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Effects of high atom densities on the NMR relaxation times in solid T_2 and DT

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Experimental NMR data on solid T_2 and DT are used to study the effects of high-atom densities on the transverse and longitudinal relaxation times. Data for the second moments, the self-diffusion coefficient, and T_1 are analyzed and compared to similar measurements in H_2, D_2, and HD in order to isolate the contributions to these quantities due to atoms. Subtle effects are seen on the second moments but no direct effect is seen on the value of T_1 even for atom densities of order 10^{20} cm^{-3}.

I. INTRODUCTION

The stable isotopes of hydrogen, H_2, D_2, and HD, have been extensively studied by means of NMR. One of the earliest applications of a then new NMR technique was to solid H_2 by Hatton and Rollin.[1] The later study of the phase transition in nH_2 by Reif and Purcell[2] is a classic paper in the field. The use of NMR techniques to measure the molecular self-diffusion coefficients (and activation energies) in H_2 and HD by Bloom[3] and later in D_2 by Meyer *et al.*[4] provided the temperature dependence of the molecular dynamics in the solid hydrogens.

Measurements of the spin-lattice relaxation time (T_1) from 4.2 to 1.4 K in both H_2 and in HD containing H_2 impurities by Hardy and Gaines,[5] along with the systematic studies of the temperature dependence of T_1 and the second moment (M_2) determinations of the resonance line by Meyer *et al.*[6] provide a relatively complete description of the NMR properties pertinent to applications such as dynamic nuclear polarization (DNP) in the solid hydrogens.

To polarize a nuclear-spin system by DNP, a static polarization of an electron-spin system is transferred to the nuclear-spin system. If we think of highly polarized systems as being "colder" than systems with a smaller polarization, the cold electron-spin system is used to reduce the spin temperature of the hotter (by virtue of its smaller magnetic moment) nuclear-spin system. As a rule, the number of electron spins available (N_e) is much smaller than the number of nuclear spins (N_n) to be cooled. The cooling is still possible if the ratio of the nuclear-spin system T_{1n} to the electron-spin system T_{1e} is sufficiently large.

The earlier relaxation studies on H_2 and D_2 can be used to predict the situations where dynamic polarization is possible. For instance in H_2, if the oH_2 concentration is sufficiently high,[7] a rotational ordering occurs at a temperature T_λ that is accompanied by a large increase in T_1. Specifically, T_1 can change from 0.28 s in the disordered state to more than 100 s in the ordered state. Thus, from the standpoint of T_1 alone, rotationally ordered H_2 could be a candidate for DNP. Since the maximum ordering temperature is about 1.5 K and the oH_2 to pH_2 conversion (a rate of about 1.9% per hour)[8] is relatively fast, there are formidable technical difficulties in polarizing H_2 with high $J=1$ concentration. On the other hand, in the orientationally disordered state, the *maximum* relaxation time observed for high oH_2 concentration samples is under 0.3 s. Reducing the oH_2 concentration (x_1) is of no help since (i) a decrease of x_1 from the "normal" value (0.75) is accompanied by a T_1 decrease to a value below 1 ms before a slight increase, at extremely low concentrations, is found and (ii) the number of polarizable nuclei is decreased. These observations virtually rule out H_2 as a candidate for DNP *if it is in the disordered state.*

The situation in D_2, from the standpoint of T_1 alone is not so pessimistic. Again, the solid can exist in a rotationally ordered or disordered state depending on the concentration of $J=1$ molecules (x_1) and the temperature. First of all, for a given concentration of $J=1$ molecules, the value of T_1 is much larger than in H_2, even in the disordered state. Secondly, the $J=0$ molecules, most of which have a nuclear spin in D_2, have *no* relaxation mechanisms of their own and must be relaxed by the $J=1$ molecules making the observed relaxation time for a mixed system of $J=1$ and $J=0$ molecules longer than that of the $J=1$ molecules alone. A relaxation time of 9 s can be obtained for nD_2 at 4.2 K while T_1's of several hundred seconds would not be difficult in the ordered state. The maximum T_λ for D_2 is larger than for H_2 and

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the conversion rate is much slower. Thus, D_2, based on T_1 values, appears to be a viable candidate for DNP.

It was the experiments on HD that originally seemed to provide the most hope for DNP in the solid hydrogens. Due to the fact that $J=0$ molecules have no intrinsic relaxation mechanism of their own, the overall T_1 of HD (where essentially all the molecules are in the $J=0$ state below 4.2 K) with a *small* impurity concentration of $o\mathrm{H}_2$ could be more than 100 s even at 4.2 K or higher. Moreover, comparison of the HD experimental results with those on H_2 provided a good understanding of the relaxation times of a mixture of spin systems, such a mixture being commonly encountered in the solid hydrogen isotopes. While HD seemed to be a good candidate for DNP, no one has achieved a large nuclear polarization in HD by DNP, although Solem did produce *some* polarization.[9]

The possibility of using a 50-50 mixture of D and T spins as a target for laser fusion was raised as a result of the theoretical work of Goldhaber *et al.*[10] The perfect such target, with both the D and T nuclear spins polarized to 100%, would provide a cross-section increase of 50% over similar target of unpolarized nuclear spins, reducing substantially the size and the cost of the laser system needed for fusion. With an ultimate goal of producing highly polarized nuclear spin systems of both D and T spins, we have started NMR experiments on solid T_2 and a high-temperature equilibrium mixture of 25% T_2, 25% D_2, and 50% DT that we will call nDT. To date, our experiments have produced results on the $o\mathrm{T}_2$ to $p\mathrm{T}_2$ conversion time as a function of temperature,[11] the spin-lattice relaxation time T_1 and the spin-spin (SS) relaxation, responsible for NMR signal dephasing. To characterize this latter quantity, we obtain the NMR line shape and measure the line's second moment, M_2. In this paper, we will present the measurements of M_2, T_1, and the self-diffusion coefficient, $D(T)$, that we have made to date and compare and contrast them with previous work on H_2, D_2, and HD.

The major difference between this present work and that on H_2 or D_2 comes from the radioactivity of the T nucleus which β decays with a half-life of 12.3 years. A solid such as T_2 is then bathed in a constant flux of electrons with energies large enough to shatter the molecules. Many different molecular fragments can be made, but it is clear from the work of Leach and Fitzsimmons[12] and Sharnoff and Pound[13] that atoms are formed. In the Leach and Fitzsimmons work, a pulsed electron source was used so that the atom recombination coefficient could be measured directly from the EPR signal decay following an electron pulse. In the Sharnoff and Pound experiment, small amounts of T_2 incorporated into a D_2 sample provided an electron flux that could not be turned off, resulting in a measurable stable atom population. Our work on ortho to para conversion in solid T_2 (Ref. 14) is best interpreted by postulating that a gas of mobile T atoms exists in the molecular solid with the number density of atoms, inferred from a model, that increases with decreasing temperature reaching a value in excess of 10^{20} atoms per cm^3 at about 6 K. Since each atom carries a free-electron spin, the atom gas should alter the behavior of the nuclear-spin system. Thus, in addition to the practical problem related to nuclear-spin polarization, this system is scientifically intersting due to problems presented by spin diffusion.

This paper is organized in the following manner: Section II contains a discussion of the expected values of the second moment if T_2 and DT were not radioactive (and behaved as the other hydrogen isotopes do) which is followed by the results obtained for the second moment in our experiments; Sec. III parallels the development in Sec. II except it deals with T_1; Sec. IV is devoted to measurements of the self-diffusion coefficient; and Sec. V contains a discussion of the results and our conclusions. The experimental techniques and apparatus have been described elsewhere[14] and will not be repeated here.

II. THE SECOND MOMENTS (SPIN-SPIN RELAXATION)

A. Basic ideas about second moments

One of the quantities that can be calculated with some ease is the "second moment" of an NMR (or EPR) line. A quantum-mechanical technique originated by Van Vleck gives a closed form expression for the second moment in terms of the Hamiltonian that expresses all the *magnetic* interactions. Moreover, the expression for the second moment depends on the "trace" of the commutator of I_x (the x component of the spin system being observed) with the magnetic Hamiltonian. Since a trace is involved, the exact eigenstates of the system do not have to be known since any complete set will suffice. The classical example of a second moment calculation is provided by the magnetic dipole-dipole interaction, described in great detail in the standard reference works on NMR by Abragam[15] and Slichter.[16]

For those systems with only magnetic dipolar interactions, the contribution to the second moment comes from just two of the six terms used to characterize the dipolar interaction. The two important terms are the ones that are *time independent in the rotating frame* of the nucleus of interest. Thus, only the term that produces a static field in the z direction and the term that corresponds to a mutual spin flip, with no dipolar energy change, need be considered. When the dipole-dipole (d-d) interaction is written

$$H_{d\text{-}d}=\frac{\gamma_1\gamma_2\hbar^2}{r_{12}^3}(A+B+C+D+E+F)\ , \tag{1}$$

only the terms A and B can possibly be time independent in the rotating frame of nucleus 1. In fact, if the nuclei 1 and 2 are different, then their mutual spin flip does not conserve "spin energy" and even that term can be discarded from the calculation. When the nuclei are identical and both the A and B terms contribute, their relative contributions are not equal, the contribution from the B term being $\frac{5}{4}$ the contribution from the A term.

The ease of calculation of the second moment is not the sole justification for its widespread use in characterizing NMR lines. A great deal of its utility comes from the fact that the second moment is *invariant to lattice motion.* This invariance stems from the fact that the coordinates that contain lattice information are "space coordinates" and they commute with "spin coordinates" making no contribution to the second moment. This is a very important idea as it indicates that temperature changes will only alter the second moment through changes in the density (the factor r_{12}^3). This result seems to contradict common experience since the NMR line in a liquid is very narrow, but in the solid it is much broader. The theory of "motional narrowing" due to Anderson[17] removes this apparent dilemma. The square root of the second moment $\sqrt{M_2}$ is used in the Anderson theory as the "benchmark" frequency. If the angular frequency that characterizes the motion (Γ) is large compared to $\sqrt{M_2}(\Gamma \gg \sqrt{M_2})$, liquidlike behavior is observed and the line has a width given by $\Delta\omega = M_2/\Gamma$. If the motional frequency is small compared to $\sqrt{M_2}(\Gamma \ll \sqrt{M_2})$, solidlike behavior is observed and the width $\Delta\omega = \sqrt{M_2}$.

Physically, the second moment is a quantitative measure of the local magnetic field in a rigid system. The second moment is obtained from Eq. (1), after calculating a trace and a lattice sum. The complete lattice sum is usually only about 20% larger than the contribution from just the first nearest neighbors and so M_2 is very sensitive to short-range order.

B. Calculation of the second moment for solid tritium

In solid tritium, either in the form of T_2 or DT, the magnetic dipolar interaction is the only interaction that must be considered. For solid T_2, only the ortho-T_2 molecules have a nonzero nuclear spin ($I=1$) and all such molecules are identical so the second moment contains contributions from both the A and B terms. The only complication with the calculation comes in performing the needed lattice sum to include the interactions with all the magnetic dipoles in the system. This is not so bad a problem as it seems since the contribution to the second moment depends inversely on the distance from the "central" spin to power six ($1/r_{12}^6$). Thus, nearest neighbors make the most significant contribution. The usual way to handle a magnetically diluted system (one where there is not a spin at every lattice site) is to sum over *all* sites (as you would with a perfect spin system) but multiply the sum by the probability that the site is occupied by a spin (i.e., multiply the ordinary lattice sum by the concentration of spins). Such an approach should be reasonably correct until the probability of the central spin having one nearest neighbor with spin become smaller than unity, $zx<1$, where z is the number of nearest neighbors and x is the concentration of spins. The lattice structure of solid T_2 is hcp above 4 K but could be fcc below 4 K depending on the $o\mathrm{T}_2$ concentration. In either case, $z=12$, so the preceding treatment of the magnetic dilution should be acceptable for x larger than 10%. Making that assumption, the second moment, M_2, becomes

$$M_2 = 17.34\frac{\gamma^4\hbar^2}{a^6}x_1(\mathrm{rad\,s^{-1}})^2 = (M_{20})x_1 \ , \tag{2}$$

where $a=3.53$ Å is the nearest-neighbor distance for T_2, and x_1 is the $o\mathrm{T}_2$ concentration. The quantity M_{20} would be the rigid lattice second moment for a sample of solid tritium with an $o\mathrm{T}_2$ molecule at every lattice site. From the density of T_2, we can calculate the quantity M_{20} to be

$$M_{20} = [6.60\times10^9\ (\mathrm{rad\,s^{-1}})^2] \ .$$

In addition to the contribution to M_2 from the intermolecular dipolar interaction between $o\mathrm{T}_2$ molecules, there are several other contributions to M_2. (1) Magnetic impurities in the system could also contribute to M_2. For all of the solid hydrogens, this situation appears to be relatively simple. As the hydrogens are liquefied, nearly all impurities other than hydrogen isotopes are excluded so that the samples are very pure in this sense. However, other hydrogen isotopes *can remain in solution* and contribute to M_2. These would include H_2, D_2, HT, HD, and DT as all have at least one molecular species with a nonzero nuclear spin. (2) A second source of line broadening (and a contribution to M_2) could come from any unpaired electron spins, possibly on free atoms. Their contribution to M_2 would be due to the large local magnetic field they generate. (3) Another contribution to M_2 could come from quenching the free rotation of the $J=1$ moleules giving rise to a nonzero average of the intramolecular interaction. The first two contributions to the second moment are independent of x_1 but the intramolecular interaction is a complicated function of x_1. At this time we will not distinguish between the first two sources of line broadening but instead lump them altogether in a term, M_{2i}, an "impurity" contribution that is independent of x_1. There is no experimental evidence for anything but a linear dependence on x_1 and so we will neglect the broadening due to quenching of molecular rotation. The complete second moment can be regarded as the sum of the impurity contribution (M_{2i}) and the contribution from the local field due to $o\mathrm{T}_2$ moleules given in Eq. (2):

$$M_2 = M_{2i} + (M_{20})x_1 \ . \tag{3}$$

Measurements of M_2, at fixed temperature, for different $o\mathrm{T}_2$ concentrations, can then be used to find M_{2i} and M_{20}. The NMR signal height in T_2 or DT is linear in x_1, so as x_1 changes due to ortho-para conversion, one can obtain M_2 as a function of x_1 in a straightforward manner.

C. Experimental values of the second moment

The second moment, M_2, is obtained from the data by fitting an analytic function to the short-time behavior of the free-induction-decay technique (FID). Depending on the visual appearance of the FID, we use one of two functions for the fit. If the FID contains a damped oscillation (called a Lowe-Norberg[18] beat), we use the function

$$S(t) = S_0\exp(-\tfrac{1}{2}a^2t^2)\frac{\sin bt}{bt} \approx S_0[1-\tfrac{1}{2}(a^2+b^2/3)t^2+\cdots] \ , \tag{4}$$

so that the second moment is

$$M_2=a^2+b^2/3 .$$

The value of b can be found from the nulls in the FID and a can be found from the decay. If there is no visible beat on the FID, we use the function

$$S(t)=S_0\exp\left\{-M_2\tau^2\left[\exp\left[-\frac{t}{\tau}\right]-1+\frac{t}{\tau}\right]\right\}$$
$$\approx S_0(1-\tfrac{1}{2}M_2t^2+\cdots) . \quad (5)$$

This latter function has "Gaussian" short-time behavior but the long-time behavior of the exponential. The time τ characterizes the transition from one behavior to the other. When using this latter function, we actually fit to the complete function and do not use the short-time limit.

1. "Pure" T_2

For our experiments on oT_2-pT_2 mixtures, the signal at $t=0$, S_0, is a reliable measure of the oT_2 concentration. To be sure, there is a small contribution to this signal from DT and HT impurities in our samples, but since the total impurity concentration (from gas analysis) is about 3% (and the impurities have a T spin of $\frac{1}{2}$), their contribution to the signal is of order 1%. Thus, for oT_2 concentrations above 50%, we can regard S_0 as linearly proportional to x_1, the oT_2 concentration. Thus, in the same fit of the FID we obtain the concentration x_1 (from the signal height) and M_2 (from the time decay). The oT_2-pT_2 conversion rate is found from the time dependence (at fixed T) of S_0.

The data for all temperatures and all samples, even mixtures of DT, T_2, and D_2 follow the general behavior indicated by Eq. (3) for at least a limited range of x_1 values (the higher ones). This is shown in Fig. 1, where the data points for samples of "pure" T_2, at low concentrations, are omitted. This enables us to fit the experimental values of M_2 versus x_1 to a straight line and extract the slope and intercept. The values of the quantities M_{20} and M_{2i} are plotted in Fig. 2 as a function of temperature.

Several trends in the data are worthy of comment: (i) the straight line fit is very good at large values of x_1; (ii) the agreement of the experimental value of M_{20} and the calculated value is not too bad at high temperatures; but (iii) the agreement becomes poorer at lower temperatures where the impurity contribution appears to grow. It should be noted that the impurity contribution is much too large for the *known* nuclear-spin impurities in our samples (HT and DT being the most important ones). This suggests that there must be another line broadening mechanism that is independent of x_1.

2. Mixtures of Dt, T_2, and D_2(nDT)

If DT is made from D_2 and T_2 with final concentrations given by the high-temperature equilibrium ratios, we will have 50 at. % DT, 25 at. % D_2, and 25 at. % T_2. We have done NMR experiments on such samples (which we will designate as *n*DT) although the actual concentrations are not always exactly the same as these nominal ones. The predicted value of the second moment for a DT mixture such as we described can be obtained by a suitable scaling of the values calculated for pure T_2. For instance, the decomposition of Eqs. (3) will still hold where x_1 is the oT_2 concentration, but the value of M_{20} must be changed to account for the differences in molar volume between *n*DT and T_2. We do not know the molar volume of *n*DT with great precision so we used the

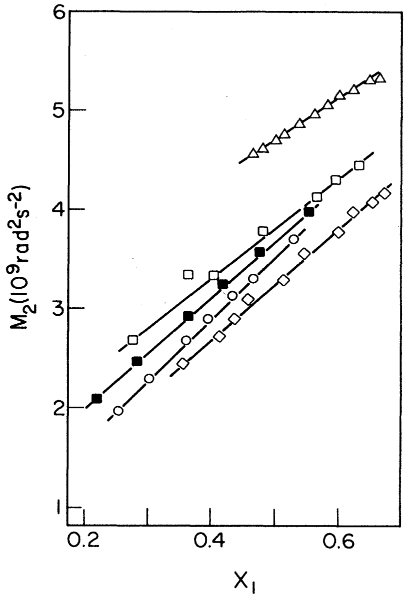

FIG. 1. The second moment M_2 in pure T_2 is plotted as a function of the oT_2 concentration at five temperatures. The temperatures are: 6.4 K (△); 8.0 K (□); 9.5 K (■); 12.6 K (○); and 14.9 K (◇). The lines are drawn as a guide only.

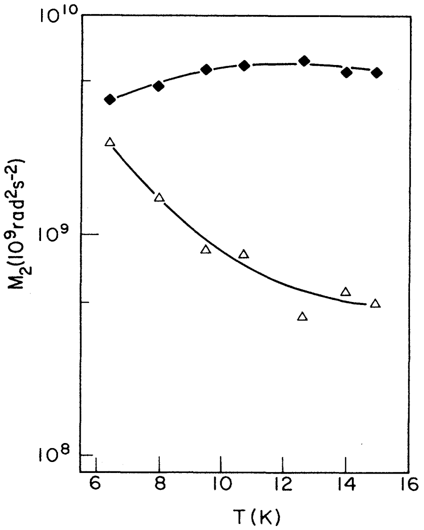

FIG. 2. The coefficients determined from the data of Fig. 1 by fitting to Eq. (3) in the text. The dashed line represents the theoretical M_2 for pure oT_2. The symbol (◆) represents M_{20} while the symbol (△) represents M_{2i}.

weighted averaged volumes of its constituents leading to

$$M_{20}(\mathrm{DT}) = M_{20}(\mathrm{T}_2)(V_{T_2}/V_{\mathrm{DT}})^2$$
$$= 6.23\times 10^9\ (\mathrm{rad\,s^{-1}})^2 \ . \qquad (6)$$

The term that is independent of x_1 is expected to be considerably larger in "DT" than in T_2 since 50% of the molecules are DT. This contribution can also be predicted from the scaled value of M_{20} by taking into account the differences in the factor $I(I+1)$ for the various nuclei. Additionally, there is a contribution to M_2 for the T resonance from the D nuclei on DT molecules and nuclei on D_2 moleules that is slightly uncertainty due to the exact $o\mathrm{D}_2$ and $p\mathrm{D}_2$ concentrations, but since this overall contribution from D spins is smaller than our probable error in measuring M_2, it should not affect any but the most detailed results. If the $J=1$ concentration in the sample is zero, the predicted value of M_2 is

$$1.24\times 10^9\ (\mathrm{rad\,s^{-1}})^2 \ ,$$

whereas the infinite temperature values of the $J=1$ concentrations would lead to

$$M_2 = 2.4\times 10^9\ (\mathrm{rad\,s^{-1}})^2 \ .$$

Extracting x_1 from the signal height measurement is less precise because of the large "background" signal from the T spins on the DT molecules than it is in pure T_2, but it still can be done. Observed M_2's for such "garden variety" DT samples are given in Fig. 3, and the parameters M_{2i} and M_{20} taken from the straight line fits are plotted in Fig. 4. The same general trends observed in T_2 are seen here along with one very interesting new feature.

The interesting new feature is seen in Fig. 5 where the M_2 data at our lowest temperature are shown. Here, the second moment actually increases between the first and second data points. One possible interpretation of this effect is that the atom poulation has not reached its equilibrium value at the time the first data point was taken but has by the time the second data point was taken. Everything is regular after the second point. This interpretation permits us to crudely estimate the time constant for the atom distribution to reach its equilibrium value at this lower temperature. The 10%–90% rise time is about 24 min so that the estimated atom recombination coefficient (α) is

$$\alpha = 1.66\times 10^{-23}\ \mathrm{cm^3\,s^{-1}} \ .$$

While such an estimate based on such scant data cannot be very accurate, it at least should provide the correct order of magnitude of the atom recombination coefficient at 4.7 K.

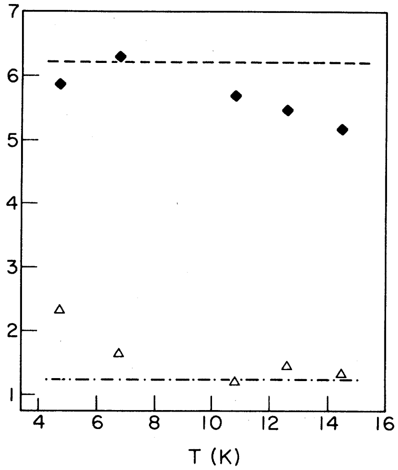

FIG. 4. The coefficients determined from the data of Fig. 3 by fitting to Eq. (3) in the text. The dashed line represents the theoretical value of M_{20} while the dot-dashed line represents the M_2 for the DT background. The symbol (◆) represents M_{20} while the symbol (△) represents M_2i.

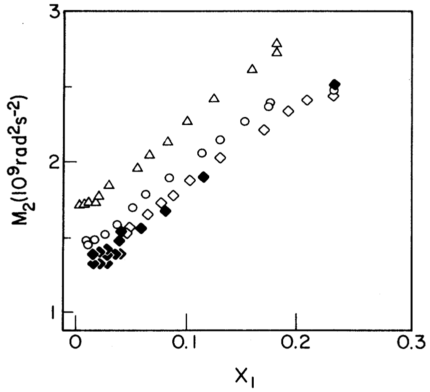

FIG. 3. The second moment M_2 in nDT at four temperatures is plotted as a function of the $o\mathrm{T}_2$ concentration x_1. The four temperatures are: 6.8 K (△); 10.8 K (○); 12.6 K (◇); and 14.5 K (◆).

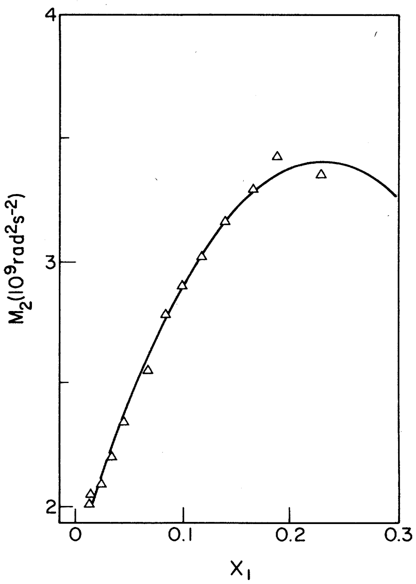

FIG. 5. The second moment at 4.7 K for nDT is shown as a function of the $o\mathrm{T}_2$ concentration. At the highest concentration, M_2 is reduced, possibly due to the atom concentration being smaller than its equilibrium value.

III. THE SPIN LATTICE RELAXATION TIME (T_1)

The relaxation times reported here include measurements on pure T_2 where the ortho to para ratio is varied as well as measurements of T_1 in the isotopic mixture, *n*DT. In both cases, at fixed temperature, the oT_2 concentration changes with time so the T_1's can be obtained for various oT_2 concentrations. For relaxation in DT, the pD_2 concentration is important and it varies in time also. Unfortunately, while the total D_2 concentration is known, the pD_2 concentration is not directly measured in our experiments nor easily inferred.

A. Spin lattice relaxation in pure H_2 and T_2

All of the earlier theories of the longitudinal or spin lattice relaxation time in solid H_2 were extended and summarized in the extensive work of Harris.[19] The intramolecular interaction in oH_2 couples the molecule's nuclear spin ($I=1$) with its rotational spin ($J=1$) so that changes in the orientation of an oH_2 molecule (J_z) provide a nuclear-spin relaxation mechanism. Para-H_2 molecules have no nuclear spin ($I=0$) and at low temperatures only the $J=0$ rotational state is occupied, so they have no direct influence on the relaxation process. For a less obvious reason, a molecule with $J=0$ but I nonzero (such as HD) still has no appreciable longitudinal relaxation mechanism. This results from the fact that the direct coupling between nuclear spins and phonons is extremely weak because the density of phonon states at the nuclear Larmor frequency is very small. Thus, the rotational degrees of freedom of the $J=1$ molecules in solid hydrogen samples have a catalytic effect on the spin lattice relaxation; they couple nuclear spins to the lattice phonons effectively because the spectrum of rotational transitions (at constant J) is broad and overlaps the spectrum of nuclear-spin transitions. This makes the coupling of the phonons to the rotational degrees of freedom much stronger than their coupling to the nuclear spins. The strength of this coupling is such that no experiments to date have seen a "breakdown" that would produce a "bottleneck" in the relaxation process. Thus, the "real" relaxation problem is that between nuclear spins and the rotational spins: The rotational spins are always in thermal equilibrium at the lattice temperature.

The preceding general ideas lead to a few simple rules for spin-lattice relaxation in the molecular hydrogen isotopes containing no free-electron spins: (i) at low temperatures all the molecules either have $J=0$ or 1, but none of the molecules have a direct spin-lattice coupling of any consequence; (ii) molecules with nuclear spin but $J=1$, have a link to the lattice governed by their quadrupole-quadrupole (EQQ) coupling to other molecules having $J=1$ so that their T_1 is a function of the concentration of $J=1$ molecules (x_1) *of any origin* (H_2, D_2, or T_2); (iii) molecules with nuclear spin but $J=0$, have no measurable direct link to the lattice nor any coupling to other rotating molecules and hence have an intrinsic T_1 of infinity; and (iv) nuclei with the same magnetic moment (such as HD and H_2 for the proton resonance) can "cross-relax" allowing nuclei with $J=0$ to equilibrate with the lattice through like nuclear spins on moleules with $J=1$.

To avoid confusion with the usage of the symbol T_1 to denote the measured relaxation time, we will use the symbol T_{11} to denote the spin-lattice relaxation time of $I=1$ nuclear spins in an alloy of $J=0$ and $J=1$ molecules of the same species. This quantity T_{11} can, in principle, be calculated with no adjustable parameters as it depends on the EQQ coupling constant and the concentration. The agreement between the calculated and measured values of T_{11} at high concentrations is truly impressive. Although there is no closed form theoretical expression for T_{11}, valid for all concentrations, there does appear to be a universal behavior for all the solid hydrogens. This is shown in Fig. 6 where the data on H_2 and T_2 are different only because of molar volume differences, and the data on oH_2 relaxation in D_2 indicate that any hydrogen quadrupole moment is effective at spin relaxation.

B. Spin lattice relaxation in isotopic mixtures

The spins on a molecule with $J=0$ can be brought into equilibrium with the lattice through mutual spin flips (cross relaxation) that eventually reach a molecule with $J=1$ (spin diffusion) that has a shorter relaxation time labeled T_{11}.

By using the spin temperature approximation, the following expression for the total relaxation time T_1 for all the spins of a given gyromagnetic moment can be obtained:

$$T_1=\frac{C_0+C_1}{C_1}T_{11}(x_1)\ , \tag{7}$$

where C_0 and C_1 are the *spin* specific-heat capacities [proportional to the number of spins, N_0 or N_1 and $I(I+1)$ where I is the nuclear spin]. This expression has been derived independently by Nakamura and Fujio[20] for

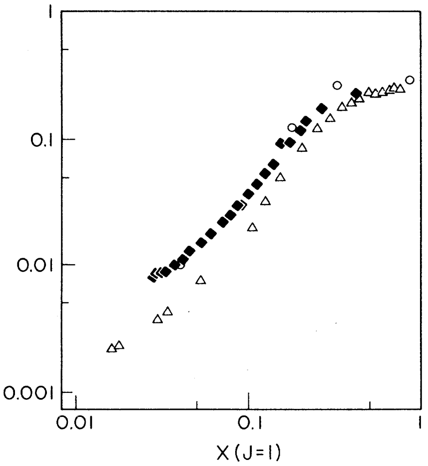

FIG. 6. The quantity T_{11} used in Eq. (7) is plotted as a function of the total $J=1$ concentration, $x(J=1)$, for oH_2 in pH_2 (△) at 4.2 K; oT_2 in pT_2 (◆) at 6.4 K; and 1% nH_2 in D_2 (○) with various $J=1$ concentrations at 4.2 K.

relaxation of HD molecules with H_2 impurities present. Moreover, measurements by Hardy and Gaines[5] on H_2 and HD containing controlled amounts of H_2 have verified the correctness of this simple picture.

The previous equation forms the basis for producing very long relaxation times in DT. If solid DT is produced with a few percent of T_2 and D_2 impurities, then $C_0 \gg C_1$ and

$$T_1 = (C_0/C_1)T_{11} = (3/8x_1)T_{11}(x_1) .$$

As the metastable $J=1$ concentration decays, T_{11} goes through a minimum for x_1 below a percent and increases slightly at lower x_1's. Thus, below the minimum in T_{11}, the quantity T_1 can increase significantly due to the factor $(1/x_1)$. In HD, T_1's of 1000 s have been produced by Hardy and Gaines and Honig and co-workers[21] for small values of x_1. The relaxation time in DT as a function of time is shown in Fig. 7. Increasing time leads to reduced $J=1$ concentration and T_1 does change after there is no detectable change in M_2 indicating that decreasing $J=1$ D_2 concentration changes T_1.

At very low concentrations, we see slight increases in T_1 with time. One possible explanation is that D_2 is converting very slowly producing this change. More likely is that the D_2 is also in a dynamic equilibrium just as the T_2 is, so another explanation is needed. Possibly the slight increase comes from the breakdown of the spin-flip term in the dipolar Hamiltonian seen in the M_2 data. If the nuclear spins are not on "speaking terms," T_1 can increase as spin diffusion takes longer.

C. The effects of free-electron spins on T_1

Since most of the features of our observed relaxation times are adequately predicted by Eq. (7), it appears that the unpaired electron spins that noticeably effect M_2 have little to no effect on T_1. Considering the large densities of unpaired electron spins in the solids inferred from the *o-p* conversion rates, it is quite remarkable that there is so little effect of these spins on T_1. The simple hopping model we used to interpret the *o-p* conversion rate data is also useful here in estimating the effect on T_1 of the mobile electron spins. If we denote their contribution to the overall spin lattice relaxation rate as R_e, then

$$R_e = c\frac{\Omega\Gamma}{\Omega+\Gamma} , \tag{8}$$

where Γ is the electron-spin hopping frequency (determined from the *o-p* conversion rates), c is the electron-spin concentration, and Ω^{-1} is the relaxation time of a nuclear spin caused by a nearby electron spin. We could imagine that the nuclear spin and the electron spin are "in contact" and use the hyperfine interaction to calculate Ω.

In the preceding picture of relaxation of nuclei by free-electron spins, the electron spin hops to a site occupied by a nucleus and interacts with the nucleus through the hyperfine interaction, characterized by the splitting in an atom of H by the field of 509 G (and 544 G for T). The T_1 due to this interaction has been worked out in Abragam and is given by

$$\frac{1}{T_1} = \frac{A^2}{2}\frac{\tau}{1+\omega^2\tau^2} = \Omega , \tag{9}$$

where A is the hyperfine coupling constant, τ is the electron-spin correlation time, and ω is the difference frequency between the electron spins and the nuclear spins (essentially the electron-spin resonance frequency). The minimum relaxation time corresponds to $\omega\tau = 1$ and has the value $4\omega/A^2$. By taking τ to be the inverse of Γ, the hopping frequency that has been deduced from the analysis in Sater *et al.* and found to be less than $\Gamma =$ at 19 K, we see that $\omega\tau \gg 1$ for our experiments so that the observed relaxation rate due to the hopping electron spins is given by

$$R_e = c\Omega = 2c(A^2/2\omega)^2\Gamma , \tag{10}$$

since $A/\omega \ll 1$ at the fields we use. Because of the inequality $A/\omega \ll 1$, we have $\Omega \ll \Gamma$ except near the maximum in the rate. At 6 K, the quantity Γ is approximately $3\times10^{-2}\ \mathrm{s}^{-1}$, so if $\Omega/\Gamma \ll 1$, the relaxation rate in general equals $c\Gamma$. Taking $c = 4.6\times10^{-3}$, we estimate a T_1 at 10^6 s. Even at the maximum of Eq. (8), the relaxation time is still 30 min (the *o-p* conversion time). Thus, for our *short* relaxation times resulting from the EQQ interaction, we are justified in ignoring the contribution from the free-electron spins, even though they are in motion.

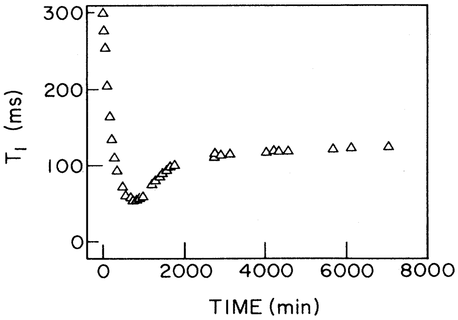

FIG. 7. The relaxation time T_1 measured in *n*DT is plotted as a function of time at $T=6.8$ K. The changing *o*T_2 concentration produces the minimum seen.

IV. THE SELF-DIFFUSION COEFFICIENT

There are not very many experimental techniques that can measure a diffusion coefficient. Radioactive tracers can be used if the element in question has a radioactive isotope. NMR can be used for self-diffusion measurements because "spatial motion" can destroy spin phase memory and hence produce a measurable decay of a spin echo. We have used appropriate spin-echo techniques to measure the spin-diffusion coefficient, D(T), for HD, *n*DT, and T_2. These measurements are quite important to the interpretation of the data on second moments and even the ortho to para conversion time data because they yield quantities such as the motional correlation time as a function of the temperature.

To measure D(T), we used a Carr-Purcell, Meiboom-

Gill[22] pulse sequence to obtain a spin-spin relaxation time, T_{SS}. This quantity was related to the correlation time for diffusion (τ_c) by a motional narrowing expression

$$\frac{1}{T_{SS}}=\tau_c M_2^{\text{inter}} . \tag{11}$$

In turn, the diffusion coefficient was related to the "hopping frequency" (Γ) or the correlation time (τ_c) by

$$D=\langle r^2\rangle\Gamma/12=\langle r^2\rangle/(12\tau_c) ,$$

where the nearest-neighbor separation is used for r.

All of the measurements of the diffusion coefficient have been fitted to the "thermally activated" form

$$\text{D(T)}=D_0\exp(-E_a/kT) , \tag{12}$$

where E_a/k is the activation energy in degrees Kelvin. The quantities D_0 and E_a obtained in this work and by others are summarized in Table I.

Examination of these results reveals that the two measurements of D(T) for HD are in disagreement. If we drop the earlier determination of D(T) in favor of our more recent one, the activation energies become a monotonic function of the isotope mass. This is shown in Fig. 8. An interesting addition to the preceding data comes from the measurement of D(T) for HD impurities in $p\text{H}_2$ (Ref. 25) where

$$D_0=5.7\times10^{-3}\ \text{cm}^2\,\text{s}^{-1}$$

and $E_a/k=196.8$ K were obtained. For the measurements on the nonradioactive hydrogen isotopes, D_0 is subject to considerable scatter and both different models and different relationships are used to extract D_0 from a relaxation time measurement so it it now possible to generalize. Nevertheless, the values we obtain for nDT and T_2 appear to be anomalously large. The value of E_a/k obtained for H_2 and D_2 agree well with the calculation of Ebner and Sung, and the trend of values for E_a/k, seen for the isotopes where no calculations exist, appears reasonable, but we will elaborate on diffusion results in a subsequent paper.

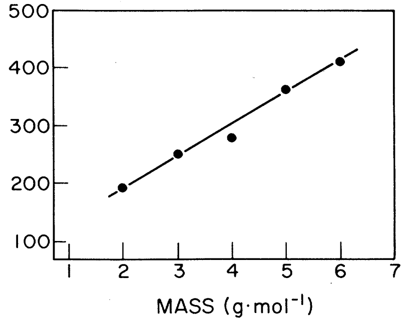

FIG. 8. The activation energy, E_a, is plotted for the various hydrogen isotopes as a function of the isotope mass. The straight line is drawn as a guide.

V. DISCUSSION AND CONCLUSIONS

The data on D(T) is interesting in its own right, but the main reason for introducing it into this discussion is to quantify the molecular motion as a function of temperature so that the temperature below which the second moment attains its rigid lattice value can be predicted. We will call this temperature the "freezing temperature" (T_f). Even in H_2, which solidifies at 14 K, the NMR linewidth does not reach the value predicted by the rigid lattice M_2 until $T<10$ K. For solid H_2, $T_f=10$ K.

A. The "freezing temperature" for T_2

The experimental values of M_2 in HD as a function of temperature are shown in Fig. 9. Below 10 K, the experimental M_2 agrees perfectly with the calculated "rigid lattice" value for a powdered sample. Above 10 K, it can be seen that the apparent M_2 is reduced. If we interpret this effect as a motional effect, the "freezing" temperature for HD is about 12 K. Using our measurement of D(T) for HD, we find that $\Gamma/\sqrt{M_2}=1$ at 12.4 K, consistent with the M_2 data. Using D(T) for T_2 to find the temperature where $\Gamma=\sqrt{M_2}$, it is found that the second moment of T_2 should attain its rigid lattice value below 16 K. This estimate cannot be taken too seriously but it is not bad. For instance, if we use the law of corresponding states

TABLE I. Values of the diffusion coefficient.

Isotope	$E_a(K)$	D_0 (cm^2 s^{-1})	Comment
H_2	191	1.4×10^{-3}	experiment (Ref. 3)
	200	3.0×10^{-3}	experiment (Ref. 6)
	198	2.0×10^{-3}	experiment (Ref. 23)
	197	0.6×10^{-3}	theory (Ref. 24)
HD	302	0.17	experiment (Ref. 3)
	250	2.6×10^{-3}	experiment (this work)
D_2	276	0.4×10^{-3}	experiment (Ref. 4)
	290	0.7×10^{-3}	theory (Ref. 24)
nDT	368	0.138	experiment (this work)
T_2	411	0.392	experiment (this work)

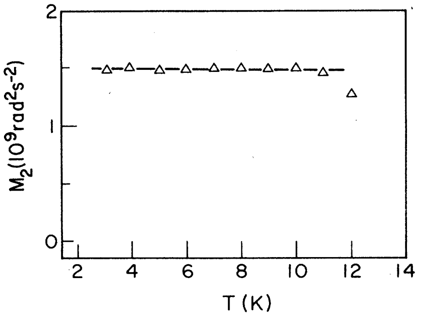

FIG. 9. The second moment of HD is plotted as a function of temperature. The straight line represents the calculated rigid lattice value.

(and the triple point and critical point temperatures) to extrapolate behavior from HD to T_2, we find that a temperature at 12.4 K for HD corresponds ot a temperature of 15.4 K for T_2, in reasonable agreement with our diffusion-motional narrowing argument. Thus, we take $T_f = 15$ K for T_2.

From the T_2 data, it can be seen that M_{20} *has not* reached its rigid lattice value by estimated freezing temperature of 15 K, although the triple point is near 19 K. The apparent reduction in the second moment could be due to motion; most likely the motion of atoms since that of molecules should be frozen out at these temperatures.

B. Second moments

Several trends are evident from Fig. 2. It should be noted that M_{20} appears to be increasing from 20 K to 12 K, but peaks there and decreases again at lower temperatures. We interpret the temperature dependence above 12 K as a motional effect. The apparent value of M_{20}, reflecting the oT$_2$-oT$_2$ dipolar interaction, depends on the temperature, peaking near 12 K. There is still significant *molecular motion* above 15 K so it is not surprising that M_{20} falls below its "rigid lattice value" at the higher temperatures. It is surprising to note the decrease in M_{20} at the lower temperatures. The temperature dependence below 12 K cannot be due to molecular motion which should be frozen out.

In addition to the question raised by the earlier discussion, namely below what temperature should we observe "rigid lattice" behavior, there is another point to be addressed, namely the magnitude of the "impurity" contribution to M_2 and its origin. The increase in M_{2i} that occurs at lower temperatures is suggestive of an atom buildup. Such a buildup has been indicated from measurements of the oT$_2$-pT$_2$ conversion rate. The value of M_{2i} obtained from the data is higher than that calculated for the impurities known to be in the sample and also higher, for the three low-temperature points, than the *actual* M_2 obtained at the lowest concentration.

To explain why the value of M_{2i} is larger than the actual M_2 obtained for the lowest concentration at the three low-temperature points, we note that the oT$_2$ concentration at the end of a run is not zero. At the higher temperatures, the equilibrium concentration, as measured from the signal heights, is found to be as large as 18%, decreasing to 1.8% at 8 K before rising to 2.3% at 6.4 K. These latter concentrations are in excess of the Boltzmann values calculated from the known spacing of the molecular rotational levels and have been interpreted as arising from a "pumping" of the $J=1$ level due to atomic recombination. Therefore the "ending" M_2 is predictably larger than that expected from just the impurities. We will examine the possible contribution to M_2 from atoms trapped in the solid using just the three points at the lowest temperatures.

C. The local field of atoms

The effects of atoms, with their unpaired electron spin, on the second moment of the nuclear spins is an issue of central importance to this study. Unfortunately, there is no existing framework for us to use in quantifying the effect of electron spins located on atoms on the observed M_2 of the nuclear spins in our sample.

The portion of the second moment that is independent of $J=1$ concentration increases as the temperature is reduced. This is seen in both the T_2 data and the nDT data. Such an increase could be due to quenching the rotation of the $J=1$ molecules so that the intramolecular interaction produces a contribution to M_2 but this contribution would not be independent of x_1. In our data, the increase in M_2 at low temperatures, while less pronounced in nDT than it is in T_2, indicates that quenched rotation is not the cause of the increase. Thus, the atoms may be producing this additional contribution to M_2. We will try to estimate the order of magnitude of their contribution.

The initial assumption that we make is that the atom concentration is 1% or below, so that we are considering a "dilute" magnetic system. The second moment calculated for a rigid lattice of T_2 molecules can be scaled to estimate the electron-spin contribution. This scaling involves some obvious numerical factors such as: a reduction by $\frac{4}{9}$ since spin flips are not energy conserving; a reduction by $\frac{3}{8}$ to correct for the spin differences; an increase by $(\gamma_2/\gamma_1)^2$ where γ_2 is the electron-spin gyromagnetic moment and γ_1 is the nuclear-spin gyromagnetic moment; and finally, a "lattice scaling" by the factor $(a_0/a_1)^6$ where a_0 is the near neighbor distance in T_2 and a_1 is the average distance between electron spins. This last factor introduces the square of the electron-spin concentration (c). This gives for the atom contribution to the second moment,

$$(M_2)_{\text{atom}} = 4.1 \times 10^{14}\ (\text{rad}\,\text{s}^{-1})^2 c^2\ .$$

Converting this (rough estimate) second moment contribution to a spread in frequency, δ, we obtain

$$\delta = (2 \times 10^7\ \text{rad}\,\text{s}^{-1})c\ .$$

From the data, we must remove the contributions from the known DT and HT impurities in the T_2 and then subtract the contribution from the remaining oT$_2$. After these two corrections, our "excess" second moment, converted to an angular frequency, does appear to be linear in the atom density inferred from the ortho to para conversion experiments in T_2 (c_a) and the model we used, but the experimental result, $\delta=(0.8\times10^7\ \mathrm{rad\,s^{-1}})c_a$, gives a coefficient three time smaller than the estimated one. This could be reconciled if the *actual* atom concentration, c, is a factor of 3 smaller than that inferred from the $o\mathrm{T}_2$-$p\mathrm{T}_2$ conversion experiments.

D. The spin-lattice relaxation time

Since one of our original goals was to produce long T_1's suitable for dynamic polarization experiments, much of our analysis has focused on this problem. There are two *apparent* methods of producing such long T_1's in an isotopic mixture: (i) distill the sample until almost no $J=1$ molecules remain; and (ii) let the $J=1$ to $J=0$ conversion in the solid remove the $J=1$ impurities. The former technique, used by Hardy and Gaines, could be applied to DT but it would be very costly. Even if the distillation was successful, there might still be problems because of some unique features of the radioactive hydrogen isotopes. The latter technique, used by the Honig group, has been tried in this work but it still does not produce long T_1's.

The problem in producing long T_1's in the *radioactive* hydrogen isotopes based on Eq. (7) does not come from the rate of *o-p* conversion but from the fact that rapid recombination of atoms produced by the β decay *repopulates* the $J=1$ state leading to a dynamic equilibrium where, below 8 K, x_1 is much larger than the value predicted from the Boltzmann distribution applied to the rotational levels. This dynamic equilibrium value of x_1 appears to be about 1.5%, leading to a value of T_{11} of about 1 ms and hence a value of T_1 of order 100 ms. Unfortunately, the rapid recombination combined with an *o-p* rate that decreases below 10 K in the solid, seems to doom even the distillation approach unless a way is found to inhibit the recombination.

There is a less apparent way to increase T_1 that does work to a limited extent. The specific-heat factors appear in Eq. (7) because of cross relaxation. If nDT is aged at a given temperature until the $o\mathrm{T}_2$ concentration has reached its lowest value, the factor C_0/C_1 is approximately 12.5. If this sample is suddenly mixed with an equal amount of $n\mathrm{H}_2$ (because of the different nuclear spin there is additional cross relaxation and no change in the specific-heat ratio), where 75% of the molecules are in the $J=1$ state, the new effective $J=1$ concentration is 38% and T_{11} is driven to a value above 100 ms producing a T_1 in excess of 1 s.

One final method, as yet untried, for obtaining long T_1's in a 50-50 mixture of D and T molecules would be to start with equal amounts of $p\mathrm{D}_2$ and $n\mathrm{T}_2$ (an effective $J=1$ concentration of 87%) and cool the sample below the quadrupole-quadrupole ordering temperature (T_λ) where a dramatic increase in T_1 is observed in H_2 or D_2. For such a mixture, T_λ should be of order 3 K and a temperature of 2 K would probably be low enough to see a large increase in T_1. Working at high magnetic fields would also be advantageous as T_1 in H_2, according to Sullivan and Pound, increases significantly as the field increases.

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