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Nuclear Longitudinal Relaxation in Hexagonal Close-Packed H_2†

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Measurements of the nuclear-longitudinal relaxation time T_1 in hcp H_2 are presented. The experiments were performed mainly on solid samples with mole fractions X of molecules with rotational angular momentum $J=1$ equal to or less than $X=0.5$. Pulsed techniques were used at NMR frequencies of 5.5 and 29 MHz. The temperature range was between 0.4 and 13.8 K. The recovery of the NMR signal after saturation was always exponential as a function of time for all samples above $T \approx 7$ K, and could then be characterized by a single relaxation time T_1. For $X < 0.2$ and $T < 7$ K, the recovery gradually departed from exponential behavior, indicating a more complex relaxation which was studied and discussed in some detail. From the initial slope of the signal recovery at small times, an average value $\langle 1/T_1 \rangle$ was obtained that might characterize the relaxation rate of the entire NMR line. At temperatures below the onset of thermally activated diffusion, the relaxation mechanism is believed to be caused by the nuclear-spin flips induced by modulation from the electric quadrupole-quadrupole coupling between $J=1$ molecules, and the results are compared with theories that predict the dependence of T_1 on X in its high-temperature limit. As X decreases, the temperature variation of T_1 between 10 and 4 K becomes surprisingly large and an extrapolation to the limiting high-temperature value $T_1(\infty)$, which is of theoretical interest, becomes rather uncertain. Results for $T_1(\infty)$ for H_2 and D_2 are found to scale in their dependence on the $J=1$ mole fraction down to $X \approx 0.15$. The departures from scaling below this mole fraction are tentatively attributed to the difficulty in extrapolating the data to $T_1(\infty)$. Approximate scaling of T_1 data for H_2 and D_2 in their temperature dependence for $X=0.5$ and 0.3 was demonstrated. In the region above 10 K where diffusion affects T_1, the time $\tau=\tau_0 e^{+E/k_BT}$ between diffusion jumps could be determined from data at 5.5 MHz and compared with that from transverse relaxation measurements (T_2) by Hass *et al.* Excellent agreement is obtained for the activation energy which is found to be $E/k_B = 200 \pm 10$ K in both experiments. This energy and τ_0 from both experiments are discussed in relation to the prediction of Ebner and Sung.

I. INTRODUCTION

In this paper we present nuclear longitudinal relaxation measurements in solid hexagonal close-packed (hcp) H_2 at zero pressure for ortho mole fractions $X \leq 0.5$ and over a temperature range between 0.4 and 14 K. This work is a continuation of previously published research from this laboratory[1] describing T_1 measurements for $X \geq 0.5$. In the last few years, there has been increasing interest in relaxation of dilute ortho-H_2 mixtures as witnessed by a number of theoretical papers.[2-5] For the study of relaxation times, two temperature regions have to be considered: The first one is below ≈ 10 K, where classical diffusion is very slow. There the nuclear-relaxation mechanism is caused by modulation of the intramolecular nuclear-spin interactions by intermolecular electric quadrupole-quadrupole (EQQ) interaction between ortho molecules.[6] We shall label this relaxation time by $T_{1,Q}$. The second region is above ≈ 10 K where, in addition, the thermally activated diffusion contributes to the relaxation by modulating the inter- and intramolecular nuclear-dipolar interactions.[6] The corresponding relaxation time is $T_{1,D}^{\text{diff}}$. One of the most difficult theoretical problems seems to have been so far the correct prediction of the variation with X of the limiting high-temperature relaxation time $T_{1,Q}(\infty)$. Because dilute mixtures are expected to show only little temperature dependence in $T_{1,Q}$ above about 4 K, it would be particularly significant to study $T_{1,Q}$ experimentally above 4 K in order to obtain its asymptotic value $T_{1,Q}(\infty)$ before the onset of diffusion. So far, the only available experimental data for $X \leq 0.5$ have been those of Hass, Poulis, and Borleffs[7] at $T > 12$ K; those of Hardy and Gaines[8,9] at 4.2 K; and those of Harris and Hunt[10] between 1.2 and 4.2 K, all taken at a NMR frequency of about 30

The purpose of the present paper is to describe a systematic study of the longitudinal relaxation time T_1 at frequencies of 5.5 and 29 MHz and to compare the data in the nondiffusion region with existing theories that use the EQQ relaxation mechanism. In the diffusion region, the relaxation rate caused by diffusion will be used to determine the characteristic time τ between diffusive jumps, and these results will be compared with those obtained from transverse relaxation time measurements.[7]

In Sec. II we present a short summary of the theories on relaxation in solid H_2. In Sec. III the experimental techniques are described and in Sec. IV the results are presented and discussed.

II. THEORETICAL REVIEW

We first consider the relaxation caused by the EQQ interaction between the ortho molecules, i.e., those with rotational angular momentum $J=1$. This relaxation rate, which is a consequence of the *intra*molecular nuclear-spin interactions, is given by[3]

$$(T_{1,Q})^{-1}=\tfrac{16}{3}\pi^3\{c^2J_1^1(\omega)+d^2[\tfrac{9}{5}J_2^1(\omega)+\tfrac{36}{5}J_2^2(2\omega)]\}, \tag{1}$$

where c denotes the constant of spin-rotational coupling and d that of the intramolecular-dipolar coupling, with respective values of 113.9 and 57.7 kHz. The spectral density functions $J_j^k(\omega)$ are taken at frequency $\omega=0$, because their widths are much larger than the frequencies ω at which the NMR experiments are carried out. Also, in general, $J_j^k(0)$ is proportional to Γ^{-1}, the EQQ interaction parameter.[3-6] The most recent analysis[11] of optical[12] and NMR and thermodynamic[13] data shows that Γ is practically independent of X, and has an average value of approximately $\Gamma/k_B[H_2]=0.82\pm0.03$ K.

For $X\gtrsim0.5$, a Gaussian approximation for $J_j^k(0)$ has been used,[3,6] giving for a powder of H_2 crystals and for $\Gamma\ll k_BT$,

$$T_{1,Q}=0.543\,\frac{\Gamma}{k_B}\,X^{1/2}\times\left(1-\frac{9}{14}\,\frac{\Gamma}{k_BT}-\frac{1857}{1792}\,\frac{\Gamma X}{k_BT}\right)^{1/2}. \tag{2}$$

The weak temperature dependence[3,4] should be noted. For $X\geq0.5$ and at 10 K, Eq. (2) yields $0.98\geq T_{1,Q}/T_{1,Q}(\infty)\geq0.96$. Hence experimental values at 10 K can be expected to be closely identified with $T_{1,Q}(\infty)$.

Hama and Nakamura[4] have considered departures from the Gaussian approximation and their result is

$$T_{1,Q}(\infty)=\frac{0.499\,X^{1/2}}{1+0.024\,X^{-1}}\,\frac{\Gamma}{k_B}\ (\text{sec})\ . \tag{3}$$

At low ($J=1$) concentration, the simple Gaussian approximation cannot be used because it does not take into account the various configurations of ($J=0$) or ($J=1$) neighbors to a lattice site. Sung's original statistical theory,[2] corrected by Harris,[3] gives then

$$T_{1,Q}(\infty)=1.76[\Gamma/k_B]X^{5/3}\ (\text{sec}). \tag{4}$$

Most recently, Hama, Inuzuka, and Nakamura[5] have presented a calculation valid over the whole range of ortho concentration. They use a Gaussian form for the spectral density function for particular configurations of $J=1$ clusters and then average over the configurations. Furthermore, the authors have used an approximate treatment for the correlation effect between nearest neighbors as expressed by a correlation parameter η. This effect comes from clusters of spins having a radius $r<\eta R$ within a distance R from an isolated spin. Here R is the mean distance between isolated spins. The spins in this cluster would flip more frequently than an isolated spin due to the strong EQQ interaction between them. Consequently they should contribute less to the relaxation rate (second moment of the spectral density function) of the neighboring isolated spin than would another isolated spin. To first order they are simply not counted. For $\eta=0$, the correlation effect is neglected and the relaxation time $T_{1,Q}(\infty)$ so obtained is larger by about 10% than the statistical $X^{5/3}$ result by Harris[3] for $X\geq0.2$. For $\eta=0.8$, the correlation effect is properly taken into account, leading to a lower $T_{1,Q}(\infty)$ than for $\eta=0$ by roughly a factor of 2 for $X<0.02$. There is then excellent agreement between the theoretical fit and the experimental results by Hardy and Gaines[8] at $T=4.2$ above $X>0.02$. For $X>0.5$, where the fit was made to the T_1 data by Amstutz *et al.*,[1] the effects of correlations are no longer important. However, in order to achieve the fits just discussed, a value of $\Gamma_{\text{eff}}/k_B=0.71$ K had to be taken.[5] This value is smaller than those quoted above. A value of $\Gamma_{\text{eff}}/k_B=0.8$ K is obtained for the fit if the theory by Hama and Nakamura [Eq. (3)] is used above $X=0.5$. Their approximation is hence better than the simple Gaussian one. However, this treatment has not yet been extended to the region of low ortho concentrations.

The relaxation rate from modulation of the *inter*molecular dipolar interaction by diffusion has been calculated by Moryia and Motizuki.[6] These authors expressed the transverse and longitudinal relaxation times as a function of a correlation time τ_c. To avoid confusion below [Eqs. (6) and (9)], we label as $\tau_{c,1}$ and $\tau_{c,2}$ the times appearing in the respective expressions for T_1 and T_2. The fact that they turn out to be numerically somewhat different is simply due to the imperfection of the theory, but it should be emphasized they represent the same quantity. From the T_2 data[14] Moryia and Motizuki have estimated $\tau_{c,2}$. For the NMR frequencies used in the experiments to be described, $\tau_{c,2}\gg\omega^{-1}$. Under these conditions, the relation for the relaxation rate produced by *inter*molecular interactions reduces to[6]

$$T_1^{\text{diff}}=\tfrac{3}{4}2\ln2\,(T_2'')^2\,\omega^2\tau_{c,1}=\tfrac{3}{4}(M_2^{\text{inter}})^{-1}\,\omega^2\tau_{c,1}\ . \tag{5}$$

Here T_2'' is the rigid-lattice linewidth and M_2^{inter} is the second moment of the rigid lattice.[15] This latter quantity is determined from the intermolecular nuclear dipole-dipole interactions and is expected from theory to be proportional to X. This has been closely confirmed by experiments.[16] The more refined treatment of diffusion relaxation by Torrey[17] considers the time τ between diffusive jumps, which one can expect to be of the same magnitude as τ_c. In the limit $\omega\tau \gg 1$, the theory of Torrey and Resing[17] gives for longitudinal relaxation an expression which upon identification with Eq. (5) yields

$$\tau = 1.71\,\tau_{c,1} \quad . \tag{6}$$

Also we will assume that the relaxation rates from the *inter*molecular dipolar interactions modulated by diffusion and those from the *intra*molecular interactions are additive,

$$1/T_1 = 1/T_1^{\mathrm{diff}} + 1/T_{1,Q} \quad , \tag{7}$$

where T_1 is the observed longitudinal relaxation time. Here we have made the reasonable assumption that the diffusion-jump frequency τ^{-1} is much smaller than that associated with the reorientation due to EQQ interactions in the rigid lattice, which is of the order of Γh^{-1} under the conditions present in these experiments. Hence we assume $T_{1,Q}$ not to be affected by diffusion. In the temperature region where $(M_2^{\mathrm{inter}})^{1/2} \ll \tau^{-1} \ll \omega$, one has also[6]

$$T_2 \approx T_2^{\mathrm{diff}} = 2\ln 2\,(T_2'')^2 \tau_{c,2}^{-1} = (M_2^{\mathrm{inter}})^{-1} \tau_{c,2}^{-1} \quad . \tag{8}$$

Identifying with the result of Resing and Torrey[6] for T_2 in the same region, one obtains

$$\tau = 1.09\tau_{c,2} \quad . \tag{9}$$

The anticipated weak temperature dependence of $T_{1,Q}$ as measured in the nondiffusion region should permit the determination of T_1^{diff} via Eq. (7) from the experimental data above 11 K. Comparison of the jump time τ calculated from T_1 and T_2 data should make possible a check on the internal consistency of theory and data.

III. EXPERIMENT

The relaxation-time measurements were carried out using a phase-coherent Arenberg pulse system that was operated at 5.5 and at 29.5 MHz. The oscillator frequency was monitored by an electronic counter and was kept within 200 Hz of the NMR line center. Measurements of T_1 were carried out using a 90°-t-90° radio-frequency pulse sequence. A 90° pulse had a width approximately 4 μsec, a rf field amplitude of about 15 G, and had a Fourier component wide enough to rotate the spins in the entire line shape by $\frac{1}{2}\pi$ except at the lowest temperatures for $X = 0.5$ and 0.3. The amplitude of the free-induction decay $M(t)$ was measured at times t' between 20 and 100 μsec after the leading edge of the second 90° pulse. At mole fractions below $X \simeq 0.2$, a boxcar integrator was used for signal averaging. Most samples were prepared by accurate mixing of samples of normal ($X = 0.75$) and para ($X = 0$) hydrogen. Measurements of the mole fraction were also made before and after the experiments using the standard technique of gas thermal conductivity. For mole fractions $X \geq 0.4$ the samples were allowed to convert from $X = 0.75$ and thermal-conductivity measurements were made after the samples were removed.

IV. RESULTS AND DISCUSSION

A. Presentation of Results

The determination of T_1 was made from the semilogarithmic plot of $M(t=\infty) - M(t)$ vs time t. If the relaxation process of the entire NMR line is characterized by a single time T_1, then such a plot is a straight line within the experimental scatter. This was the case for all ortho concentrations at $T > 7$ K. However, for $X \gtrsim 0.2$ and below 7 K the plot became increasingly nonlinear. The departure from an exponential recovery was already noted by Hardy and Gaines[8] during their experiments at 4 K. We have made a study of the recovery from saturation of various parts of the free-induction decay by sampling $M(t)$ at time $t' = 20$, 60, and 100 μsec after the second 90° pulse. The recovery plots are shown in Fig. 1 for a representative sample $X = 0.089$, where we have determined a T_1 from the initial slope of the semilogarithmic plot.

In Fig. 2 we show the temperature dependence of the relaxation times as defined from the initial slope of the recovery curve $M(t=\infty) - M(t)$. The difference becomes gradually larger as T decreases, and as the nonexponentiality becomes more pronounced. Line-shape measurements at approximately the same ortho mole fraction show[13,16] progressive broadening as T decreases. This is caused by the intramolecular dipolar interaction that reflects the orientational ordering of the $J = 1$ molecules.[16] Hence one might attribute the observed curving of the recovery plot to spin-lattice relaxation of the various configurations of ($J = 1$) molecules that have various degrees of ordering, and hence different relaxation times.

We will now assume the the cross-relaxation rate through the NMR line structure is determined by the spin energy diffusion across the absorption line. A random-step model, discussed by Bloembergen *et al.*[18] for an inhomogeneously broadened line having a width T_2^* is used. If the intermolecular dipolar width is T_2'', then the cross-relaxation rate is given by

$$T_x^{-1} = T_2^{*3}/T_2''^{4} \quad . \tag{10}$$

For the concentration $X = 0.089$ we have calculated the cross-relaxation time using experimental line shapes obtained in this laboratory.[13] We have represented T_x in Fig. 2 by a dashed line and it is seen to increase strongly with decreasing T. In the temperature range when T_x becomes compara-

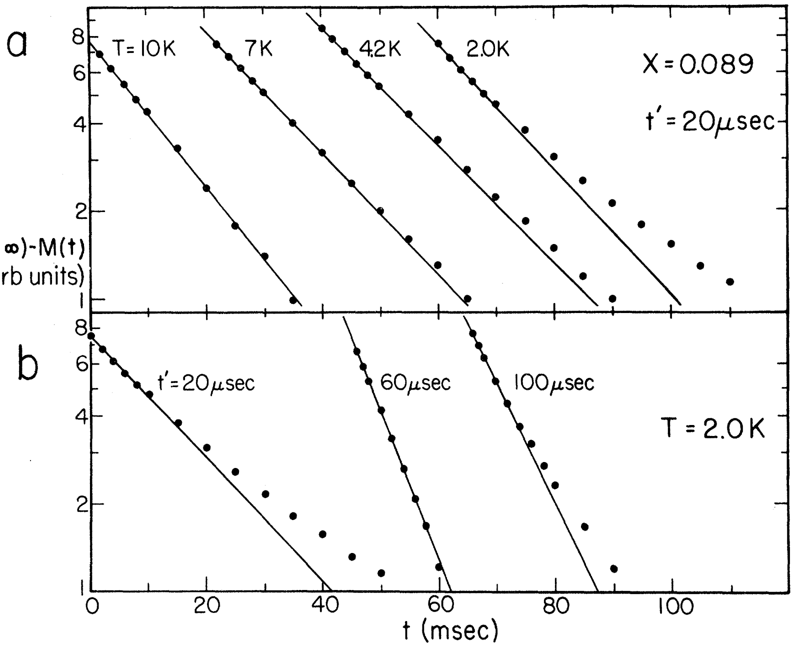

FIG. 1. (a) Recovery from saturation for a mixture with $X=0.089$ showing the nonexponential behavior as the temperature is decreased below about 10 K. (b) Recovery rate from saturation as a function of the sampling time t' after the second 90° pulse at 2 K.

ble with T_1 we have just the condition where the recovery from saturation is no longer exponential but reflects the relaxation times of the various spin configurations. These spins tend to relax independently to the lattice, instead of first coming to equilibrium with each other. In solid D_2, the calculated T_x according to the simple random-step model is lower and has a faster temperature variation than found experimentally.[19] Accordingly it is not unexpected that in H_2, the cross relaxation between the various parts of the NMR line becomes a bottleneck at higher temperatures than estimated from Eq. (10).

Figure 3 shows the relaxation time for two representative samples. For $X=0.019$ we note that T_1 passes through a minimum near 10 K. The measurements were taken by sampling the free-induction-decay (FID) signal 30 μsec after the second 90° pulse. For $X \leq 0.1$ one can calculate from Eq. (5) and T_2 experiments[7,14] that $T_{1,Q}^{-1} \gg [T_1^{\mathrm{diff}}]^{-1}$ for $\omega/2\pi = 5.5$ MHz and for all temperatures up to the melting point. Hence the observed T_1 will not reflect any noticeable effect from diffusion. However, the unexpected temperature behavior of $T_1 = T_{1,Q}$ prevents an accurate extrapolation to $T_{1,Q}(\infty)$. We have no satisfactory explanation for the temperature variation of T_1 above 4 K. A change in Γ causing this effect would be very surprising. Hence further studies of the spectral density function in this temperature range by other methods would be very useful.

The curve for $X=0.51$ in Fig. 3 shows the effect of diffusion at high temperatures. As expected from Eq. (5), the temperature dependence is stronger for the frequency of 5.5 MHz. In the temperature range between 4 and 10 K, the anomalous behavior previously noted for $X=0.02$ is no longer observed, and $T_{1,Q}(\infty)$ can be obtained quite well through extrapolation, or using the data at 10 K together with the temperature dependence predicted by Eq. (2). As T decreases below 4 K and orientational ordering progresses, T_1 de-

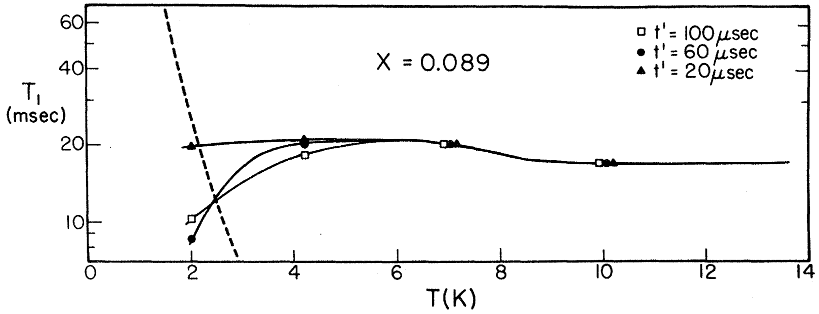

FIG. 2. Temperature dependence of T_1 defined from the initial slope of the recovery plot (Fig. 1) for $X=0.089$. Sampling times t' were 20, 60, and 100 μsec after the second 90° pulse. The dashed line represents the calculated cross-relaxation time according to Eq. (10).

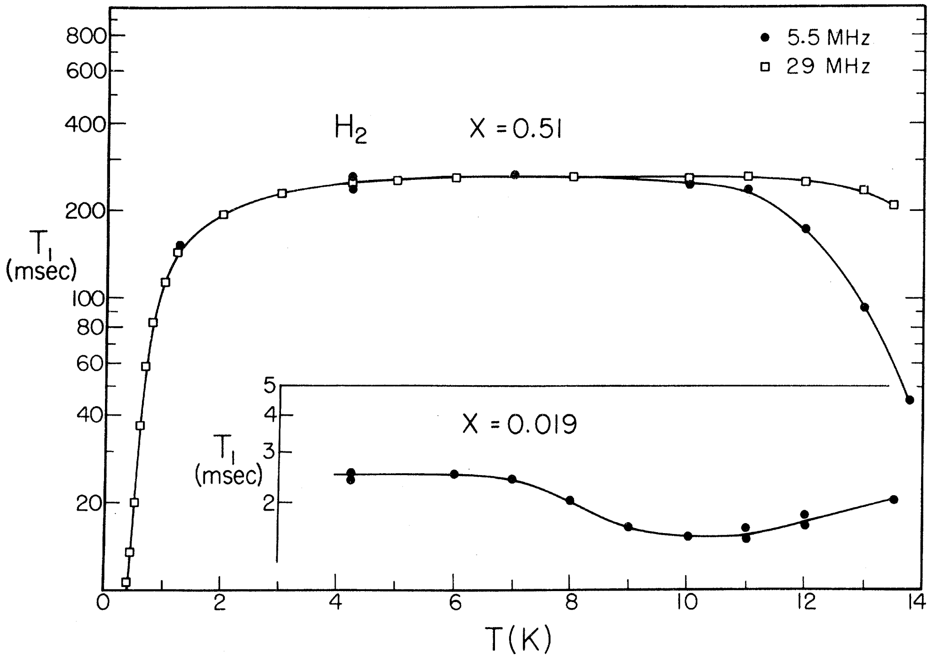

FIG. 3. Relaxation time T_1 for two representative mixtures with $X = 0.50$ and 0.019. For the latter sample, T_1 was obtained from the initial slope of the recovery plot using sampling time $t' = 20$ μsec.

creases. This is interpreted as resulting from the slowing down of the orientational fluctuations, bringing the modulation frequency from EQQ interaction closer to the frequency range of the NMR experiment. However, no theory has been proposed for T_1 in this temperature region. Because the orientational ordering of the average $J = 1$ molecule at a given T is smaller at the low ($J = 1$) content, it is not surprising that T_1 should decrease less than for the intermediate X.

Two considerations so far have limited the T_1 studies of low ($J = 1$) concentrations to temperatures above 3 K. The first is that the recovery plot is nonexponential. What is then measured from the initial slope of this plot is an average $1/T_1$, and this point was already made by Hardy and Gaines.[8] Also a study of the relaxation rate of the various segments in the line was considered to be of little promise. The second is the slow diffusion induced by resonant conversion between ($J = 0$) and ($J = 1$) molecules[20] that produces clustering of ($J = 1$) molecules as the temperature decreases.[21] The plots of the recovery from saturation would then change with time while the ($J = 1$) molecules rearrange, and this effect should become evident as X decreases. At 4 K and above, the distribution of ($J = 1$) molecules in the lattice will stay nearly random.[22] Hence T_1 measurements at $T \gtrsim 4$ K are representative of random distributions of the various configurations of ($J = 1$) molecules in the lattice, and should be independent of time.

Tables I and II present smoothed results for all the samples we have investigated. In Table I, the combined results for 5.5 and 29.5 MHz are presented for $T = 10$ K, since in this region no appreciable dependence on frequency has been detected down to 5.5 MHz. In Table II, which covers the diffusion region, the results for these two frequencies are presented separately. For $X = 0.5$ and 0.7, a further comparison in the diffusion region can be made with the results reported by Amstutz *et al.*[1] at 38 MHz. The data reported by Harris and Hunt[19] at $X = 0.42$ join on to our measurements at $X = 0.44$ and for convenience their smoothed values are included in Table I. Comparison with the data of Hardy and Gaines[8] and with those of Hass, Poulis, and Borleffs[7] reveals some systematic discrepancies especially for $X < 0.3$. For instance, the present T_1 data at 4.2 are systematically higher than those of Hardy and Gaines. This is shown in Fig. 4. This discrepancy is not understood. Although Hardy and Gaines used a 180°-t-90° sequence (instead of our 90°-t-90° sequence) their sampling time t' after the second pulse was 30 μsec, hence comparable to ours. Perhaps the discrepancy might be caused by uncertainties in the mole fraction. As mentioned before, one does not expect that there should be any difference in T_1 at 4 K between measurements at 5 MHz (used in this work) and 30 MHz (used by Hardy and Gaines). As for the data by Hass *et al.* at 30 MHz, which we have extrapolated to 10 K to afford comparison with our 5.5-MHz data in the nondiffusion region, they lie systematically below our curve of data for $X > 0.2$, and then lie above for $X < 0.2$.

TABLE I. Longitudinal relaxation time $T_1 = T_{1,Q}$ (in msec) at temperatures below the diffusion region. Here no difference is found between the data at 5.5 and 29 MHz. The numbers between parantheses represent data corrected slightly for diffusion above 9 K. The uncertainties (±) in X include both the range over which ortho-para conversion proceeded during the experiments and the uncertainty in the measurement. The uncertainty in T_1 was on the average about ± 2%, but in the worst cases could be as high as 6%. For convenience we also list the values of T_1 (denoted by an asterisk) taken in this laboratory by Hunt (Ref. 10) for $X = 0.42$, which join on smoothly to the present data for $X = 0.44$.

T (K) \ X	0.019 ± 0.002	0.046 ± 0.002	0.092 ± 0.004	0.205 ± 0.006	0.223 ± 0.007	0.318 ± 0.007	0.44 ± 0.01	0.510 ± 0.030	0.702 ± 0.028
∞	1.55	5.70	18.3		95.5	170	231	260	300
10	1.55	5.70	18.3		95.5	(170)	(231)	(260)	(299)
9	1.66	5.80	18.6		96.0	(170)	(231)	(260)	(300)
8	2.05	6.30	19.8		96.5	170	231	260	300
7	2.43	7.20	22.5		97.5	170	229	260	296
6	2.50	7.30	22.8		98.5	170	227	260	290
5	2.50	7.30	22.8		99.0	170	225	256	279
4	2.50	7.30	22.8	91.5	99.5	170	223	248	266
3				91.5	101	170	210*	232	
2.5				92.5	102	168	198*	216	
2				94.5	106	166	180*	196	
1.5				96.0	108	162	160*	168	
1.2				95.0		156	125*	142	
1.0				92.5		145		117	
0.8				90.0		123		82.5	
0.7				88.5		108		57.0	
0.6				86.5		91.0		35.0	
0.5				84.5		69.5		20.0	
0.4						46.5		10.0	

B. Scaling between H_2 and D_2 Relaxation Times

The similarity in the theoretical expressions for the ($J = 1$) molecule relaxation time T_1 in D_2 and H_2 in the high-temperature regime[3] leads us to expect a scaled behavior expressed by the ratio of Eqs. (6.35a) and (6.35b) and that of Eqs. (7.24a) and (7.24b) in Ref. 3. Taking $\Gamma/k_B[H_2] = 0.82$ K and $\Gamma/k_B[D_2] = 1.02$ K as average values[11] for all mole fractions X, one obtains

$$T_{1,Q}(\infty)D_2/T_{1,Q}(\infty)H_2 \approx 8.1 \quad \text{for } X \gtrsim 0.4 \qquad (11a)$$

[this is in region where $T_{1,Q}(\infty) \propto X^{1/2}$] and

$$T_{1,Q}(\infty)D_2/T_{1,Q}(\infty)H_2 \approx 9.2 \quad \text{for } X \lesssim 0.2 \; ; \qquad (11b)$$

[this is in the regime where $T_{1,Q}(\infty) \propto X^{5/3}$].

Furthermore, Eq. (2) leads us to expect for both isotopes a scaled behavior in temperature, as given by

$$T_{1,Q}(X, T)/T_{1,Q}(X, \infty) = f(X, \Gamma/k_B T). \qquad (12)$$

For a given X, a plot of $T_{1,Q}(T)/T_{1,Q}(\infty)$ vs $\Gamma/k_B T$ should be the same for H_2 and D_2. That scaling according to Eq. (11a) is nearly true is shown in Fig. 5 by a plot of the ratio $T_{1,Q}(\infty)D_2/T_{1,Q}(\infty)H_2$ vs X. We have used the results for D_2 tabulated

TABLE II. Longitudinal relaxation time T_1 (in msec) in the diffusion region $T \gtrsim 8$ K. Here the data for a given intermediate X depend strongly on frequency. The errors in both X and T_1 are as described in Table I.

	5.5 MHz						29 MHz		
T (K) \ X	0.019 ± 0.002	0.046 ± 0.002	0.092 ± 0.004	0.223 ± 0.007	0.327 ± 0.007	0.510 ± 0.030	0.44 ± 0.01	0.499 ± 0.012	0.702 ± 0.028
13.8						43.5			
13.5	2.05	6.65	18.3	52.5	56.5	60.5	188	208	245
13.0	1.93	6.30	18.3	65.5	78.0	94.5	202	231	262
12.5	1.83	6.05	18.3	76.5	108	133	211	246	277
12.0	1.75	5.90	18.3	84.0	135	172	218	253	288
11.5	1.66	5.80	18.3	89.5	150	206	223	258	295
11.0	1.59	5.75	18.3	93.0	158	230	226	259	298
10.0	1.55	5.70	18.3	95.5	170	248	231	259	299
9					176	256	231	259	300
8					178	260	231	259	300

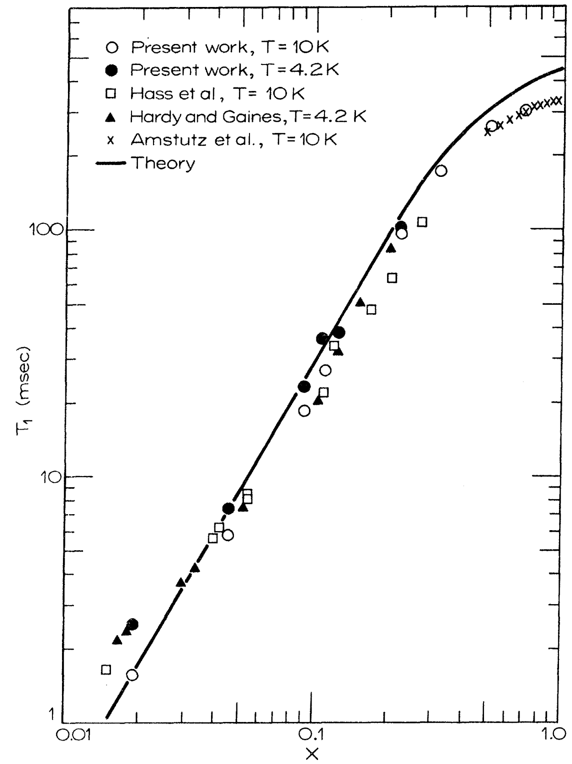

FIG. 4. Comparison of T_1 at 4.2 (solid circles) and 10 K (open circles) with the results of Gaines and Hardy at 4.2 K (solid triangles) and those of Hass, Poulis, and Borleffs extrapolated to 10 K (open squares). The solid line is the theoretical curve of Hama, Inuzuka, and Nakamura using $\Gamma/k_B = 0.82$ K.

by Weinhaus *et al.*[23] and the present results plus those of Amstutz *et al.*[1] for H_2. For $X \lesssim 0.2$, in view of the uncertainties of the extrapolation to $T=\infty$, we have taken for both H_2 and D_2 the points at 10 and 8 K, respectively. Above $X=0.2$, the ratio is indeed constant within the experimental uncertainty, and in excellent agreement with the predicted value. Hence the systematic errors made in the calculation of the respective $J_j^k(0)$ for H_2 and D_2 by using the Gaussian approximation[3] cancel out when the ratio of the spectral densities is formed. Below $X=0.2$, there is a drop in the experimental ratio $T_{1,Q}D_2/T_{1,Q}H_2$. However, as mentioned before, there is also an uncertainty as regards the choice of $T_1(\infty)$ for both H_2 and D_2. Hence the departure from the scaling expected by Eq. (11b) should not be regarded as serious. A similar scaling plot has been presented in Ref. 5. In Fig. 6 we demonstrate qualitative scaling in temperature [Eq. (12)] for $X=0.33$ and 0.51 using the values of Γ quoted above. Considering the possible systematic errors in the respective determinations of T_1, shown by error bars, and possible temperature gradients within the respective samples, as

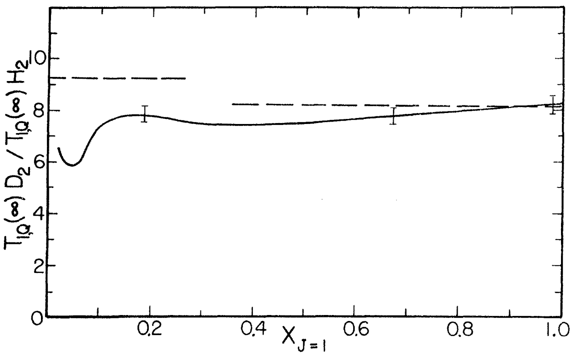

FIG. 5. Scaling plot (solid line) of the relaxation times ratio for D_2 and H_2 at the high-temperature limit as a function of X. For $X<0.3$, $T_1(H_2)$ at $T=10$ K and $T_1(D_2)$ at 8 K was provisionally taken as the high temperature limit $T_1(\infty)$. The dashed lines are the theoretically expected ones, Eqs. (11a) and (11b), applying, respectively, for the regions of high and low mole fractions X.

caused by the heat of $(J=1)$ to $(J=0)$ conversion, confirmation of Eq. (12) appears satisfactory, although admittedly a better scaling was expected in view of the excellent experimental confirmation of Eq. (11a).

C. Comparison of T_1 with the Theory of Hama *et al.*

In Fig. 4, we show the comparison of T_1 data for H_2 with the curve calculated by Hama *et al.*[5] Here the correlation parameter $\eta = 0.8$ was used and we have taken $\Gamma/k_B = 0.82$ K. We want to stress, as has been done by Hama *et al.*,[5] the excellent agreement as far as the dependence on X is concerned. At the same time there remains the slight discrep-

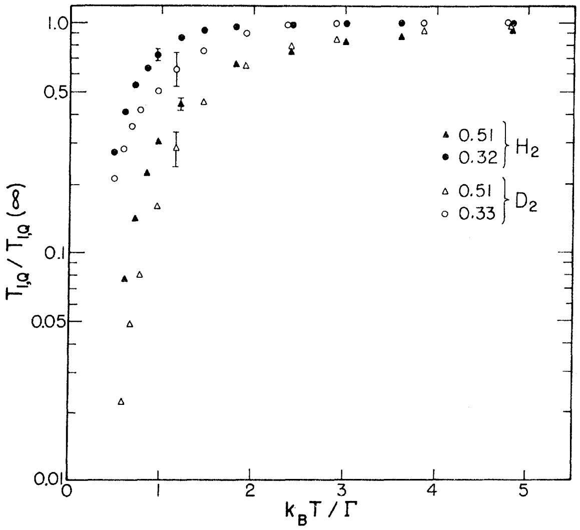

FIG. 6. Plot of the reduced relaxation time versus reduced temperature, according to Eq. (12) for both H_2 and D_2 at $X=0.5$ and 0.3, using respective parameters Γ as indicated in the text.

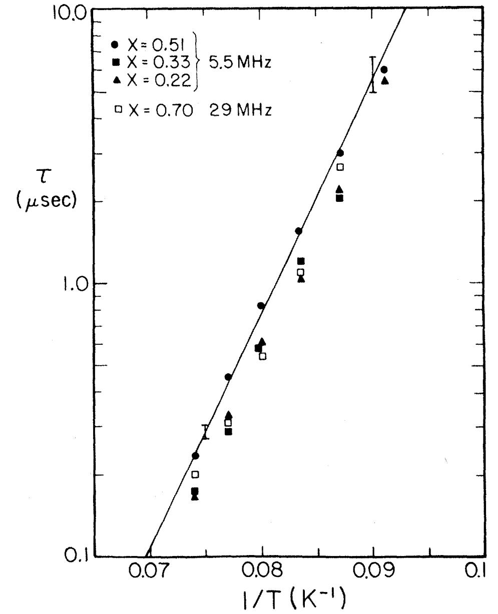

FIG. 7. Time τ between diffusive hops as determined from the present T_1 data and from T_2 results by Hass, Poulis, and Borleffs (Ref. 7). The various symbols label the T_1 data while the solid line represents within experimental error the τ from the T_2 results.

ancy of about 15% that reflects the approximations made in calculating the spectral density function.

Perhaps fourth-moment corrections to this function can be successfully extended to the low ortho-concentration range to bring theory and experiment in nearly perfect agreement.

Although the temperature dependence of T_1 for mixtures with small mole fraction X has not been specifically calculated even in the high-temperature limit, one might expect only a very slow temperature variation, based on Eq. (2). Therefore, the strong variation observed (see Fig. 3) is surprising, and should stimulate further research. We note that this dependence was already evidenced by the measurements of Hass *et al.* above 11 K.

D. Relaxation Time in the Diffusion Region

We have made an analysis of T_1 in the diffusion region for ortho mole fractions $X > 0.2$. Using the $T_{1,Q}$ results near 10 K in the nondiffusion region, listed in Table I, together with Eq. (7), we have calculated T_1^{diff} for the 5.5-MHz data. Using relations (5) and (6) for $\omega\tau \gg 1$, the numerical tabulations by Resing and Torrey,[17] and the M_2^{inter} data of Ref. 16, we have obtained the time between jumps, which is expected to obey a relation of the type

$$\tau = \tau_0 e^{+E/k_B T} . \qquad (13)$$

Here E is the diffusion activation energy. Accordingly, the results were plotted on a semilogarithmic scale in Fig. 7. The symbols represent averaged values at regularly spaced temperatures, rather than individual points. This mode of representation was preferred to the drawing of four different straight lines. The data with the largest uncertainty are those for $X = 0.7$ at 29 MHz, since there the effect of diffusion on T_1 is rather small (see Table I). For the 5.5-MHz data, there seems to be a slight dependence of τ on X, but it is clear that the activation energy E is closely the same for the four sets of measurements. Also shown in Fig. 7 are the τ results calculated from the T_2 data by Hass *et al.*, using Eq. (8), and the M_2^{inter} data by Amstutz *et al.*[16] To avoid confusion with the other data, only the average value of τ from all the T_2 results was plotted. The error bars here indicated the spread between the curves for different mole fractions X for $0.75 \geq X \geq 0.16$. Over this concentration range, an average value $E/k_B = 200 \pm 10$ K was obtained from the T_1 measurements, in excellent agreement with that obtained from T_2 data and with the value 197 K predicted by Ebner and Sung[24] for classical diffusion. We have not included in Fig. 7 the results from T_2 data for $X = 0.06$ which indicate a vastly different activation energy, namely, about half that for $X > 0.16$.

The results for both E/k_B and τ_0 from T_1 measurements are presented in Table III. Using the average value of $\tau_0 = 7.9 \times 10^{-14}$ sec and the relation $D_0 = R^2/6\tau_0$ for random walk one obtains $D_0 = 3.0 \times 10^{-3}$ cm²/sec which is to be compared with the value $D_0 = 6 \times 10^{-3}$ cm²/sec predicted by Ebner and Sung.[24] This is in reasonable agreement considering the variation observed in τ_0, the uncertainty associated with the random walk equation above, and the approximations associated with the Ebner and Sung theory. However, we have failed to observe the predicted[24] diffusion via quantum tunneling with an activation energy of $E/k_B = 112$ K. This was already noted elsewhere[24] from the analysis of early T_2 data.[14]

TABLE III. Activation energies and coefficients τ_0 for our T_1 data and for the T_2 data of Hass, Poulis, and Borleffs (Ref. 7).

$X(J=1)$	E/k_B (K)	τ_0 (sec)		
0.223	200	6.4×10^{-14}	5.5 MHz	T_1 data
0.327	203	4.7×10^{-14}		
0.510	197	1.1×10^{-13}		
0.702	200	6.8×10^{-14}	29 MHz	
Average for mole fractions $0.16 \leq X \leq 0.75$	198	1.0×10^{-13}		T_2 data Hass, Poulis, and Borleffs

V. CONCLUSIONS

The principal results from new data of the longitudinal relaxation time T_1, taken between 0.4 and 13.5 K, are the following.

(i) Recovery from saturation can be characterized by a single relaxation time for all investigated samples (namely, for $X \geq 0.02$) above 7 K. Below this temperature, the recovery is nonexponential for $X < 0.2$. Hence it is difficult to define a T_1 in this region characteristic of the whole NMR absorption line. The results we have quoted refer to the initial slope of the recovery just after saturation, which gives an average $\langle 1/T_1 \rangle$.

(ii) In the nondiffusion region, the temperature dependence of T_1 reflects the orientation ordering of the $(J=1)$ molecules and is strong for intermediate ortho-para mixtures. Even for dilute mixtures, there is a noticeable temperature variation.

(iii) Reasonable scaling of the T_1 data for H_2 has been achieved with those of D_2, both as a function of X in the high-temperature limit and as a function of T at constant X.

(iv) In the diffusion region, the time τ between hops has been evaluated from both T_1 and T_2 data, and has been found to be consistent order-of-magnitudewise. Both data gave the same diffusion activation energy.

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[15] More rigorously, the relaxation rates caused by the diffusion modulation of the intramolecular dipolar interaction should also be taken into account. This aspect has been considered in recent experiments of T_1 in low fields and of T_2 in high fields for solid D_2 [F. Weinhaus, H. Meyer, S. M. Meyers, and A. B. Harris (Ref. 19)]. It turns out that the quantity that should appear in Eqs. (5) and (8) is not just M_2^{inter} but $(M_2^{\text{inter}} + M_2^{\text{intra}})$, where M_2^{intra} is the contribution to the rigid-lattice second moment from intramolecular dipolar interaction. For D_2 in the region of 10 K, M_2^{intra} is not small in comparison with M_2^{inter}. However, for H_2 one always has for the $T \geq 10$ K, $M_2^{\text{inter}} \gg M_2^{\text{intra}}$ and hence Eqs. (5) and (8) are sufficiently good approximations.

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