

## Nuclear-Spin Relaxation in the Rotating Frame in Solid $D_2$ <sup>†</sup>

F. Weinhaus, H. Meyer, and S. M. Myers\*

*Department of Physics, Duke University, Durham, North Carolina 27706*

A. B. Harris

*Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

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The decay of the nuclear magnetization along a spin-locking field in the rotating frame has been studied in solid deuterium, at a frequency of 4.7 MHz, following the method of Rowland and Fradin. Measurements were made between 4 and 13 K, on samples having *para* ( $J=1$ ) mole fractions  $X$  ranging from 0.04 to 0.9. The lab-frame transverse relaxation time  $T_2$  was measured in the range 13–17 K. These data permitted the observation of thermally activated diffusion between 9 and 17 K, corresponding to a change in the characteristic time  $\tau$  between molecular jumps of some seven orders of magnitude. The activation energy is  $(276 \pm 20)$  K, independent of concentration. No evidence could be detected of the slow diffusion from quantum tunneling of vacancies predicted by Ebner and Sung. For the temperature range below about 8 K, the rotating-frame formalism has been adapted to the specific spin-lattice relaxation mechanisms present in  $D_2$ , and account has been taken of the intramolecular spin-spin interactions. Effects of translational molecular motion were not seen in this region. This is consistent with the very slow rates expected theoretically by Oyarzun and Van Kranendonk. At intermediate and high ( $J=1$ ) mole fractions  $X$  and below about 8 K, the exponential decay of the spin-locked magnetization was preceded by a short transient of approximately 0.1-sec duration. This transient is thought to be associated with the internal equilibration of the nuclear-spin energy systems. Its lifetime  $T_x$  is much longer than  $T_2$  of the rigid lattice because the NMR line is inhomogeneously broadened by the intramolecular spin-spin interactions. The magnitude of  $T_x$  has been correlated with previously reported cross-relaxation times for the lab frame.

### I. INTRODUCTION

For low magnetic fields, comparable in magnitude to the dipolar local field, relaxation-time measurements can give information about diffusion not available from high-field measurements.<sup>1–3</sup> This is due to the fact that in the low-field regime, where the Zeeman and dipolar Hamiltonians are comparable in size, changes in dipolar energy due to atomic or molecular motion are very rapidly communicated to the Zeeman system, providing for spin-lattice relaxation. Indeed one can detect jump times comparable to the spin-lattice relaxation time, whereas in the high-field regime the limiting time is the rigid lattice (RL) spin-spin relaxation time  $T_2^{RL}$ . Another possibility, as we shall see, is the study of energy diffusion through an inhomogeneously broadened line. Since in the low-field case the Zeeman energy, which is the quantity measured, is comparable with other terms in the Hamiltonian, the flow of energy into those terms can be monitored. In practice, it is most convenient to achieve the low-field regime in the “rotating frame.”

In the present experiment, rotating-frame studies of solid  $D_2$  were made. Thermally activated diffusion was monitored between 9 and 13 K using this technique. The diffusion was also followed in the range 13–17 K, via the transverse relaxation

time  $T_2$  in the lab frame, using the formalism of Resing and Torrey.<sup>4</sup> In the region below about 8 K, thermally activated diffusion has a negligible effect on the nuclear-spin system. Also, the quantum diffusion observed in  $H_2$  by Amstutz, Thompson, and Meyer<sup>5</sup> and treated by Oyarzun and Van Kranendonk<sup>6</sup> should be too slow to be detected in  $D_2$ . Here the rotating-frame measurements have provided useful information on the flow of energy among the terms of the spin Hamiltonian. In particular, the inhibition of cross relaxation associated with inhomogeneous broadening of the NMR line by intramolecular spin-spin interactions was studied by monitoring the decrease of the Zeeman energy with time. These results were successfully correlated with previous studies in the lab frame below 5 K.<sup>7</sup>

In Sec. II the rotating-frame theory of Rowland and Fradin<sup>8</sup> will be reviewed briefly and adapted to the specific case of  $D_2$ . The relevant constants in the theory will be derived, and the effect of the intramolecular spin-spin interactions will be included. For the region below 8 K where the intramolecular interaction broadens the line, an estimate will be made of the time for internal equilibration of the nuclear-spin system. Also a generalization of the relation derived by Resing and Torrey<sup>4</sup> for the  $T_2$  of a motionally narrowed line will be given. Section III will describe the pulsed-NMR method used, and outline the other experi-

mental procedures. The experimental data and analysis will be presented in Sec. IV and the conclusions given in Sec. V.

## II. THEORETICAL REVIEW

### A. Rotating-Frame Relaxation-Time Measurements

Nuclear relaxation in weak applied fields has been discussed by Redfield<sup>9</sup> and by Hebel and Slichter<sup>10</sup> using the concept of a spin temperature and a "weak-collision" theory. Slichter and Ailion<sup>2</sup> modified this treatment for the "strong-collision" regime, and applied it to the case where the low fields were achieved by an adiabatic transformation to a reference frame rotating about the static field at the Larmor frequency. More recently, Rowland and Fradin<sup>8</sup> have also discussed relaxation in the rotating frame. These authors, however, attained the rotating-frame conditions using the "spin-locking" pulse sequence of Hartmann and Hahn.<sup>11</sup> The effect of either of these two methods is to align the net magnetization in a plane perpendicular to the static field and along a rotating field of the order of the dipolar field in magnitude. Thus to the spins the rotating field appears to be static. The advantage of doing the experiments in the rotating frame is that a large static field is still present which provides for a good signal-to-noise ratio.<sup>1-3</sup>

Redfield<sup>12</sup> has shown that in the presence of a radio-frequency field large enough to saturate the absorption, the system can be characterized by a spin temperature in the rotating frame. Thus the system is describable by a density matrix

$$\rho = e^{-\mathcal{H}/k_B\Theta} / \text{Tr} e^{-\mathcal{H}/k_B\Theta} . \quad (1)$$

Here Tr indicates that the trace is to be taken,  $\Theta$  is the spin temperature of the system,  $k_B$  is Boltzmann's constant, and  $\mathcal{H}$  is the effective Hamiltonian in the rotating frame.

It is well known that in solid  $D_2$ , the molecules with rotational angular momentum  $J=1$  have a total nuclear spin  $I=1$ , while a fraction  $\frac{5}{8}$  of those with  $J=0$  have a spin  $I=2$ , the rest having  $I=0$ . In the solid  $D_2$  system, the interaction Hamiltonian consists principally of three systems or terms:

(i)  $\mathcal{H}_Z$ , the Zeeman interaction with the external magnetic field; (ii)  $\mathcal{H}_d$ , the intermolecular nuclear dipole-dipole interaction between molecules; (iii)  $\mathcal{H}_q$ , the intramolecular nuclear interaction which depends on the orientation of the molecule with respect to the static field.<sup>13</sup> The orientational alignment of the  $J=1$  molecules is caused by the intermolecular electric quadrupole-quadrupole (EQQ) interaction between these molecules. Making the standard rotating-coordinate transformation,<sup>12,14</sup> one can express the effective Hamiltonian as

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_d^0 + \mathcal{H}_q^0, \quad (2)$$

where the Zeeman term is

$$\mathcal{H}_Z = \mathcal{H}_Z^z + \mathcal{H}_Z^x, \quad (3a)$$

with

$$\mathcal{H}_Z^z = -\gamma\hbar \sum_k (H_0 - \omega/\gamma) I_{zk}, \quad (3b)$$

$$\mathcal{H}_Z^x = -\gamma\hbar H_1 \sum_k I_{xk}, \quad (3c)$$

the summation being over all nuclear spins,

$$\mathcal{H}_d^0 = \frac{1}{4} \gamma^2 \hbar^2 \sum_{i,k} (3I_{zi} I_{zk} - \vec{I}_i \cdot \vec{I}_k) \left( \frac{1 - 3 \cos^2 \vartheta_{ik}}{R_{ik}^3} \right) \quad (4a)$$

$$\equiv \frac{1}{4} \sum_{i,k} F_{ik} (3I_{zi} I_{zk} - \vec{I}_i \cdot \vec{I}_k) \quad (4b)$$

is the truncated intermolecular dipolar term, and

$$\mathcal{H}_q^0 = -\frac{5}{4} d \hbar \sum_k' \langle 3 \cos^2 \varphi_k - 1 \rangle_T (3I_{zk}^2 - 2) \quad (5a)$$

$$\equiv -\frac{1}{3} d \hbar \sum_k' A_k (3I_{zk}^2 - 2) \quad (5b)$$

is the truncated intramolecular term. Here  $\omega$  is the frequency of the rotating field  $H_1$ ,  $\gamma$  is the deuteron gyromagnetic ratio,  $I_k$  is the total nuclear-spin operator for the  $k$ th molecule,  $\vartheta_{ij}$  is the angle that the intermolecular vector  $\vec{R}_{ij}$  makes with the  $z$  axis,  $\varphi_k$  is the angle between the axis of the  $k$ th molecule and the  $z$  axis, and  $d$  is the intramolecular coupling constant, which is 25.24 kHz in  $D_2$ .<sup>13</sup> In Eq. (5a) the brackets  $\langle \rangle_T$  indicate that a thermal average is to be taken and the prime on the summation indicates that sum is to be restricted to molecules having  $I=1$  and  $J=1$ , where  $J$  is the angular momentum of molecular rotation. The terms analogous to those of Eq. (5) for  $J=0$  molecules are negligible.<sup>13</sup>

Rowland and Fradin<sup>8</sup> have already discussed the low-field relaxation of just such a system, i.e., one with Zeeman, dipolar, and quadrupolar terms in the Hamiltonian. For the case in which there is rapid transfer of energy within the spin system, they make use of the spin temperature in the rotating frame to calculate the magnetization along the effective field. When the frequency  $\omega$  of the rf field is equal to the Larmor frequency, and  $H_0 \gg H_1$ , then  $\langle M \rangle_T$ , which lies along  $H_1$ , decays to a zero value. The time constant  $T_R$  for this decay is then given by

$$\frac{1}{T_R} = \frac{1}{H_1^2 + H_D^2 + H_Q^2} \left( \frac{H_1^2}{T_b} + \frac{H_D^2}{T_D} + \frac{H_Q^2}{T_Q} \right). \quad (6)$$

Here the intermolecular dipolar local field  $H_D$  is defined as

$$H_D^2 = H_1^2 \text{Tr}(\mathcal{H}_d^0)^2 / \text{Tr}(\mathcal{H}_Z^x)^2 \quad (7)$$

and the intramolecular (quadrupolelike) local-field  $H_Q$  is defined as

$$H_Q^2 = H_1^2 \text{Tr}(\mathcal{H}_Q^0)^2 / \text{Tr}(\mathcal{H}_Z^x)^2. \quad (8)$$

Also,  $T_b$  is the relaxation time for the magnetization along the  $H_1$  field and has been shown by Redfield<sup>12</sup> to be just the high-field laboratory-frame relaxation time  $T_1$ . Finally,  $T_D$  and  $T_Q$  are the relaxation times for the inter- and intramolecular nuclear spin interactions, respectively.

We can generalize the expression for  $H_D^2$  evaluated by Hebel<sup>14</sup> to the situation of  $D_2$  where there are two systems of spins with the same gyromagnetic ratio. We obtain

$$H_D^2 = \frac{1}{4\gamma^2\hbar^2} \sum_j \bar{B}_{ij} I_j(I_j + 1) = \frac{5-3X}{5} \gamma^2 \hbar^2 \sum_j R_{ij}^6 \quad (9a)$$

$$= M_{\frac{1}{2}}^{\text{inter}} / 3\gamma^2 = 0.0253(5-3X) (G^2). \quad (9b)$$

Similarly, the evaluation of  $H_Q^2$  from our Eq. (8) and from Eq. (3.16d) and (3.19b) in Ref. 13 yields

$$H_Q^2 = \left(\frac{2\pi}{\gamma}\right)^2 \frac{2X\bar{d}^2}{3(5-3X)} \left(\sum_k \bar{A}_k^2 / \sum_k 1\right) \quad (10a)$$

$$= M_{\frac{1}{2}}^{\text{intra}} / 3\gamma^2. \quad (10b)$$

In Eqs. (9) and (10), the superior bars indicate powder averages, and  $M_{\frac{1}{2}}^{\text{inter}}$  and  $M_{\frac{1}{2}}^{\text{intra}}$  are, respectively, the intermolecular and intramolecular contributions to the second moment of the absorption line shape due to all the nuclear spins in the system. The experimental determination<sup>15</sup> of  $M_{\frac{1}{2}}^{\text{inter}}$  agrees very well with the expression given in Eq. (9b). In the case of Eq. (10b), the calculation of  $M_{\frac{1}{2}}^{\text{intra}}$  involves thermal averages which can only be calculated in the high-temperature limit. Furthermore, the experimental determination of  $M_{\frac{1}{2}}^{\text{intra}}$  is subject to a large uncertainty at high temperatures. Accordingly, at temperatures and concentrations for which experimental determinations of  $H_Q^2$  is meaningful we will use experimentally determined values for it; otherwise (i. e., when  $H_Q$  is of the order or smaller than  $H_D$ ) we shall use theoretical expressions for it [c. f. Eq. (4.13) of Ref. 13].

Returning to Eq. (6) we write the relaxation rates as the sum of two terms, one due to diffusion, the other due to rigid-lattice  $T_1$  mechanisms:

$$\frac{1}{T_D} = \frac{1}{T_D^{\text{diff}}} + \frac{\alpha}{T_1}, \quad (11a)$$

$$\frac{1}{T_Q} = \frac{1}{T_Q^{\text{diff}}} + \frac{\beta}{T_1}. \quad (11b)$$

The parameters  $\alpha$  and  $\beta$  describe the efficiency of  $T_1$  processes for inter- and intramolecular nuclear relaxation, respectively. If the nuclear spins are flipped independently,  $\alpha = 2$ , since the dipolar

energy is relaxed if either of the nuclear spins is flipped. It can be shown that this is the case for spin flips caused by the terms involving the interaction of Eqs. (5). The much smaller effects due to correlated spin flips caused by the spin-rotation coupling term  $c\vec{I} \cdot \vec{J}$  in the nuclear spin Hamiltonian<sup>13</sup> can be safely neglected, so we set  $\alpha = 2$ . The value of  $\beta$  is shown in Appendix A to be given by

$$\beta = (15 - 9X) / 10X. \quad (12)$$

Finally, we consider the relaxation rates appearing in Eqs. (11) due to diffusion. Slichter and Ailion<sup>2</sup> have treated in detail the dipolar relaxation due to slow vacancy diffusion. They have employed two assumptions: (i) the systems corresponding to the terms in the Hamiltonian couple together strongly to attain a common spin temperature between jumps; (ii) the actual time for a jump is so short compared to the nuclear precession period that the spin orientation does not change during a jump. This "strong-collision" theory for diffusion extended for rapid moving vacancies<sup>1</sup> leads to

$$(T_D^{\text{diff}})^{-1} = \frac{2(1-p)}{\tau} \left(\frac{G-1}{G}\right) \left(\frac{G-2}{G}\right), \quad (13)$$

where  $\tau$  is the mean time a molecule rests between jumps and  $G$  is the number of nearest neighbors. The factor  $(1-p)$  is a lattice sum of the order of unity ( $p = 0.223$  for hcp lattice) which accounts for the fact that the local field at a nucleus after a jump is not statistically independent of the local field before the jump. The factor of 2 in Eq. (13) occurs because motion of either of the two interacting spins modulates the dipolar energy.

An expression similar to Eq. (13) is obtained in Appendix B for  $T_Q^{\text{diff}}$ :

$$(T_Q^{\text{diff}})^{-1} \approx 2/\tau. \quad (14)$$

At first glance the appearance here of the factor of 2 is surprising, because in this case the nuclear spin is interacting with a field not produced by nuclear spins on a different molecule. However, when a molecule jumps, it changes not only its own orientational state, but also that of its neighbors because of the EQQ interaction. Hence the environments of two nuclear spins are disturbed by each molecular jump. Since  $H_Q^2$  is of the same magnitude as  $H_D^2$ , and since the diffusion theories are not too accurate anyway, we use the approximation of writing

$$\frac{H_D^2}{T_D^{\text{diff}}} + \frac{H_Q^2}{T_Q^{\text{diff}}} \approx (H_D^2 + H_Q^2) \frac{2(1-p)}{\tau} \frac{G-1}{G} \frac{G-2}{G}. \quad (15)$$

Using the values of  $\alpha$  and  $\beta$  given above, and substituting Eq. (15) into Eq. (11), we write Eq. (6) as

$$\frac{1}{T_R} = \left( \frac{H_1^2 + 2H_D^2 + [(15 - 9X)/10X]H_Q^2}{H_1^2 + H_D^2 + H_Q^2} \right) \frac{1}{T_1} + \left( \frac{H_D^2 + H_Q^2}{H_1^2 + H_D^2 + H_Q^2} \right) \frac{2(1-p)}{\tau} \frac{G-1}{G} \frac{G-2}{G} \quad (16)$$

Since the quantities in large parentheses are both of order unity, this expression shows that  $\tau$  should be observable when it is comparable to or less than  $T_1$ . Before continuing, we should point out that Eq. (16) has the correct form in the  $X=0$  limit. To see this we use Eq. (10a), according to which  $H_Q^2 \propto XA^2$ , where  $A^2$  is the average of  $A_k^2$  over all configurations of the ortho-para mixture. Note that  $A_k^2$  vanishes if the  $k$ th molecule has no  $J=1$  neighbors to cause orientational alignment. For small  $X$ ,  $A^2$  is proportional to  $X$ ,<sup>13</sup> and hence  $H_Q^2 \propto X^2$ . Thus, in the  $X=0$  limit, Eq. (16) becomes

$$\frac{1}{T_R} = \left( \frac{H_1^2 + 2H_D^2}{H_1^2 + H_D^2} \right) \frac{1}{T_1} + \left( \frac{H_D^2}{H_1^2 + H_D^2} \right) \times \frac{2(1-p)}{\tau} \frac{G-1}{G} \frac{G-2}{G} \quad (17)$$

independent of  $H_Q$ , as expected.

#### B. Quantum Diffusion

Thermally activated vacancy diffusion falls off very rapidly with decreasing temperature, and is negligible below about 8 K in solid  $D_2$ . However, three mechanisms remain which may change the spatial distribution of the  $I=0$ ,  $I=1$ , and  $I=2$  nuclear spins: (a) quantum mechanical exchange between nearest neighbors due to the overlap of their molecular wave functions; (b) resonant conversion of two neighbors due to the magnetic interaction between nuclei. This process is distinguished by having  $\Delta J = +1$  for one molecule and  $\Delta J = -1$  for the other; (c) uncorrelated  $I=2 \rightleftharpoons I=0$  transformations with  $\Delta I_x = 0$  among the  $J=0$  molecules.

Changes with time of the distribution of  $I=1$  nuclear spins have been observed in solid  $H_2$  by Amstutz *et al.*<sup>5</sup> These authors found that the characteristic NMR spectrum of nearest-neighbor ortho pairs increased in amplitude with time following a drop in temperature, indicating that molecules were moving into this energetically favored configuration.<sup>16</sup> Oyarzun and Van Kranendonk<sup>6</sup> subsequently treated mechanisms (a) and (b) theoretically. They concluded that mechanism (a) is negligible, but that the resonant conversion has a characteristic time of  $\tau \approx 30$  min in 1% ortho  $H_2$ . This time takes into account the slowing down of the conversion rate by the EQQ interaction from ( $J=1$ ) neighbors. The estimate is consistent with the Amstutz *et al.* result. However, applying the same formalism to  $D_2$  gives  $\tau \approx 80$  h, while  $T_1 \approx 1$  sec. Hence this motion cannot be detected in the

rotating-frame experiment.

The uncorrelated ( $I=0 \rightleftharpoons I=2$ ) transformation has been shown to occur in a time  $\tau_{2 \rightarrow 0} \approx 0.4$  sec.<sup>17</sup> However, since there is no means whereby this mechanism can cause energy exchange with the lattice, it must conserve the total nuclear spin energy. Hence it will not produce an observable effect in the rotating-frame experiment.

As a result of the above considerations, the second term of Eq. (16) can be neglected below the region of significant thermally activated vacancy diffusion, giving

$$\frac{1}{T_R} = \frac{H_1^2 + 2H_D^2 + (15 - 9X)H_Q^2/10X}{H_1^2 + H_D^2 + H_Q^2} \frac{1}{T_1} \quad (18)$$

#### C. Cross Relaxation

The validity of Eq. (18) depends specifically on the flow of energy among the terms of the Hamiltonian, occurring rapidly in comparison with the spin-lattice relaxation time. When exchange occurs at the rate  $(T_2^{RL})^{-1}$ , this condition is well satisfied. However, at low temperatures the NMR linewidth of the ( $J=1$ ) molecules, given approximately in terms of the second moment by  $[m_2(I=1)]^{1/2}$ , is much broader than that of the ( $J=0$ ) molecules  $[m_2(I=2)]^{1/2}$ . This inhomogeneous broadening arises from the intramolecular nuclear spin-spin interaction as the ( $J=1$ ) molecular rotation is quenched by the EQQ interaction.<sup>13</sup> It has the effect of making mutual nuclear spin flips non-degenerate, thereby inhibiting energy flow. The cross relaxation will then be characterized by an energy exchange time  $T_{12}$ , which is much longer than  $T_2^{RL}$ . We will not attempt to calculate this parameter for the low-field regime, but rather will assume that it is the same as for the high-field case. Then one can use the result of Bloembergen *et al.*<sup>18</sup> for the diffusion of energy through an inhomogeneously broadened line, as modified in Ref. 10 to apply to solid  $D_2$ . This calculation gives

$$T_{12} \approx \frac{[m_2(I=1)]^{1/2}}{[M_2^{int \text{er}}]^2} \{ [m_2(I=1)]^{1/2} - [m_2(I=2)]^{1/2} \}^2 \quad (19)$$

This is obviously an approximation, since at high fields the total Zeeman energy is conserved and one is concerned only with its redistribution among the nuclear spins. Nevertheless, since the mechanism of energy exchange is basically the same in both cases, it is probably a reasonable one. As will be seen, the cross relaxation is observable as a short transient of duration  $T_x$  in the exponential decay of the magnetization along the rotating field. This transient corresponds to the coming into equilibrium of the various nuclear spin energy systems, shown in Fig. 1. We can calculate the relation between the experimentally observed time constant  $T_x$  and the cross-relaxation time  $T_{12}$

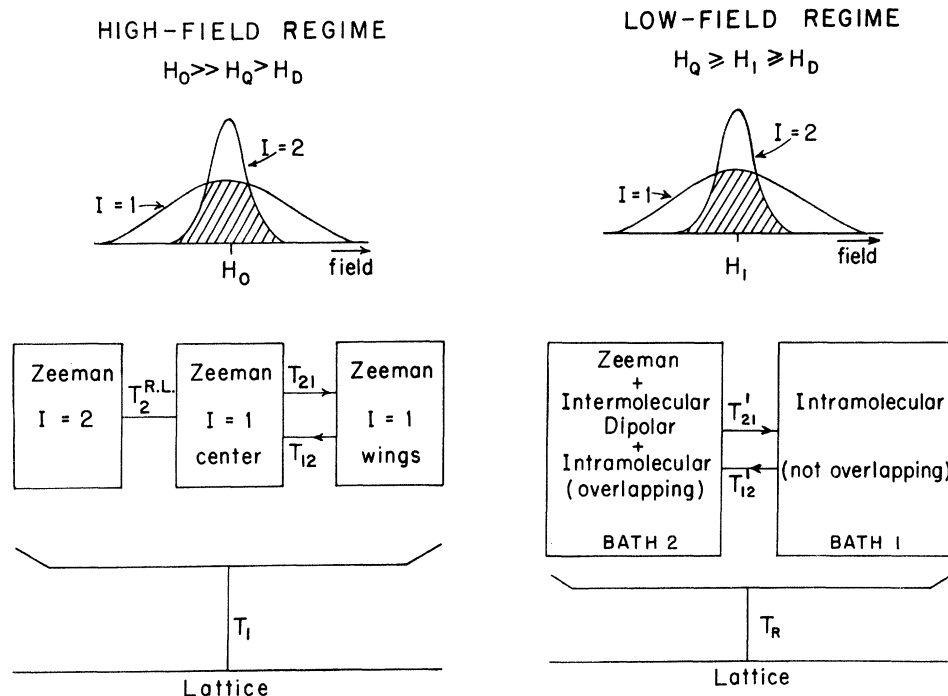


FIG. 1. Symbolic representation of the NMR spectra and energy baths from the  $I=1$  and  $I=2$  spins in the high-field ( $H_0$ ) and low-field ( $H_1$ ) regimes. The spin-lattice relaxation mechanisms are those induced by intermolecular electric quadrupole-quadrupole interaction and by diffusion. Once the energy baths have come into internal equilibrium via cross relaxation, they relax to the lattice with a characteristic time  $T_1$  and  $T_R$  in the high-field and low-field situations, respectively.

by solving the differential rate equation of the two energy baths shown on the right-hand side of Fig. 1. For simplicity we assume that the equilibration time of the energy baths is much smaller than  $T_R$ . Our calculation, which is briefly presented in Appendix C, gives then

$$T_x^{-1} = T_{12}^{-1} \left( \frac{H_1^2 + H_D^2 + H_Q^2}{H_1^2 + H_D^2 + \Phi^2 H_Q^2} \right). \quad (20)$$

Here the factor  $\Phi^2$  represents the fraction of the quadrupole bath that overlaps in energy with the dipolar and Zeeman baths, with

$$\Phi^2 \approx [m_2(I=2)/m_2(I=1)]. \quad (21)$$

#### D. Laboratory-Frame Transverse Relaxation Time $T_2$

It has long been known that motional narrowing of the high-field NMR line provides a means of probing diffusion in condensed systems.<sup>20</sup> However, this technique is primarily useful in the region given by

$$[M_2^{\text{inter}}]^{1/2} \ll \tau^{-1} \ll \omega. \quad (22)$$

In the region defined by Eq. (22), the expression for  $T_2^{-1}$  given by Kubo and Tomita<sup>21</sup> becomes

$$(T_2^{\text{diff}})^{-1} = \tau_c M_2^{\text{inter}}, \quad (23)$$

where  $\tau_c$  is the decay time for the correlation function which characterizes the modulation by diffusion

of the nuclear dipole-dipole interaction. Obviously  $\tau_c$  and  $\tau$  are comparable. A microscopic theory<sup>4</sup> based on an approximate treatment of the random walk gives the result

$$\tau = 1.09\tau_c \quad (24)$$

for the fcc lattice. Within the approximations used to obtain Eq. (24), we find the result for the hcp lattice to be identical to that for the fcc lattice.

It must be realized, of course, that the theory<sup>4</sup> used to obtain Eq. (24), and to a lesser extent that given by Slichter and Ailion,<sup>2</sup> is approximate. Equation (24) was derived by using the approximation of isotropic hopping and by neglecting the correlation which prevents two nuclear spins from occupying the same lattice site. As a consequence of this latter approximation the formal expressions are not well defined for a discrete lattice. Therefore, exact agreement between the values of  $\tau$  obtained from the two techniques is not to be expected. However, the temperature dependences are not sensitive to theoretical details and should therefore be correctly related to the activation energy.

As we have seen above, diffusion modulates the intramolecular interactions  $\mathcal{K}_Q$ , and one expects that in analogy with Eq. (14) that Eq. (23) should be generalized to read

$$(T_2^{\text{diff}})^{-1} = \tau_c (M_2^{\text{inter}} + M_2^{\text{intra}}) \quad (25)$$

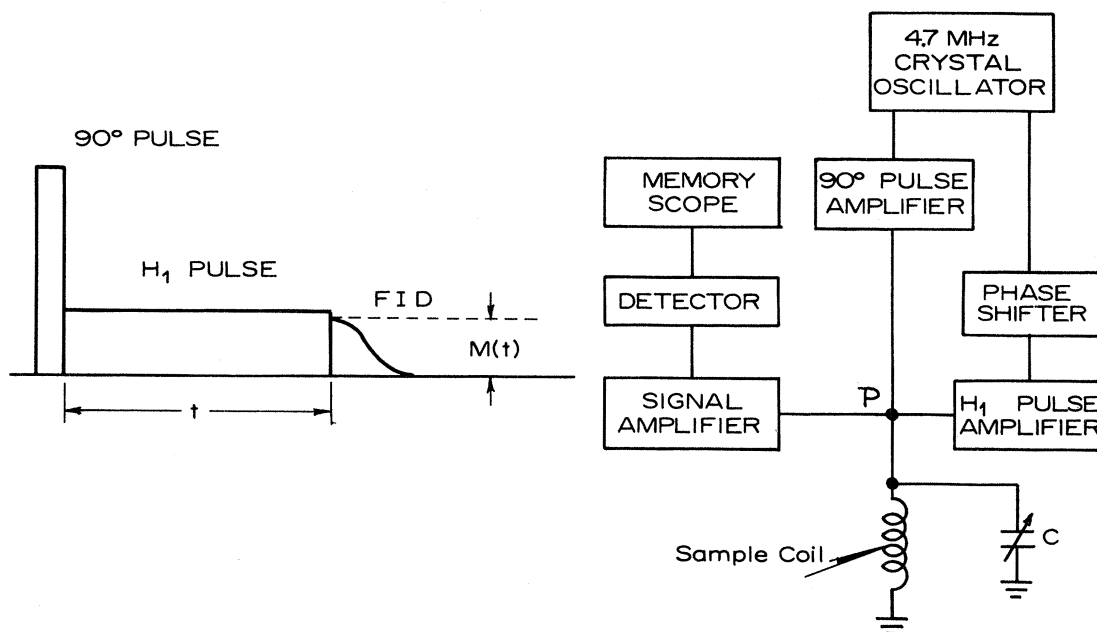


FIG. 2. Pulse sequence for the spin-locking technique and schematic representation of the NMR pulse generating and detecting system.

This result is discussed in Appendix B.

From the measurements of  $T_2^{-1}$ , we will determine  $\tau$  and compare it with that from longitudinal relaxation measurements in the rotating frame. The data are taken only in a temperature range where Eq. (22) is satisfied. Under these conditions,  $T_2^{\text{diff}} \gg [M_2^{\text{inter}}]^{-1/2}$ .

### III. EXPERIMENTAL PROCEDURE

For the low-field experiment, the decay of the nuclear magnetization along a transverse rf field rotating at the nuclear resonant frequency was studied, using the spin-locking procedure of Hartmann and Hahn.<sup>11</sup> The method is schematically indicated in Fig. 2. A sequence started with a  $90^\circ$  rf pulse, which rotated the equilibrium magnetization along the static field  $H_0$  into the transverse plane. In a time short compared to  $T_2^{\text{RL}} \approx 0.3$  msec, another rf pulse, of variable amplitude and  $90^\circ$  out of phase with the preceding pulse, was applied. The second pulse, whose field  $H_1$  was colinear with the transverse magnetization, lasted for a variable time  $t$ . At the end of the second pulse the amplitude  $M$  of the free-induction decay (FID) was measured. Specific-heat considerations give the following limits<sup>8</sup>:

$$M(t \rightarrow 0) = M_0 H_1^2 / (H_1^2 + H_D^2 + H_Q^2), \quad (26)$$

$$M(t \rightarrow \infty) \approx M(t=0) H_1 / H_0 \approx 10^{-4} M(t=0) \approx 0. \quad (27)$$

Here  $M_0$  is the amplitude of the FID after the initial  $90^\circ$  when no subsequent  $H_1$  rf pulse is applied. A

semilogarithmic plot of  $M(t)$  vs  $t$  yielded the desired relaxation time  $T_R$ .

The electronics of the NMR system are block diagrammed in Fig. 2. A stable 4.7-MHz crystal oscillator drove two pulse amplifiers, one through a variable phase shifter. These amplifiers were triggered from a timing network. The  $90^\circ$  pulse had an amplitude of 190 V peak to peak, and a width of 65  $\mu\text{sec}$ , while  $H_0$  could be continuously varied up to 150 V peak to peak and over a time between 0.3 msec and 14 sec without appreciable drop in the amplitude. The first pulsed amplifier has been used in previous work,<sup>22</sup> while the long ( $H_1$ ) pulse amplifier was of the Blume type,<sup>23</sup> with an extra pentode amplifier stage added. The nuclear signal was amplified, detected, and displayed on a memory scope. The sample coil circuit was parallel tuned, the capacitor  $C$  being adjusted to maximize the impedance at  $P$  with all components connected.

The conversion factor from V to G in the rf coil was determined by measuring the voltage amplitude and duration of a carefully optimized  $90^\circ$  pulse, and this factor was found to be  $0.030 \pm 0.001$  G/V. For almost pure ortho  $D_2$ ,  $H_Q \approx 0$ , while  $H_D$  is given by Eqs. (9) and its value is 0.355 G. A check on the internal consistency of Eqs. (9) was made at 4 K and  $X = 0.036$  by measuring the short-time FID amplitude  $M(t=0)$  as a function of  $H_1$ . Using Eq. (26), a plot of  $[(M_0/M(t)) - 1]^{1/2}$  vs  $H_1^{-1}$ , shown in Fig. 3, gave then a slope  $H_D = 0.35 \pm 0.01$  G, in good agreement with that predicted above. The nonzero

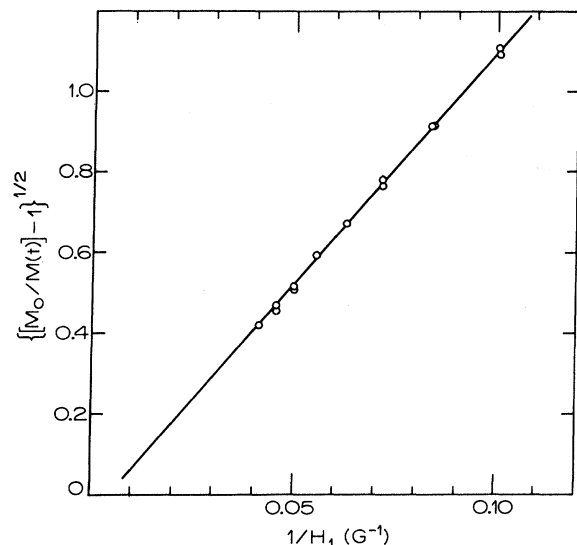


FIG. 3. Determination of the field  $H_D$  from rotating-frame experiments with various spin-locking fields. For further explanation, see text. The solid  $D_2$  sample had the composition  $X=0.036$  and the temperature was 4.2 K.

intercept, however, is not understood at this time.

The lab-frame transverse relaxation time  $T_2$  was determined in the conventional way by measuring the FID corrected for magnet inhomogeneity and also by measuring the amplitude of the echo produced by a  $90^\circ$ - $t$ - $180^\circ$  pulse sequence. A semi-logarithmic plot of the echo amplitude vs  $2t$  yielded  $T_2$ .

The cryostat, the technique of  $J=1$  mole fraction

measurement and the gas sample purity have been discussed elsewhere.<sup>22</sup>

#### IV. RESULTS AND DISCUSSION

##### A. Classical Diffusion Region

The experimental values of the rotating-frame relaxation time  $T_R$  and of  $T_2$  are shown in Fig. 4 for a representative mole fraction  $X=0.89$ . For temperatures above about 9 and 12 K, respectively, both  $T_R$  and  $T_2$  exhibit an exponential behavior vs  $T^{-1}$ . For temperatures below 8 K,  $T_R$  is unaffected by diffusion and is only weakly temperature dependent down to 4 K. Figure 5 shows a plot of  $T_2$  vs  $T^{-1}$  for  $X=0.05$ , 0.54, and 0.89 that indicates that  $T_2$  is practically independent of  $X$ . The solid line represents the fit

$$T_2 = 3.68 \times 10^8 e^{-287/T} \text{ sec},$$

which is close to that quoted in an earlier paper.<sup>22</sup> In Fig. 6 we present the characteristic time  $\tau$  between jumps, as calculated via Eq. (25). Figure 6 also shows the characteristic time  $\tau$  between jumps calculated from low-field techniques, using Eqs. (16) and (17) and the assumptions made in Sec. II. Here the correction for the nondiffusion term was made by subtracting the extrapolated value of  $1/T_R$ , shown in Fig. 4 by the dashed line, from the measured  $1/T_R$  data at the corresponding temperature. The average activation energies determined from the slopes of the data derived from spin-locking experiments and from  $T_2$  data are 272 and 287 K, respectively, with an error of  $\pm 10$  K. There is a discontinuity<sup>24</sup> by a factor of about 2 be-

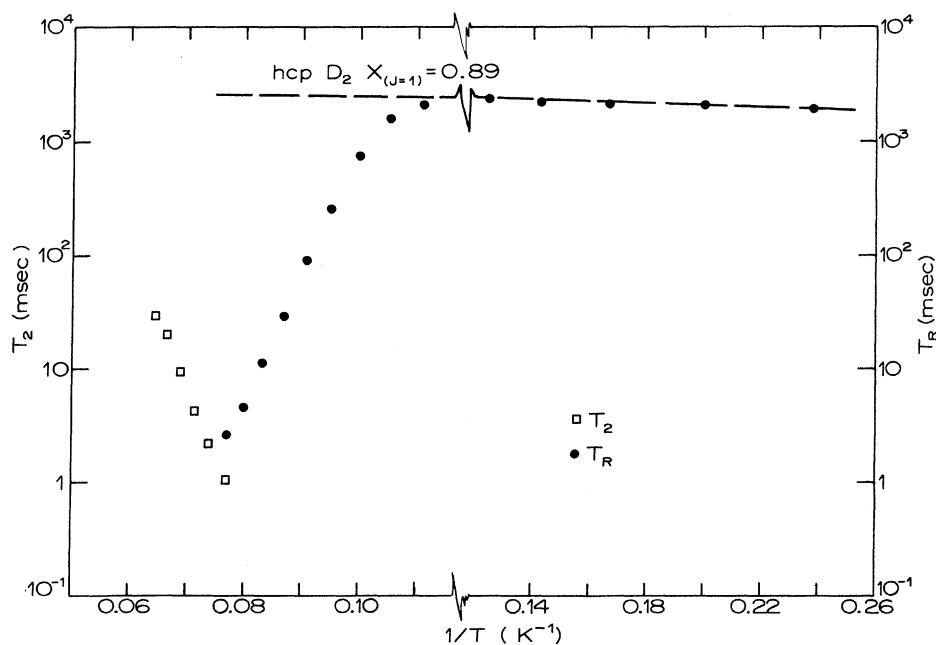


FIG. 4. Representative set of relaxation data for a sample of  $D_2$  with  $X=0.89$ . Left vertical scale: transverse relaxation time  $T_2$ ; right scale: longitudinal relaxation time  $T_R$  in the rotating frame. The dashed curve is the extrapolation from the nondiffusion region.

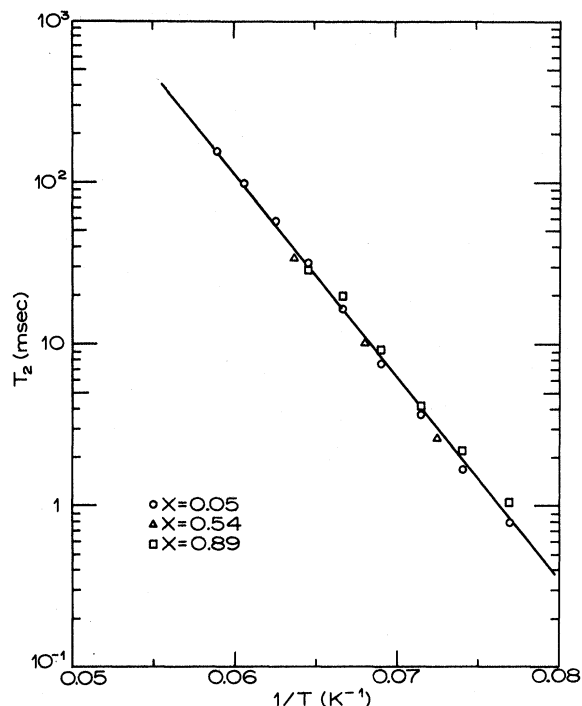


FIG. 5. Results for the transverse relaxation time  $T_2$  for three samples of  $D_2$  with different mole fractions  $X$ . The straight line is the representative average for the three sets of points.

tween the  $\tau$  obtained from  $T_2$  and  $T_R$  data, which is not understood but which might be due to the approximations made in the theory leading to Eqs. (16) and (24). However, from Fig. 6 it is clear that from  $T=17$  to 9 K, and over a range of about 7 decades in  $\tau$ , the diffusion is characterized essentially by one activation energy  $E/k_B = 276 \pm 20$  K. A slight dependence of  $E$  on  $X$  is not excluded, but is within the experimental error. If we chose an intermediate value of  $\tau$  between the low-field and high-field data, we obtain  $\tau = \tau_0 e^{E/k_B T}$ , with  $\tau_0 = 5.4 \times 10^{-13}$  sec for a choice of  $E/k_B = 276$  K. Clearly, the value of  $\tau_0$  strongly depends on this choice, decreasing by a factor of  $\sim 2$  for a choice of  $E/k_B \sim 10$  K higher. The value of  $E/k_B$  is in good agreement with the theoretical prediction by Ebner and Sung,<sup>25</sup> 290 K. Their diffusion constant  $D_0 = 7 \times 10^{-4}$  cm<sup>2</sup>/sec is also in good agreement with the value of  $D_0 = R^2/6\tau_0 \approx 4 \times 10^{-4}$  cm<sup>2</sup>/sec that can be derived from our experiment.

Wang, Smith, and White<sup>26</sup> have recently reported a less direct determination of the activation energy in  $D_2$ , based on experimental  $T_1$  values in the laboratory frame. Their values of  $306 \pm 15$  K for  $X < 0.05$  and  $336 \pm 15$  K for higher mole fractions agree roughly with the above results in which the dependence on  $X$ , if any, is much smaller.

Ebner and Sung<sup>25</sup> also predict that diffusion of a

molecule by quantum tunneling through the double-potential well barrier to a nearest-neighbor vacancy should be observable below about 14 K. The diffusion in this range should then be characterized by an activation energy of 132 K. However, our data down to 9 K fail to show evidence for this prediction.

### B. Nondiffusive Region

The decay of the FID amplitude  $M(t)$  as a function of the duration of the spin-locking  $H_1$  pulse is shown in Fig. 7 for  $D_2$  samples with  $X=0.05$ , 0.33, and 0.89. For  $X=0.05$ , where  $H_Q^2$  resulting from the intramolecular spin-spin interaction in the ( $J=1$ ) molecules is very small,  $M(t)$  exhibits an exponential decay with time. However as  $X$  is increased, a transient precedes the exponential regime. The parameter  $T_R(X, T)$  was taken from the exponential portion of the decay in all cases. Using Eq. (18), the predicted value of  $T_R$  was calculated for temperatures between 4 and 8 K,

### DIFFUSION CHARACTERISTIC TIME $\tau$

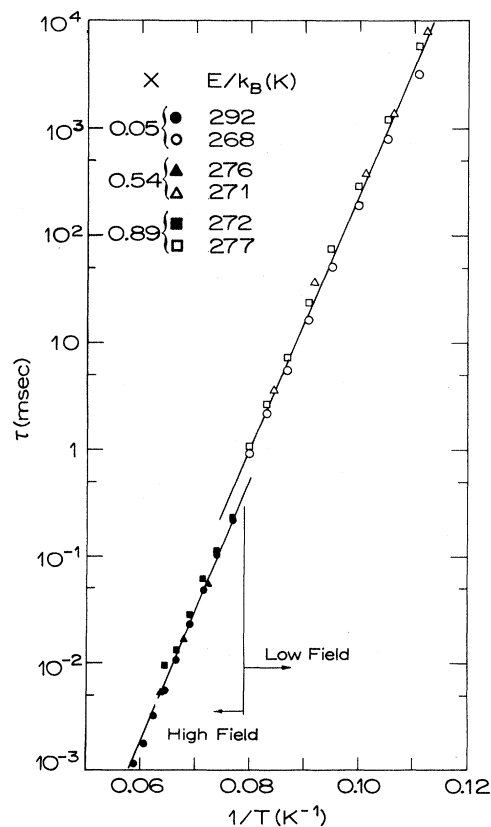


FIG. 6. Characteristic time  $\tau$  between jumps in the classical diffusion region for  $D_2$  samples with various mole fractions  $X$ . The solid symbols pertain to the high-field  $T_2$  measurements, while the open symbols refer to rotating-frame measurements.



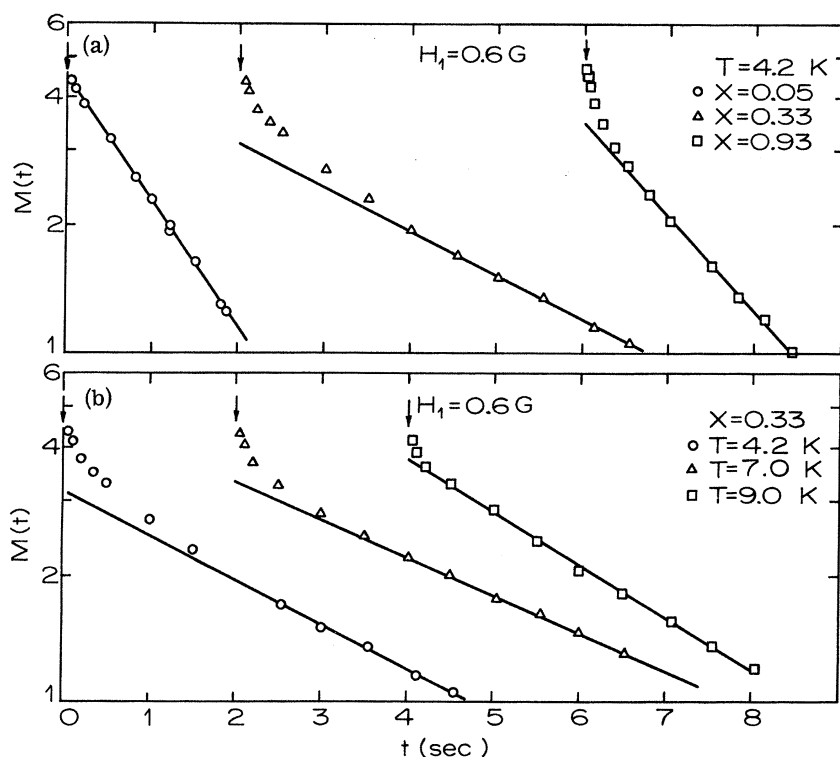


FIG. 7. Decay of the free-induction signal  $M(t)$  in the nondiffusion region. For economy of space, only one common time scale is used in this figure. The vertical arrows indicate the respective  $t = 0$  points. (a) The decay for samples with various mole fractions  $X$  at 4.2 K, illustrating the transient at higher  $X$ , attributed to cross relaxation between the two baths shown in Fig. 1. (b) Temperature dependence of the transient for  $X = 0.33$ . The steeper slope at  $T = 9$  K (shorter  $T_R$ ), already reflects the onset of diffusion.

assuming no diffusion of any kind over this temperature region. The lab-frame relaxation time  $T_1$  was determined from measurements on the  $D_2$  sample during the same experiment. The field  $H_Q$  was obtained from Eq. (8) and using the experimental second moment  $M_2$  presented elsewhere.<sup>15,19</sup> The other parameters such as  $H_1$  and  $H_D$  were determined as described before in Sec. III. The calculated value  $T_R(X, T)$  is presented in Table I together with the experimental results. This calculated value of  $T_R$  may be in error by as much as 10% due to the uncertainty in  $T_1$  and in  $H_Q^2/H_D^2$ . Considering this, the agreement between the calculated and the experimental  $T_R$  is quite satisfactory.

In Fig. 7 we also present the decay of  $M(t)$  vs  $t$  as a function of temperature for  $X = 0.33$ . It can be readily seen that the transient time increases as the temperature is decreased. We have labeled the characteristic time associated with the transient by  $T_x$  and have obtained it from the FID decay  $M(t)$  using a fit of the type

$$M(t) = A - B e^{-(t/T_R)} + B e^{-(t/T_x)}, \quad (28)$$

where  $T_R \gg T_x$ .

The observed dependence of  $T_x$  on temperature and on the mole fraction  $X$  imply that the transient is due to equilibration of the three energy systems in the Hamiltonian in the low-field regime, that is, the attainment of a common spin temperature. We

have crudely represented this by the three energy baths shown in Fig. 1. Here we have the Zeeman, intermolecular dipolar and overlapping portion of the intramolecular systems coming into equilibrium with one another in a time comparable to  $T_2^{RL}$  but the nonoverlapping portion of the intramolecular dipolar system takes a time  $T_x \gg T_2^{RL}$  to communi-

TABLE I. Comparison of the calculated relaxation time  $(T_R)_{\text{theor.}}$  from Eq. (15) with the experimental values  $(T_R)_{\text{expt.}}$ . The quoted values of  $H_Q^2/H_D^2 = M_2^{\text{intra}}/M_2^{\text{inter}}$  have been taken from previous experiments (Ref. 19). The field  $H_1$  is the applied spin-locking field and  $H_D$  is related to  $M_2^{\text{inter}}$  via Eq. (7).

$X$	$T$ (K)	$\frac{H_1^2}{H_D^2}$	$\frac{H_Q^2}{H_D^2}$	$T_1$ (sec)	$(T_R)_{\text{theor.}}$ (sec)	$(T_R)_{\text{expt.}}$ (sec)
0.036	4.2	1.66	0	1.76	1.28	1.23
0.036	7.0	1.66	0	1.61	1.17	1.16
0.33	4.2	3.60	5.1	8.70	3.5	4.12
0.33	6.0	3.60	2.2	8.35	4.2	4.27
0.33	7.0	3.60	1.4	8.35	4.7	4.66
0.33	8.0	3.60	1.0	8.35	5.0	4.76
0.91	4.2	7.09	4.6	2.05	2.1	1.91
0.91	5.0	6.40	3.2	2.19	2.2	2.08
0.91	6.0	7.09	2.5	2.37	2.3	2.16
0.91	7.0	7.09	2.1	2.52	2.4	2.27
0.91	7.0	1.60	2.1	2.52	2.3	2.26
0.91	7.0	90.4	2.1	2.52	2.5	2.38
0.91	8.0	7.1	1.7	2.63	2.5	2.48

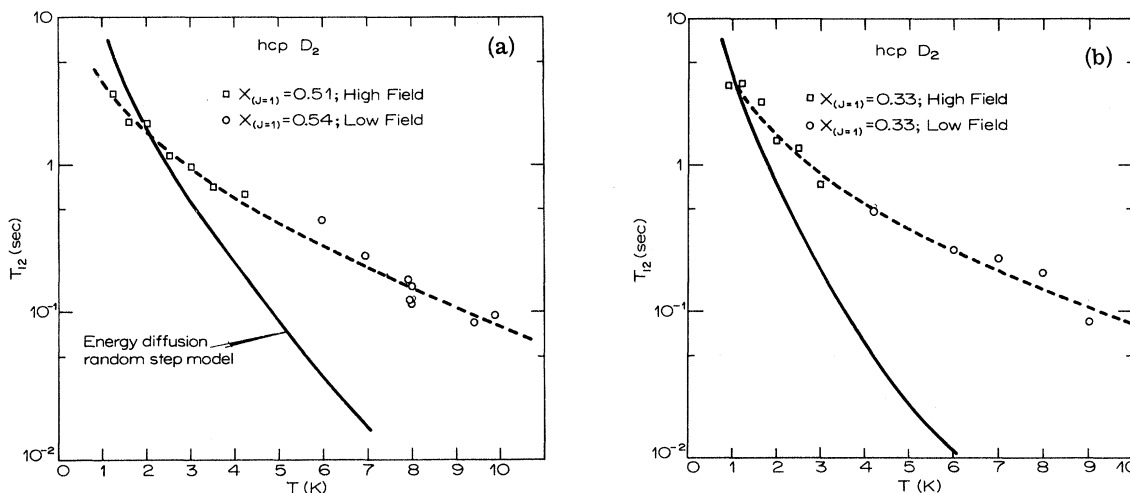


FIG. 8. Cross-relaxation time  $T_{12}$  for  $X \approx 0.5$  and  $X \approx 0.33$ . This figure shows the data taken at high fields up to 4 K and continued by the low-field (rotating frame) technique. The temperature dependence is less strong than that predicted from a simple energy-diffusion random-step model (Ref. 19), applied to the  $D_2$  problem, and shown by the solid lines.

cate with the combined bath just mentioned. Once the three systems are in equilibrium, the magnetization that expresses their common temperature decays to its equilibrium value with the characteristic time  $T_R$ . In Fig. 8, we have presented for  $X = 0.33$  and  $0.54$  the time  $T_{12}$  calculated from  $T_x$  via Eq. (C13). These data join on smoothly to those obtained from high-field pulsed-NMR techniques.<sup>19</sup> Hence the high- and low-field transients do indeed seem to be based on the same mechanism. The temperature dependence obtained experimentally is weaker than that predicted by the simple random-step energy diffusion model. The discrepancy between the predictions from the model and the experiment becomes very large as the temperature increases. Evidently at  $T$  as high as 10 K, the measured cross-relaxation time is appreciably larger than  $T_2^{RL}$ , which is somewhat of a surprise.

Finally, we check the self-consistency of the calculations we presented in Appendix C by comparing the calculated ratio  $A/B$  [Eqs. (C11) and (C12)] with that determined experimentally using Eq. (28) and the results presented in part in Fig.

TABLE II. The calculated and observed ratio  $A/B$  of the amplitudes defined in Eqs. (28), (C11), and (C12) as a function of temperature for  $X = 0.33$ .

$T(K)$	$(A/B)$ calc.	$(A/B)$ expt.
4.2	2.0	1.6
6.0	1.4	1.4
7.0	1.3	1.3
8.0	1.2	1.2
9.0	1.13	1.15

7. We have used the value of  $\Phi$  obtained from the data for  $m_2(I=2)$  and  $m_2(I=1)$  and we have used the ratios  $H_1^2/H_D^2$  and  $H_Q^2/H_D^2$  as given in Table I for  $X = 0.33$ . We find the results presented in Table II. The agreement, except for  $T = 4.2$  K, where  $T_{12}$  becomes comparable with  $T_R$ , is quite satisfactory. This tends to confirm further that the selection of energy reservoirs in Fig. 1 is a reasonable one.

## V. CONCLUSIONS

By combining rotating-frame relaxation data with measurements of the transverse relaxation time in the lab frame, it has been possible to determine the time  $\tau$  between jumps due to thermally activated diffusion in solid  $D_2$  over some seven orders of magnitude. It was shown that the activation energy is essentially constant between 9 and 17 K. Furthermore, there is fair consistency in the absolute magnitude of  $\tau$  as calculated from the theory of these two very different pulse techniques.

Below 14 K there was no evidence of another diffusion process based on quantum tunneling of vacancies, as predicted by Ebner and Sung.

Below the classical diffusion region, rotating-frame measurements gave no indication of translational molecular motion, consistent with theoretical expectations. The decays with time of the magnetization in the rotating frame were characterized by a short-lived initial transient, the time of which increased with  $X$  and with decreasing temperature. This transient was associated with the energy flow within the nuclear spin system, and related to the cross-relaxation time previously measured in the lab frame. The values of the characteristic energy-exchange time  $T_{12}$  from the

two kinds of measurements merged smoothly as a function of temperature. However, this parameter was found to have a much weaker temperature dependence than predicted by a simple random-step model. In view of this, and since solid D<sub>2</sub> offers a unique case where the inhomogeneous broadening is (i) random on an atomic scale and (ii) strongly temperature dependent, a more detailed theoretical treatment would seem most desirable.

#### ACKNOWLEDGMENTS

The authors are greatly indebted to Paul Pedroni for his help during several of the experiments, and for some of the data analyses.

#### APPENDIX A: EVALUATION OF $T_Q^{-1}$

We wish to evaluate the rate  $T_Q^{-1}$ , at which the energy of the intramolecular interactions relaxes toward the lattice in the absence of diffusion. The spin-lattice interaction is of the form

$$V_{SL} = hc \sum_k [I_{kz} J_{kz} + \frac{1}{2}(I_{k+} J_{k-} + I_{k-} J_{k+})] + hd \sum_k' \sum_m a_m O_m(I_k) O_{-m}(J_k), \quad (A1)$$

where

$$\begin{aligned} O_{\pm 2}(k) &= k_{\pm}^2, \\ O_{\pm 1}(k) &= k_{\pm} k_z + k_z k_{\pm}, \\ O_0(k) &= 3k_z^2 - k(k+1), \end{aligned} \quad (A2)$$

$$T_Q^{-1} = \frac{9\pi^2}{d^2 h^2 X \sum_k A_k^2} \left\{ c^2 \sum_k G_1(k) \{ \langle [J_k, \mathcal{H}_Q^0]^2 \rangle_T + \langle [\mathcal{H}_Q^0, I_{k+}] [I_{k-}, \mathcal{H}_Q^0] \rangle_T \} + \frac{1}{4} d^2 \sum_k G_2(k) \{ \langle [O_0(J_k), \mathcal{H}_Q^0]^2 \rangle_T + 3 \langle [\mathcal{H}_Q^0, O_1(J_k)] [O_{-1}(J_k), \mathcal{H}_Q^0] \rangle_T + 3 \langle [\mathcal{H}_Q^0, O_2(J_k)] [O_{-2}(J_k), \mathcal{H}_Q^0] \rangle_T \} \right\}, \quad (A7)$$

where

$$G_1(k) = \int_{-\infty}^{\infty} dt \langle J_{kz}(t) J_{kz}(0) \rangle_T, \quad (A8a)$$

$$G_2(k) = \int_{-\infty}^{\infty} dt \langle [3J_{kz}^2(t) - 2][3J_{kz}^2(0) - 2] \rangle_T. \quad (A8b)$$

After the powder average and that over the ortho-para mixture are taken, we may set

$$G_1(k) = \frac{4}{3} \pi J_1(0); \quad G_2(k) = \frac{16}{5} \pi J_2(0). \quad (A9)$$

The commutators in Eq. (A7) are easily evaluated and all terms contain the factor  $A_k^2$ , which then cancels the similar term in the denominator of Eq. (A7). Thus, the final result is

$$T_Q^{-1} = 144\pi^3 \left\{ \frac{1}{3} c^2 J_1(0) + \frac{1}{5} d^2 J_2(0) \right\} \quad (A10a)$$

$$= 3T_c^{-1} + \frac{3}{5} T_d^{-1}. \quad (A10b)$$

If we neglect the small terms in  $T_c^{-1}$  in Eqs. (A4) and (A10), we may write the latter as

and

$$a_0 = \frac{1}{2}; \quad a_{\pm 2} = a_{\pm 1} = \frac{3}{4}. \quad (A3)$$

We shall compare our results with the expression for  $T_1^{-1}$ , which we write in the form

$$T_1^{-1} = [2X/(5-3X)] (T_c^{-1} + T_d^{-1}), \quad (A4)$$

where, in the notation of Ref. 13,

$$T_c^{-1} = \frac{16}{3} \pi^3 c^2 J_1(0), \quad (A5a)$$

$$T_d^{-1} = 48\pi^2 d^2 J_2(0), \quad (A5b)$$

are the relaxation rates due to the two terms in Eq. (A1), and for solid D<sub>2</sub>,  $T_c^{-1} \ll T_d^{-1}$ . Here  $J_1(0)$  and  $J_2(0)$  are the spectral densities of, respectively, the first- and second-rank tensors in  $J_r$  ( $\sim J_{rz}$  and  $3J_{rz}^2 - 2$ ), which are then averaged over a powder and over configurations of the ortho-para mixture. These functions are evaluated at  $\omega = 0$ , since  $\gamma \hbar H_0$  is small compared to typical lattice energies.

We now evaluate  $T_Q^{-1}$ . The assumption of a spin temperature allows us to write

$$T_Q^{-1} = \frac{\pi}{\hbar} \frac{\int_{-\infty}^{\infty} dt \langle [\mathcal{H}_Q^0, V_{SL}]_t [V_{SL}, \mathcal{H}_Q^0] \rangle_T}{\langle (\mathcal{H}_Q^0)^2 \rangle_T}, \quad (A6)$$

where the subscript  $t$  denotes a time-dependent operator at time  $t$ ,  $\mathcal{H}_Q^0$  is given in Eq. (5), and we again set the resonance frequency to zero. Use of Eq. (A6) yields

$$T_Q^{-1} = [(15-9X)/10X] T_1^{-1}, \quad (A11)$$

which is equivalent to Eq. (12) of the text.

#### APPENDIX B: MODULATION OF INTRAMOLECULAR INTERACTIONS VIA DIFFUSION

Since the term in  $(T_Q^{\text{diff}})^{-1}$  is not dominant in the temperature range of interest, we will give here a rather crude treatment of it. We will not bother to estimate the small corrections analogous to  $(1-p)$  or  $[(G-1)G]/[(G-2)/G]$ , which appear in Eq. (13).

The model we consider is one where diffusion consists of nearest-neighbor-vacancies hopping. Since it takes three vacancy hops for a vacancy to pass by a given molecule, our picture of diffusion is the following: A single molecule sees an environment which is essentially static for a time  $\tau$ , then undergoes fluctuations over a period of  $3\tau$ .

Here  $\tau_v$  is the vacancy hopping time and  $\tau_v \ll \tau$  because  $N\tau_v = N_v\tau$ , where  $N_v/N$  is the vacancy concentration. Then this molecule settles down to a new surrounding which remains essentially constant for another interval of length  $\tau$ . Clearly, the fluctuation duration  $3\tau_v$  is negligible in view of the fact we undoubtedly have  $M_2^{1/2}\tau \ll 1$ . Hence to compute the rate of energy transfer to the lattice, we should compute the difference in a spin's energy between a time  $\frac{1}{2}\tau$  after and a time  $\frac{1}{2}\tau$  before the vacancy passes it. This picture differs slightly from that used by Slichter and Ailion. Approximately, however, we can say that for each spin displaced, an amount of dipolar energy of order  $(1-p)(2/N) \times \langle (H_d^0) \rangle_T$  is transferred to the lattice. Here the factor of 2 occurs because for pairwise interactions the energy of a spin in the field of its neighbors is twice the energy per spin. Thus, we have

$$\frac{d\langle \mathcal{H}_d^0 \rangle}{dt} = \frac{2N_v}{N\tau_v} \langle \mathcal{H}_d^0 \rangle_T (1-p). \quad (\text{B1})$$

Apart from the factors of  $[(G-1)/G](G-2)/G$  this argument reproduces Eq. (13).

The analogous argument for the effect of diffusion on  $\mathcal{H}_q^0$  runs as follows. We need to calculate the difference in intramolecular energy between times long before and long after a vacancy has passed by a particular molecule. The change in intramolecular energy is given by (c.f. Ref. 2)

$$\Delta E = \text{Tr} \rho_i (\mathcal{H}_f - \mathcal{H}_i) \propto (1/k_B \Theta) \langle \mathcal{H}_f \mathcal{H}_i - \mathcal{H}_i^2 \rangle_T, \quad (\text{B2})$$

since the density matrix before the hop  $\rho_i$ , is proportional to  $(1 - \mathcal{H}_i/k_B \Theta)$ . Here  $\mathcal{H}_f$  and  $\mathcal{H}_i$  are the values of  $\mathcal{H}_q^0$  before and after the hop. From Eq. (B2) we see that the energy associated with the motion of the  $k$ th molecule is

$$\Delta E_k = -\frac{1}{k_B \Theta} \left( \frac{hd}{3} \right)^2 \left( A_{kf} A_{ki} - A_{ki}^2 + \sum_{\delta} A_{k+\delta, f} A_{k+\delta, i} - \sum_{\delta} A_{k+\delta, i}^2 \right), \quad (\text{B3})$$

where again the subscripts  $i$  and  $f$  indicate values before and after the hop. Here  $\delta$  is summed over ( $J=1$ ) molecules  $k+\delta$  which are nearest neighbors of  $k$  before the hop. (Molecules which are nearest neighbors of  $k$  after the hop are counted in one of the other  $\Delta E$ 's.) To evaluate Eq. (B3) we use the high-temperature result<sup>13</sup>

$$A_k = \frac{12}{25} \left( \frac{\Gamma}{k_B \Theta} \right)^2 \sum_{\delta} q_{k+\delta} (3 \cos^2 \vartheta_{\delta H} - 1). \quad (\text{B4})$$

Here  $\vartheta_{\delta H}$  is the angle between  $\hat{\delta}$  and  $\hat{H}_0$ , and  $q_n$  is 1 if  $J_n=1$ , and is zero otherwise. Note that the average over the ortho-para mixture of  $A_k$  is zero because

$$\sum_{\delta} (3 \cos^2 \vartheta_{\delta H} - 1) = 0 \quad (\text{B5})$$

for an hcp lattice. Note also that  $A_{kf}$  and  $A_{ki}$  involve two different sets of  $q$ 's. The only  $q$ 's in the two sets which are correlated are those  $q$ 's which refer to molecules which are nearest neighbors of  $k$  both before and after the hop. These will give only a small contribution to the average of  $(A_{kf} A_{ki})$  over the configurations of  $J=1$  molecules in the ortho-para mixture. Thus, we set

$$(A_{kf} A_{ki} - A_{ki}^2) = -A_{ki}^2. \quad (\text{B6})$$

Next consider the term

$$(A_{k+\delta, f} A_{k+\delta, i} - A_{k+\delta, i}^2) \quad (\text{B7})$$

of Eq. (B3). The change in environment of the molecule  $k+\delta$  due to the hop of the  $k$ th molecule is a result of moving one of the  $n$  neighbors of the  $(k+\delta)$ th molecule which have  $J=1$ . Hence we set

$$A_{k+\delta, f} A_{k+\delta, i} \approx [(n-1)/n] A_{k+\delta, i}^2. \quad (\text{B8})$$

Thus Eq. (B2) becomes

$$\Delta E_k = -\frac{1}{k_B \Theta} \left( \frac{hd}{3} \right)^2 \left( -A_{ki}^2 - \frac{1}{n} \sum_{\delta} A_{k+\delta, i}^2 \right) \quad (\text{B9a})$$

$$\approx -2E_k, \quad (\text{B9b})$$

since on the average there are the same number of  $J=1$  neighbors to the  $k$ th molecule as there are to the  $(k+\delta)$ th. This then leads to the result

$$1/T_Q^{\text{diff}} = 2/\tau. \quad (\text{B10})$$

Clearly, a more detailed calculation of terms like  $A_{kf} A_{ki}$  will lead to a result of the form

$$1/T_Q^{\text{diff}} = (2/\tau) (1-p_Q), \quad (\text{B11})$$

where  $p_Q$  expresses the small correlation in the intramolecular energy before and after the hop.

We furthermore note that for  $\omega\tau \gg 1$ ,  $T_2^{-1}$  is proportional to the density of secular fluctuations. As is well known, the magnitude of these secular fluctuations determines the second moment of the absorption line. Hence we expect to have

$$(T_2^{\text{diff}})^{-1} = M_2^{\text{inter}} \tau_{\text{inter}} + M_2^{\text{intra}} \tau_{\text{intra}}, \quad (\text{B12})$$

where  $\tau_{\text{inter}}$  and  $\tau_{\text{intra}}$  are decay times for the inter- and intramolecular interactions due to diffusion. But we have just seen that both these times are essentially identical, both being nearly equal to  $G^2\tau/2(1-p)(G-1)(G-2)$ . Thus, in place of (B12) we should write

$$(T_2^{\text{diff}})^{-1} \approx M_2\tau [G^2/2(1-p)(G-1)(G-2)], \quad (\text{B13})$$

which is not too far from Torrey's result<sup>4</sup> for  $M^{\text{intra}}=0$ .

#### APPENDIX C: CROSS RELAXATION IN THE ROTATING FRAME

The energy baths in the low-field regime have been pictured as shown in Fig. 1. Here we have

chosen the baths to correspond to the terms in the Hamiltonian [Eq. (2)] rather than to the spin systems, namely,  $\mathcal{H}_z + \mathcal{H}_d^0 + \mathcal{H}_q^0$  (overlapping) and  $\mathcal{H}_q^0$  (nonoverlapping). We justify this separation into two baths as follows. Because the Zeeman and dipolar systems have comparable energies, they can communicate rapidly with each other (i. e., attain a common temperature within a time of the order of  $T_2^{\text{RL}}$ ).<sup>27</sup> Similarly we consider a small portion of the intramolecular system (corresponding to those spins whose intramolecular energy overlaps or is comparable in magnitude with their dipolar energy) as in equilibrium with the combined Zeeman-dipolar bath. However the remaining major portion of this intramolecular system takes a longer time  $T'_{12}$  to communicate with the other bath. This time will be comparable with the time for energy diffusion through the high-field NMR spectrum.<sup>7,19</sup> We shall assume in what follows that these times are equal. Once both systems are in equilibrium their common temperature decays to its limiting value with a characteristic time  $T_R$ .

To calculate the dynamics of the equilibration process through cross relaxation, we have made the approximation, as in a previous paper,<sup>19</sup> that average spin temperatures can be assigned to both energy baths. We label them by  $\Theta_2$ , the composite (intermolecular dipolar-Zeeman-overlapping intramolecular dipolar) system, and by  $\Theta_1$  the nonoverlapping dipolar system. This assumption is very crude for the latter one, since a time  $T_{12}$  is taken for the internal equilibrium process itself.

To simplify further the calculation, we neglect at first the relaxation to the lattice, taking  $T_{12} \ll T_R$ . Then we can treat the coupled energy baths in a similar way to that for two spin systems with different gyromagnetic ratios in a magnetic field  $H_1$  that relax towards a common spin temperature. Such a treatment has recently been presented by Engelsberg and Norberg.<sup>28</sup> The relaxation rate equations are taken to be

$$\frac{d\Theta_1^{-1}}{dt} = -\frac{1}{T_{12}} (\Theta_1^{-1} - \Theta_2^{-1}), \quad (\text{C1})$$

$$\frac{d\Theta_2^{-1}}{dt} = -\frac{1}{T_{21}} (\Theta_2^{-1} - \Theta_1^{-1}), \quad (\text{C2})$$

with the energy conservation equation

$$\frac{d}{dt} (E_1 + E_2) = 0, \quad (\text{C3})$$

where

$$E_1 = C(1 - \Phi^2)H_Q^2 / \Theta_1, \quad (\text{C4})$$

$$E_2 = C(H_1^2 + H_D^2 + \Phi^2 H_Q^2) / \Theta_2, \quad (\text{C5})$$

and  $C$  is the Curie constant for  $D_2$ ,

$$C = N\gamma^2 \hbar^2 (5 - 3X) / 3k_B. \quad (\text{C6})$$

Also here  $\Phi^2$  represents the fraction of the quadrupolar bath that overlaps in energy with the dipolar and Zeeman baths. The overlap in terms of the line shape is shown by the dashed region in Fig. 1, and we assume it to be approximately given by

$$\Phi = [m_2(I=2) / m_2(I=1)]^{1/2}. \quad (\text{C7})$$

Since the energies are proportional to the square of the local field, or to the second moments of the line shapes [Eqs. (9b) and (10b)] the overlap in terms of the energy baths must then be proportional to  $\Phi^2$ . To obtain a solution, we consider the following boundary conditions. At the beginning of the experiment, the spins are aligned along the external field  $H_0$  and their temperature is  $\Theta_0$ , equal to the lattice temperature  $T$ . The magnetic moment is  $M_0 = CH_0 / \Theta_0$ . We assume, similarly to Ref. 28,  $\Theta_1(t=0) \simeq \Theta_0 = T$ . Also from energy conservation arguments, we obtain

$$\Theta_2^{-1}(t=0) = \Theta_0^{-1} H_0 H_1 (H_1^2 + H_D^2 + \Phi^2 H_Q^2)^{-1}. \quad (\text{C8})$$

The solution is then

$$\frac{M(t)}{M_0} = \frac{H_1^2}{H_1^2 + H_D^2 + H_Q^2} \times \left( \frac{(H_1^2 + H_D^2 + \Phi^2 H_Q^2) + (1 - \Phi^2) H_Q^2 e^{-t/T_X}}{H_1^2 + H_D^2 + \Phi^2 H_Q^2} \right), \quad (\text{C9})$$

where

$$T_X^{-1} = \frac{1}{T_{12}} \left( \frac{H_1^2 + H_D^2 + H_Q^2}{H_1^2 + H_D^2 + \Phi^2 H_Q^2} \right). \quad (\text{C10})$$

At  $t=0$

$$M/M_0 = H_1^2 (H_1^2 + H_D^2 + \Phi^2 H_Q^2)^{-1} \equiv A, \quad (\text{C11})$$

and for  $t \gg T_X$ ,

$$M/M_0 = H_1^2 (H_1^2 + H_D^2 + H_Q^2)^{-1} \equiv B \quad (\text{C12})$$

or

$$T_X^{-1} = T_{12}^{-1} (A/B). \quad (\text{C13})$$

The coefficient  $B$  is the same as in Eq. (26) when the temperature of the equilibrated total system relaxes to the lattice with a time constant  $T_R$ . Hence  $B$  can be obtained by extrapolation of this decay to  $t=0$ . The ratio  $A/B$  can hence be measured from the experiment and can be checked for internal consistency using the known values of  $H_1$ ,  $H_D$ , and  $H_Q$  together with the approximate value of  $\Phi$ .

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\*Present address: Sandia Laboratories, Albuquerque, N. M.

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- <sup>16</sup>We note that the characteristic time for ( $J=1$ ) pair formation in  $H_2$  is dependent on temperature, becoming shorter as  $T$  increases. Taking  $\tau$  (pair)  $\approx 15$  min at 4 K and  $X=0.01$ , and estimating from a random step argument that about 10 interchanges are necessary before pair formation, the time for an interchange is still much larger than  $T_1$ , which is about 1 msec. Thus, rotating-frame techniques cannot be used to detect this phenomenon in  $H_2$ .
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