for the first time on the high concentration J=1 range in H\textsubscript{2} and D\textsubscript{2} using quadrature signal detection. Although some parts of the experiments, for example, the lineshape of H\textsubscript{2} and D\textsubscript{2} below T\textsubscript{c} and the order parameter $\delta\nu$ in D\textsubscript{2} as a function of temperature have been investigated by some workers, a most complete work has been covered in this dissertation. Especially, the work H\textsubscript{2} on the changes of the order parameters Q and $\delta\nu$ and $T_1$, the comparison of the FID and the shape of the echo sequences in H\textsubscript{2}, and the decay of echos in H\textsubscript{2} and D\textsubscript{2} is believed to be a pioneering work, with few and incomplete data available by far. In addition, one of the results of this work, especially the observations of emission of power in the long range ordered state in H\textsubscript{2} and D\textsubscript{2}, the observations in D\textsubscript{2} being the first ones in D\textsubscript{2} by the NMR signals from J=1 D\textsubscript{2} molecules and from oH\textsubscript{2} impurity molecules in D\textsubscript{2} host,
throws a new light onto the so-called Quadrupole Glass phase. The comparison of the order parameter $Q$ and the cusp in $T_1$ in the "Quadrupole Glass" intermediate $J=1$ concentration range and the higher $J=1$ concentration suggests that the Quadrupole Glass may be really something like the higher $J=1$ concentration long range ordered state. Since the observation of emission of power seems to be a characteristic of the long range ordered state, it will be a test of the above suggestion to see if emission of power is detectable in the intermediate $J=1$ concentrations. Finally, the emission of power in $D_2$ sample with 1% $nH_2$ as a probe at 40 kHz, which is observed in the 4K disordered state and disappears when the sample goes back to above $T_c$ from the ordered state is an unresolved problem.
APPENDIX

Determination of Concentration of the D$_2$ Sample

The determination of high J-1 concentration D$_2$ sample was made by the thermal conductivity cell. The thermal conductivity of the D$_2$ sample varies linearly as the J-1 concentration. In fact, higher J-1 concentration samples result in lower thermal conductivity. Thermal conductivity $\lambda_{av}$ is measured from

$$Q = \lambda_{av}(T_0, \Delta T)G\Delta T$$

where $G$ is the geometric factor, $Q$ is the heat flow in the region of the temperature gradient $\Delta T$, and $\Delta T$ is the deviation from the liquid N$_2$ temperature in the case of this measurement.

Two other samples with known J-1 concentrations, nD$_2$ (33% J-1 concentration) and a D$_2$ sample with 70% J-1 concentration were used for the determination of the high J-1 concentration which was used in the experiment. Comparison of the thermal conductivities of three gave a J-1 concentration of 80% for the sample used in the experiment.
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