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Study of the Nuclear-Magnetic-Resonance Line Shape in hcp D_2[†]

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A study of the nuclear-magnetic-resonance (NMR) absorption line shape in solid hcp D_2 in the nondiffusive region is presented. The mole fraction C of paramolecules (i.e., those with) a rotational angular momentum $J=1$) ranged from 0.02 to 0.93, and the temperature was varied between 0.5 and 10 °K. Both continuous-wave (cw) and pulse (free-induction-decay) methods were used to obtain complementing information on the NMR absorption line shape. It is shown that the line shape attributed to $J=1$ molecules broadens rapidly with decreasing temperature. At low enough temperatures, cw experiments record only the absorption from the $J=0$ molecules. Second moments M_2 were obtained from the analysis of both cw and pulse experiments. Over a restricted range of mole fractions and temperatures, M_2 both for the signal from all the molecules and for that from the $J=0$ molecules alone could be obtained separately from the free induction decay. The extrapolation of M_2 to the high-temperature limit where the line shape is determined by random intermolecular nuclear dipole-dipole interactions is in good agreement with theoretical predictions. A discussion is presented of the observed and theoretically expected temperature variation of M_2 for both $J=1$ and $J=0$ molecules. The results support the calculations by Harris which take account of admixtures of the $J=2$ excited state in the $J=0$ ground-state wave function, caused by the interactions with $J=1$ molecules.

I. INTRODUCTION

As an introduction to the present study of NMR in solid D_2, let us briefly review the results for solid H_2, presented in a previous paper.[1] As is well known, this solid can be prepared as a mixture of molecules having a rotational angular momentum $J=0$ (para) and $J=1$ (ortho), with any mole fraction C of the $J=1$ molecules between a few tenths of a percent and about 99%. Only the molecules with $J=1$ give an NMR absorption signal. The rotational motion of these molecules is affected by the electric-quadrupole-quadrupole (EQQ) coupling, mainly between nearest $J=1$ neighbors. Below about 10 °K, where there is no thermally activated diffusion, the line becomes progressively broader[1] as a result of the orientational ordering of the $J=1$ molecules.[2] Below the transition to the cubic phase, for sufficiently high $J=1$ concentrations, the familiar doublet structure[3] is observed with a splitting of about 160 kHz.

The situation for solid D_2 is similar. Here both $J=1$ molecules and the fraction $\frac{5}{6}$ of the $J=0$ molecules with nuclear spin $I=2$ give a resonance signal. The ratio of the integrated NMR signal intensities I from the two species is

$$\frac{\mathscr{I}(J=1)}{\mathscr{I}(J=0)}=\frac{2C}{5(1-C)} . \qquad (1)$$

As the temperature is decreased, the orientational ordering of the $J=1$ molecules should again be reflected in a broadening of the NMR absorption line.[2] On the other hand, for $J=0$ molecules one would expect relatively little thermal variation in the rotational state and hence little change in the shape of the NMR signal. Just as in solid H_2, the NMR spectrum shows in the ordered cubic phase a doublet structure for the absorption line of the $J=1$ molecules.[4,5] In addition, the line attributed to the $J=0$ molecules shows a small splitting[5] indicating that the $J=0$ state contains admixtures from the first excited $J=2$ state.[2]

In this paper we present a study of the NMR line shape in the orientationally disordered hcp phase of solid D_2 in the nondiffusive region below 12 °K. The results in the cubic (ordered) phase were presented in Ref. 5, where a short discussion has already been given of the second moment M_2 of the line shape in the hcp phase.

Here we show that the observed M_2 extrapolated to the high-temperature limit agrees well with that predicted for intermolecular nuclear dipole-dipole interaction in a rigid lattice. As the temperature decreases, the rapid broadening of the absorption line can be followed both by the steady-state and the pulse methods at sufficiently high mole fractions of $J=1$ molecules. Below $C\sim 0.6$, the observed M_2 from steady-state absorption measurements is mainly that of the $J=0$ molecules, because the line shape associated with the $J=1$ molecules becomes too broad to be distinguished from the background noise. However, pulse techniques allow one to measure the M_2 of the total-absorption line, and in favorable cases even to separate the contributions resulting from the $J=1$ and $J=0$ molecules. The moment M_2 of the latter is in very good agreement with the results from the cw method. The small temperature dependence of M_2 from the line shape attributed to $J=0$ molecules shows again the small admixture of the higher rotational state into the $J=0$ ground state. This is in agreement with the predictions by Harris.[2]

II. THEORETICAL BACKGROUND

The problem of the second moment M_2 of the NMR absorption line in D_2 has recently been treated by Harris.[2] He showed that, in general,

$$\langle \Delta\nu^2 \rangle \equiv M_2 = M_2^{\mathrm{inter}} + M_2^{\mathrm{intra}} , \qquad (2)$$

where ν is the frequency and where the two terms on the right-hand side are, respectively, the contributions from the intermolecular and from the intramolecular nuclear dipole-dipole interactions. When the rotation of the $J=1$ molecules is entirely free and there is no diffusion, M_2^{intra} vanishes and the *inter*molecular nuclear dipole-dipole interaction alone is responsible for the line shape. Assuming that both the $J=0$ and $J=1$ molecules are resonating, the Van Vleck second moment for the rigid lattice is given by[2]

$$M_2^{\mathrm{inter}} = \frac{3\gamma^4 h^2}{5R_0^6} (5-3C) \sum_j \left(\frac{R_0}{R_{ij}} \right)^6$$

$$= 0.0324\,(5-3C)\ (\mathrm{kHz})^2 \quad (\text{rigid lattice}) , \qquad (3)$$

where γ is the gyromagnetic ratio for the deuteron, C is the mole fraction of $J=1$ molecules, $R_0 = 3.59 \times 10^{-8}$ cm is the nearest-neighbor distance[6] in the hcp phase, and R_{ij} is the distance between the molecules i and j.

Because of zero-point vibrational motion in the lattice, the value of R_{ij} for nearest neighbors is effectively increased. This effect is negligible for other than nearest neighbors. Using the expression given by Harris [Eq. (3.19a) of Ref. 2] with the parameters he calculated for D_2, Eq. (3) becomes

$$M_2^{\mathrm{inter}} = 0.031(5-3C)\ \mathrm{kHz}^2 \quad (\text{quantum crystal}) . \qquad (4)$$

For the intramolecular dipole-dipole interactions, we see from the basic definition of the second moments that

$$M_2^{\mathrm{intra}} = M_2^{\mathrm{intra}}(J=1) + M_2^{\mathrm{intra}}(J=0) , \qquad (5a)$$

which we write as

$$M_2^{\mathrm{intra}} = \frac{2C}{5-3C}\, m_2(J=1) + \frac{5(1-C)}{5-3C}\, m_2(J=0). \qquad (5b)$$

The reason for explicitly factoring out the quantities $2C/(5-3C)$ and $5(1-C)/(5-3C)$ is that they reflect the intensity factors associated with the different nuclear spin species in D_2. The quantities $m_2(J=1)$ and $m_2(J=0)$ involve intrinsic rotational averages and vanish at infinite temperature when the rotation of the molecule is completely random. Also, $m_2(J=1)$ and $m_2(J=0)$ are the moments that would be experimentally obtained if only the resonances of $J=1$ or $J=0$ molecules, respectively, were observed. At finite temperature there is a slight departure from the random-orientational state. Harris has shown that this leads to a high-temperature expansion for m_2 of which the first terms are

$$m_2(J=1) = \tfrac{125}{3} d^2 (\Gamma/k_B T)^4 C(1-C)\left[1 - (\Gamma/k_B T)(2 + \tfrac{415}{64} C)\right] . \qquad (6)$$

Here d is the intramolecular nuclear spin coupling constant and Γ is the EQQ coupling constant[7] that governs the orientational ordering of the $J=1$ molecules.[8] Based on the work of Ref. 2, we see that $m_2(J=0)$ is negligible in comparison to $m_2(J=1)$. If we neglect this contribution in Eq. (5b), we obtain the scaling relations

$$M_{2,\mathrm{D}}^{\mathrm{intra}} = d_{\mathrm{D}}^2 f(C, \Gamma_{\mathrm{D}}/k_B T)[2C/(5-3C)] , \qquad (7a)$$

$$M_{2,\mathrm{H}}^{\mathrm{intra}} = d_{\mathrm{H}}^2 f(C, \Gamma_{\mathrm{H}}/k_B T) , \qquad (7b)$$

where the subscripts H and D denote hydrogen and deuterium, respectively. At high temperatures, the function f may be expanded in powers of $\Gamma/k_B T$, and the two leading terms of this expansion are given in Eq. (6). However, as Harris has pointed out,[2] this expansion is only valid for $\Gamma/k_B T \ll 1$, and therefore it can not be relied upon below, say, 10 °K. Accordingly, in order to get a reasonable estimate of M_2^{intra} in D_2, we have calculated it using the scaling relations of Eq. (7) in conjunction with the experimental values of M_2^{intra} for H_2. In so doing we have used the values $\Gamma_{\mathrm{H}}/k_B = 0.8$ °K and $\Gamma_{\mathrm{D}}/k_B = 1.1$ °K,[8] and the values $d_{\mathrm{H}} = 57.67$ kHz and $d_{\mathrm{D}} = 25.24$ kHz.[9]

The above treatment assumes that all molecules are contributing to the observed NMR signal. As Harris pointed out,[2] for D_2, $M_2^{\mathrm{intra}}(J=1)$ rapidly becomes much larger than M_2^{inter}. He therefore suggests that the line from $J=1$ molecules may be too broad to be detected, except at sufficiently high $J=1$ concentrations. Harris has also calculated the second moment for a rigid lattice, assuming that only $J=0$ molecules contribute effectively to the observed NMR absorption line shape. In the infinite-temperature limit, where the second moment is due only to intermolecular dipolar interaction, his result is[2]

$$M_2^{\mathrm{inter}}(J=0) = \tfrac{1}{9}(45-37C) \times 0.0324\ \mathrm{kHz}^2. \qquad (8)$$

At finite temperatures the $J=1$ molecules are no longer randomly oriented, and as a result they cause the pure $J=0$ ground state to become deformed by admixtures from the excited state $J=2$. The amplitude of this admixture is proportional[2]

TABLE I. Predicted $m_2(J=0)$ at 10 °K for various mole fractions of $J=1$ D_2 and predicted ratio $m_2(J=0)/M_2^{\mathrm{intra}}(J=1)$ in the high-temperature limit according to Harris (Ref. 2) as explained in the text.

C	0.1	0.2	0.33	0.4	0.48	0.6	0.7
$m_2(J=0)$ (10^{-3} kHz^2)	0.22	0.75	1.63	2.09	2.62	2.90	2.84
$\frac{10^2 m_2(J=0)}{M_2^{\mathrm{intra}}(J=1)}$	1.47	1.33	1.15	1.07	0.97	0.83	0.72

to Γ/B, where $B/k_B=45$ °K is the characteristic rotational-energy constant[10] for D_2. The first term in the high-temperature expansion is then

$$m_2(J=0)=(\Gamma/B)(\Gamma/k_BT)^4\varphi(C) , \tag{9}$$

where the function $\varphi(C)$ is computed as described by Harris.[2] This expression is also expected to be valid only at temperatures such that $\Gamma/k_BT\ll 1$. For convenience to the reader, we present in Table I this contribution for various mole fractions at $T=10$ °K. Also, using only the first term in $(\Gamma/k_BT)^4$ in the series of Eq. (6), we calculate the limiting high-temperature ratio $[m_2(J=0)/M_2^{\mathrm{intra}}(J=1)]$ for various mole fractions and present it in Table I. We assume that this ratio remains approximately constant as the temperature decreases. Physically, one might reason as follows. If the $J=0$ molecules actually contain $J=1$ induced admixtures of higher rotational states, then one would expect their degree of rotational ordering to be proportional to that of the $J=1$ molecules. Since $M_2^{\mathrm{intra}}(J=1)$ also reflects the degree of order, one would then expect $m_2(J=0)$ to scale approximately with $M_2^{\mathrm{intra}}(J=1)$, regardless of temperature.

III. EXPERIMENTAL CONSIDERATIONS

Two different but complementary experimental techniques were used in this study. They are the continuous-wave and the free-induction-decay methods. The first one is best for recording the shape near the center of the absorption line, while the second one (provided the amplifier recovery time is short enough) records best the wings of the line.

The continuous-wave NMR spectrometer was the low-level Robinson oscillator used previously,[1] and the techniques of recording and processing the absorption lines were the same as before. The resonant frequency was about 5.5 MHz. Because of the long relaxation times, typically 2–10 sec, care was taken to avoid saturation of the line. The line-shape derivatives and M_2 were examined as a function of the rf level of the spectrometer, and only data taken at power levels well below saturation were used.

The pulse measurements were done at 4.7 MHz with the equipment used in previous relaxation experiments.[11] The pulse duration ranged from 10 to 30 μsec. It should be noted that a 90° pulse consistently corresponded to about 70 μsec, but in the present measurements, the recovery time of the detection system was balanced against the signal-to-noise ratio in selecting the pulse widths. The dead time for the detector following a pulse was about 50 μsec. The signals were registered on a Tektronix storage oscilloscope from which the readings were taken. The second moment is best obtained from the normalized free-induction-decay signal $G_1(t)$ using the relation[12]

$$G_1(t)/G_1(t=0)=1-(2\pi)^2\tfrac{1}{2}M_2t^2+\cdots . \tag{10}$$

As will be shown below, the free-induction-decay method allows one to obtain separately, under favorable circumstances, the M_2 of the total line shape and the M_2 from the absorption by $J=0$ molecules alone. Furthermore, by Fourier transformation of the free-induction-decay signals, the absorption line shapes can be obtained for comparison with those from the cw measurements. As M_2 becomes larger than about 10^7 Hz^2, the decay of the signal from the $J=1$ molecules is faster than 50 μsec, and hence it can only be estimated roughly from the free-induction-decay experiment. Then only the signal decay from the $J=0$ molecules can be recorded, where M_2 is of the order of 10^5 to 10^6 Hz^2. Constable and Gaines[13] (CG) have, however, used the "solid echo technique" to measure $m_2(J=1)$ of the order of 5×10^7 Hz^2.

The D_2 gas used was the same as in Refs. 5 and 11 and the analysis of the $J=1$ mole fraction was carried out using the same technique as in Ref. 11. The cryostat used in these experiments was also the same as in a previous work[1] and permitted a temperature range between 0.4 and 25 °K to be covered in a continuous way.

IV. RESULTS AND DISCUSSION

We first present the results obtained by the cw method and then, separately, those from the free-induction-decay method. Because of the good agreement between the two techniques where the data overlap, a more complete discussion of the results is left for a third paragraph.

A. cw Method

The difficulties encountered in the measurements on D_2 were considerably more severe than for H_2. The relatively small linewidth as registered by the NMR spectrometer required a greater stability in both the applied dc magnetic field and the frequency of the spectrometer. The smaller signal-to-noise ratio and the broadening of the wings of the line with decreasing temperature also contributed to the scat-

TABLE II. Smoothed values of the observed M_2 in kHz^2 attributed mainly to the resonance of $J=0$ molecules. The data presented have been obtained from cw experiments. Those marked with an asterisk have been determined both from cw and free-induction-decay experiments and agree within the experimental scatter of ±10%.

C/T(°K)	10	8	6	5	4	3	2.5	2.0	1.6	1.25	1.0	0.8	0.7	0.6	0.5
0.02	0.166	0.166	0.166	0.166	0.167	0.167	0.167	0.168	0.168	0.169	0.170				
0.05	0.163	0.164	0.165	0.166	0.168	0.170	0.172	0.175	0.179	0.184	0.190				
0.13	0.159	0.159	0.160	0.161	0.162	0.164	0.166	0.168	0.172	0.176	0.181				
0.22	0.144	0.146	0.190	0.152	0.156	0.162	0.167	0.175	0.184	0.198	0.213				
0.33	0.135	0.137	0.139	0.141	0.144*	0.151	0.157	0.166*	0.180	0.201*	0.228	0.265	0.294	0.332	0.388
0.48	0.122	0.124	0.128	0.131	0.136*	0.145	0.153	0.166*	0.183	0.209*	0.240	0.280			
0.56	0.115	0.118	0.122	0.126	0.131	0.140	0.150	0.163	0.182	0.210	0.246				

ter. In Table II, the smoothed values of M_2 are presented as a function of T for various mole fractions at regular temperature intervals. The scatter of the data was on the average about ±10%. To show the trend of the data more clearly, these smoothed M_2 values are presented to three figures. The lines for which moments are recorded in this table are almost Gaussian. A representative example is that at $C=0.33$, where over the whole temperature range the ratio $M_4/M_2^2=2.8\pm0.4$. Here M_4 is the fourth moment. Also for $C=0.33$, the agreement with free-induction-decay measurements by Constable and Gaines[13] is well within the experimental uncertainty for both experiments over the overlapping temperature range 0.5–4 °K. The present data, however, are in disagreement with a previous study in this laboratory[14] where a larger M_2 was measured at $C=0.33$ and 4.2 °K. The older results may have been affected by magnetic field inhomogeneities. In Table III, the smoothed data taken by the cw method for $C=0.93$ are presented. These data are representative of the second moment of the total line shape.

The extrapolation to the high-temperature limit has been carried out on M_2 vs $1/T^2$ and $1/T$ plots. Such extrapolations exhibited increasing scatter as the observed temperature dependence of M_2 increased. Actually, the true M_2 of the line resulting from the resonance of both $J=1$ and $J=0$ molecules changes faster as a function of T when C assumes intermediate values [see Eq. (6)]. However, the signal from the $J=1$ molecules becomes weaker as C decreases [Eq. (1)] and is spread over such a large frequency band that it becomes progressively unobservable with decreasing temperature. Thus, below about $C=0.5$ and below about 3 °K, the M_2 observed by the cw technique is to be attributed to the absorption from $J=0$ molecules only.

TABLE III. Smoothed values of M_2 in kHz^2 of the whole absorption line. The values at $C=0.48$ and 0.71 have been obtained from free induction decays. The values at $C=0.93$ have been obtained by the cw technique. Those numbers with an asterisk were taken at $C=0.91$ by the pulse method and agree within experimental scatter with those obtained by means of the cw technique.

C/T(°K)	10	8	6	5	4	3.3	2.5	2.0	1.6
0.48	0.20	0.28	0.48	0.65	0.85	1.25	1.90	2.75	4.55
0.71		0.25	0.46	0.63	0.88	1.15			
0.93	0.16	0.20*	0.26	0.32	0.43*	0.56*			

In Fig. 1 the extrapolated $M_2(T=\infty)$ vs C is compared with the theoretical predictions, Eqs. (3), (4), and (8). As can be seen, the experimental results seem to point towards agreement with the rigid-lattice model, or at least to a smaller correlation between motions of nearest neighbors due to zero-point motion than in solid H_2. This is consistent with the conclusions from a tabulation[8] of the Γ values obtained in various experiments, and which indicates less zero-point motion in D_2 than in H_2. Certainly the NMR data indicate that in the high-temperature limit, $J=0$ and $J=1$ molecules both contribute to M_2. This is clearly shown by the disagreement with Eq. (8), calculated for resonance by $J=0$ molecules only.

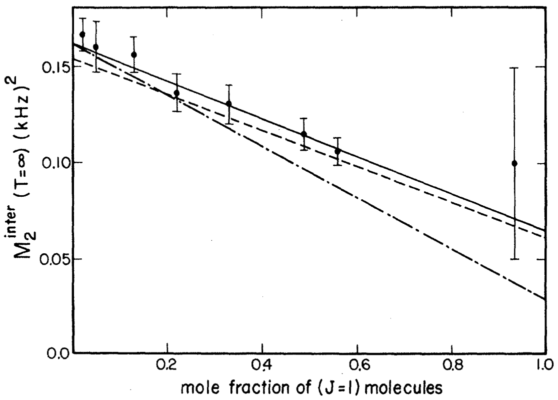

FIG. 1. Extrapolated high-temperature limit $M_2(T=\infty)$ plotted vs the mole fraction of $J=1$ molecules. Solid line: theoretical prediction for a rigid lattice. Dashed line: prediction for a lattice with correlation of motions (Ref. 2) between nearest neighbors. Dot-dashed curve: prediction from Eq. (8), assuming only $J=0$ molecules resonate.

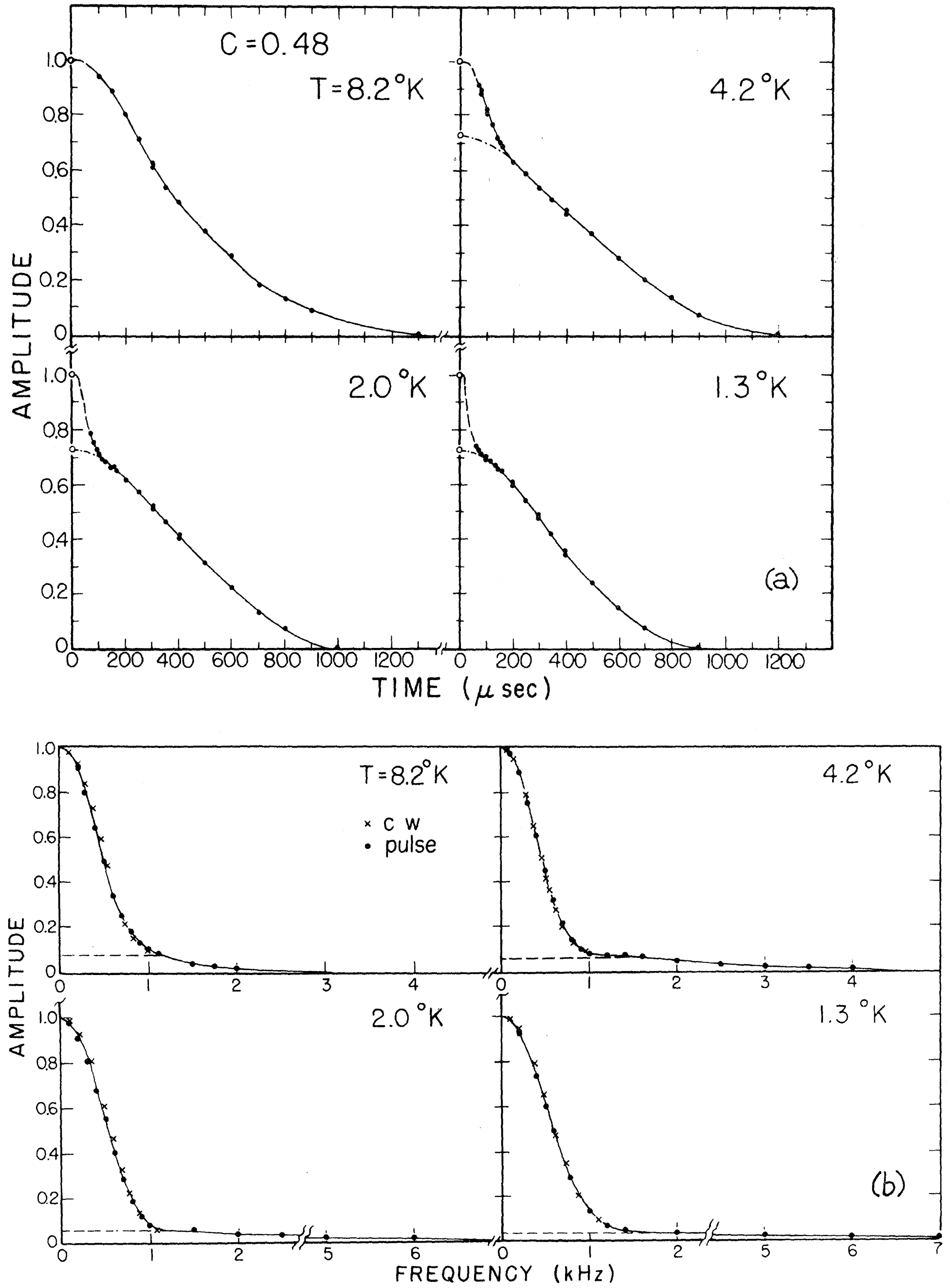

FIG. 2. (a) Normalized free induction decay for $C = 0.48$ at various temperatures vs time. The point at $t = 0$ was obtained as described in the text. (b) Normalized Fourier transforms (closed circles) for the free-induction-decay curves shown in (a). These are the NMR absorption line shapes and they are compared with those observed directly by means of the cw method (crosses). The broadening of the part attributed to $J = 1$ molecules is very striking and explains why it cannot be observed with the cw method. The dashed horizontal lines indicate the baseline of the NMR absorption observed by the cw method.

B. Pulse Experiments

These measurements were carried out mainly at high and intermediate mole fractions of $J = 1$ molecules. The purpose was to observe more clearly than with the cw method the rapid broadening of the absorption which resulted from the $J = 1$ molecules becoming orientationally ordered with decreasing T. In Table III, we present smoothed values of M_2 for the total-absorption line taken by the pulse method in addition to those mentioned in Sec. IV A. The uncertainty in the determination of M_2 from Eq. (10) was found to increase strongly as the time for the free induction decay decreased, and varied between ± 10 and ± 50%. An additional uncertainty comes from the finite pulse width, and is increasingly important as the free-induction-decay time becomes comparable with the pulse width. It is estimated that at the lowest temperatures, this error could cause a reduction in $M_2(J = 1)$ by as much as a factor of 1.5. For $C = 0.48$ the values for M_2 due only to the $J = 0$ molecules could also be extracted from the pulse measurements at and below 4.2 °K and are included in Table II. They are in excellent agreement with those obtained from cw measurements and are not listed separately. As an example, we show in Fig. 2(a) the data obtained for $C = 0.48$ for which the intensity ratio at $t = 0$ is $\mathcal{I}(J=1)/\mathcal{I}(J=0) = 0.369$. The signal at $t = 0$ was calculated at each temperature assuming Curie's law and using as a normalization a measurement at 18.5 °K, where the decay of the signal with t was sufficiently slow to allow an accurate extrapolation to $t = 0$. This figure shows the progressively faster decay of the signal from the $J = 1$ molecules as T decreases. Thanks to the normalization point at $t = 0$, a plot of $G_1(t)$ vs t^2 yielded reasonably well-determined values for M_2. With the aid of the normalization point reduced by the ratio of signal intensities, $\mathcal{I}(J=0)/[\mathcal{I}(J=0)+\mathcal{I}(J=1)]$, we could also calculate the contribution to M_2 from the $J = 0$ molecules alone for sufficiently low temperatures. This is shown in Fig. 2(a) by the dot-dashed curves for $T = 4.2$, 2.0, and 1.3°K. When these curves join into the observed decay curves, the signal from the $J = 1$ molecules has practically decayed to zero, and the remaining one is that from the $J = 0$ molecules. Figure 2(b) shows the Fourier transform of the decays at the various temperatures and illustrates dramatically the broadening of the line and its decomposition into a sharp one, mainly the contribution of the $J = 0$ molecules, and a broad one due to the $J = 1$ molecules. Also in Fig. 2(b), we present the line as observed by the cw NMR method. As can be seen, this last method only detects the sharp line when the other one becomes very broad with a low signal-to-noise ratio. The dashed horizontal line at each temperature represents the "base line" of the absorption observed by the cw technique. The agreement of the line shape observed by both methods over a frequency range of ± 2 kHz is excellent. For $C \sim 0.9$, where the intensity of the signal from $J = 1$ molecules is still relatively high, and the broadening with decreasing temperature is not too fast, both cw and pulse methods give the same total line shape and consistent values for M_2 well within the scatter of the experiment, about ± 10%.

C. Discussion

In this section we are mainly interested in the contributions to M_2 from the intramolecular dipolar interactions. First, using the results from pulse measurements (Table III) we plot in Fig. 3, for $C = 0.48$, $M_2^{\text{intra}} = M_2\,(\text{observed}) - M_2^{\text{inter}}$, where M_2^{inter} is the value predicted for the rigid lattice, and is consistent with the extrapolated $M_2(T = \infty)$ result within the experimental error. Ignoring the small contribution of the $J = 0$ molecules, this plot then gives $M_2^{\text{intra}}(J=1)$. Second, we plot $M_2^{\text{intra}}(J=1)$ obtained by scaling the H_2 results [Eqs. (7a) and (7b)]. We note that the predicted $M_2^{\text{intra}}(J=1)$ and the observed one differ by a factor of the order of 2. Third, we plot the high-temperature expansion for $M_2^{\text{intra}}(J=1)$ derived by Harris [Eq. (6)] over the temperature range where it appears to converge reasonably well. We note that within the experimental uncertainties it joins on smoothly to the observed $M_2^{\text{intra}}(J=1)$ curve. The same observations were made on plots for $C = 0.91$ and 0.78. However, for all $J = 1$ concentrations for H_2, it was observed that the experimental[1] $M_2^{\text{intra}}(J=1)$ did not join smoothly to the theory by Harris and had a discontinuity indicating the experimental value to be larger by a factor of about 2. This seems consistent with the observations in D_2, but the reasons for this discrepancy are still not understood. We will assume, however, that $M_2^{\text{intra}}(J=1)$ for D_2, predicted by scaling the H_2 results, is too high by a factor of 2 for all mole fractions of $J = 1$ molecules. Lastly, we plot in Fig. 3 for the same mole fraction the differences $m_2(J=0) = M_2\,(\text{observed}) - M_2^{\text{inter}}$, where M_2 (observed) is the moment for the line when the contribution from the $J = 1$ molecules is too broad to be observed.[15] This quantity $m_2(J=0)$, being a difference of two comparable numbers, becomes progressively less certain as T in-

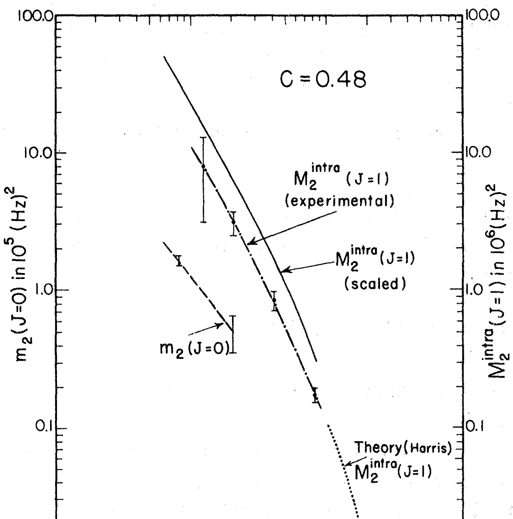

FIG. 3. Second moment M_2^{intra} for the mole fraction $C = 0.48$ vs T. $M_2^{\text{intra}}(J=1)$ scaled from the H_2 results is represented by the solid curve. The experimental data for $M_2^{\text{intra}}(J=1)$ are represented by the dot-dashed curve. The dotted curve for $T \geq 10$ °K is that predicted by Harris (Ref. 2). Note that the scale for these three curves is on the right-hand side of the graph. The dashed curve to the left represents experimental data and is attributed mainly to $m_2(J=0)$. The error bars are representative uncertainties for the dashed curve.

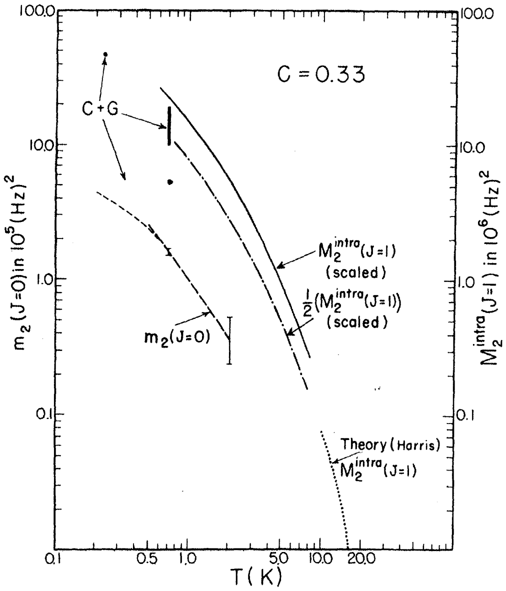

FIG. 4. Second moment M_2^{intra} for $C=0.33$ vs T. $M_2^{intra}(J=1)$ scaled from the H_2 results (Ref. 1) is represented by the solid curve. The dot-dashed curve is $M_2^{intra}(J=1)$ divided by 2, as explained in the text. The dotted curve for $T \geq 10$ °K is that predicted by Harris (Ref. 2). The scale for these three curves is on the right-hand side of the graph. The curve to the left is that attributed to $m_2(J=0)$. The point, the vertical bar, and the shorter dashed curve below 0.4 °K refer to measurements by Constable and Gaines (Ref. 13) as described in the text. Above 0.4 °K, the longer dashed curve represents both the results by Constable and Gaines (Ref. 13) and those of this paper. The error bars are representative of the uncertainties of $m_2(J=0)$.

creases and therefore is only presented below 2 °K. Within the large combined experimental error, we note that

$$m_2(J=0) \sim (1.2 \times 10^{-2}) M_2^{intra}(J=1) ,$$

which is in good agreement with the estimation in Table II.

For $C=0.33$, where line-shape measurements were carried out as low as 0.5 °K, M_2 was also found to increase substantially as T decreased. This is shown in Fig. 4, where we present $m_2(J=0)$ from our experiments together with the results obtained by Constable and Gaines.[13] We note that even at 0.2 °K, $m_2(J=0)$ has not reached its limiting $T=0$ value. We also plot the value $M_2(J=1) \sim M_2^{intra}(J=1)$ measured by CG[13] at 0.23 °K, which was taken implicitly by these authors to be the limiting low-temperature value. They also presented in their Fig. 3(b) a solid echo picture at 0.7 °K. From the broadening of the $J=1$ decay signal, we very crudely estimate $M_2^{intra}(J=1)$ to be about 14 ± 5 kHz^2. A direct determination of $M_2^{intra}(J=1)$ above about 1 °K appeared impracticable by both pulse and cw methods because of the low $\mathcal{I}(J=1)/\mathcal{I}(J=0)$ ratio.

Following the arguments presented above, we plot both $M_2^{intra}(J=1)$ and $\frac{1}{2}M_2^{intra}(J=1)$ predicted by scaling the H_2 results. Also we show the predictions by Harris for $T \geq 10$ °K. We find $m_2(J=0) \sim 1.4 \times 10^{-2} [\frac{1}{2}M_2^{intra}(J=1)$, scaled]. This again is in good agreement with the expectations from Table II.

The important conclusion then is that since $m_2(J=0)$ has not reached its limiting value at 0.23 °K, neither has $M_2^{intra}(J=1)$. The saturating value of the latter at $T=0$ may well be of the order of 1×10^8 Hz^2 or even larger. Self-heating of the sample from $J=1$ to $J=0$ conversion[13] may well prevent the measurement of the limiting second moment.

We also note that for solid D_2 with $C=0.33$, estimations from a combination of thermodynamic measurements[16,17] show that the entropy per mole of $J=1$ molecules is less than $0.1R$ at 0.2 °K. Therefore, just as in solid H_2, M_2^{intra} shows a strong temperature variation when the entropy is close to zero. Furthermore, under these conditions no Pake doublet is observed for either solid. This behavior appears to be different from that which one would expect for a simple molecular field approximation.

Constable and Gaines[13] have noted that $M_2^{intra}(J=1)$ at 0.23 °K corresponded to that predicted in the molecular field approximation with the state $J_z = \pm 1$ being lowest in energy. This would correspond to an entropy $R \ln 2$ at this temperature. For the reasons just outlined, we feel that this interpretation may not be correct.

V. CONCLUSION

The study of the NMR line shape in hcp D_2 in the nondiffusion region has led to the following conclusions.

(a) The second moment extrapolated to $T=\infty$ is in good agreement with that predicted for a rigid lattice of interacting nuclear dipoles.

(b) As the temperature is decreased, the line can be progressively separated into two parts. The first one, due to the absorption of $J=1$, $I=1$ molecules, broadens out and therefore becomes so faint that it is no longer observable with the cw method below $C \sim 0.7$. Free-induction-decay and solid echo techniques,[13] however, are able to follow this process. This broadening is expected from the theory of Harris[2] and from an appropriate scaling of the results for hcp H_2. The second part broadens out at a much slower rate and is due to the NMR absorption of the $J=0$, $I=2$ molecules.

(c) For D_2, the temperature-dependent part of M_2 of the total line, namely, $M_2^{intra}(J=1)$, observed for $T \leq 8$ °K, joins on smoothly to the predicted curve by Harris, based on a high-temperature expansion series valid above about 10 °K. However, for hcp H_2, the measured[1] $M_2^{intra}(J=1)$ tends to be higher by a factor of about 2 than the extrapolated theoretical curve of Harris. It is also found that $M_2^{intra}(J=1)$ for D_2, predicted by scaling the H_2 data[1] below 8 °K, is higher by a factor of about 2 than the experimentally observed $M_2^{intra}(J=1)$. This discrepancy, which is consistent with that just mentioned, is not understood.

(d) The temperature-dependent parts of the moments from the $J=0$ and the $J=1$ molecules, respectively, namely, $m_2(J=0)$ and $M_2^{intra}(J=1)$, are found to be approximately proportional to each other. The proportionality constant is in good agreement with that predicted by Harris.[2] His hypothesis is that the $J=0$ molecules have a small admixture from the $J=2$ excited state due to the ordering of the $J=1$ molecules and therefore also become progressively aligned as the temperature decreases.

(e) At the intermediate mole fraction $C=0.33$ of $J=1$ molecules and where no transition to the cubic phase occurs, the NMR linewidth from either $J=1$ or $J=0$ molecules shows no tendency to reach a limiting value at 0.2 °K, even though the entropy is close to zero. This is similar to the situation in solid H_2.

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