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NUCLEAR MAGNETIC RESONANCE AND RELAXATION IN SOLID HYDROGEN

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Recently the molecular solids of hydrogen and deuterium have been the object of several experimental[1-4] and theoretical studies.[5-8] The moment of inertia of these molecules is sufficiently small that we may consider both the ortho and para molecules to occupy their lowest rotational state: $J=0$ for para-H_2 or ortho-D_2 and the threefold degenerate $J=1$ state for ortho-H_2 or para-D_2. For H_2 at normal pressure and ortho concentration a transition, possibly of first order, is observed at 1.6°K in which the crystal structure changes[9] and the entropy associated with the rotational degrees of freedom decreases.[1] In the present note we consider the interpretation of nmr data at temperatures between the transition and 4.2°K and reach the following conclusions. Firstly, the correlation time associated with molecular rotation is much shorter than previously estimated[5] from measurements of the spin-lattice relaxation time.[10] Secondly, such a rotational correlation time is to be expected from the intermolecular interactions of the molecular quadrupole moments as suggested by Nakamura.[6] Thirdly, from nmr linewidth data, we have deduced the magnitude of the crystal-field splittings for the $J=1$ rotational manifold to be 0.22 and 0.024 cm^{-1} for normal H_2 and D_2, respectively.

The secular part, $\mathcal{H}_N'$, of the nuclear spin Hamiltonian $\mathcal{H}_N$ of an isolated molecule is[11]

$$\mathcal{H}_N' = -(\mu/i)H_0(i_{1z}+i_{2z}) - hc\vec{J}(\vec{i}_1+\vec{i}_2) - (5hd_D/4i)[3\cos^2\theta-1][3i_{1z}i_{2z}-\vec{i}_1\cdot\vec{i}_2] + (5hd_Q/4)[3\cos^2\theta-1] \times[3i_{1z}^2+3i_{2z}^2-2i(i+1)], \quad (1)$$

where the parameters have the values given in Ref. 11, $\vec{i}_1$ and $\vec{i}_2$ are the two nuclear spins each of magnitude i, and θ is the angle between the molecular axis and the direction of the magnetic field. In Eq. (1) the terms in the Hamiltonian represent, respectively, the Zeeman energy, the energy of the nuclear spins in the magnetic field caused by the rotation of the molecule, the intramolecular dipolar interaction, and (for D_2 only) the interaction of the nuclear electric quadrupole moment with the intramolecular electric field gradient. The role of the nonsecular terms in $\mathcal{H}_N$ is discussed below. We assume a rigid lattice and, following Nakamura's suggestion,[6] consider nearest-neighbor molecules to interact mainly via a quadrupole-quadrupole interaction which is given in a convenient form by Van Kranendonk.[12] Thus the rotational Hamiltonian is

$$\mathcal{H}_{\mathrm{rot}} = \sum_i B_J J_i(J_i+1) + 4\pi\epsilon\left(\frac{280\pi}{9}\right)^{1/2} \sum_{i<j,\,mn} C(224;mn)Y_2^m \times(\Omega_i)Y_2^n(\Omega_j)Y_4^{m+n}(\Omega_{ij})^*, \quad (2)$$

where the first term due to the rotational kinetic energy predominates so that J_i is nearly a good quantum number. Here $\epsilon = e^2Q_e^2/5R^5 = 0.38\ \mathrm{cm}^{-1}$ (see Ref. 6), R is the intermolecular separation, $C(224;mn)$ a Clebsch-Gordan coefficient,[13] eQ_e the molecular quadrupole moment, and B_J the rotational constant. Also, the arguments Ω_i and Ω_{ij} of the spherical harmonics are the angular orientations of the axis of ith molecule and of $\vec{R}_i-\vec{R}_j$, respectively, relative to the magnetic field when $\vec{R}_i$ is the position of the ith molecule. Finally, we assume the usual intermolecular dipolar interactions.

As Abragam[14] shows, the nonsecular terms in $\mathcal{H}_N$ are responsible for a spin-lattice relaxation time T_1 which for H_2 is given as

$$1/4\pi^2T_1 = \tfrac{2}{3}c^2J_1^{\,1}(\omega_0) + \tfrac{3}{2}d_D^{\,2}[J_2^{\,1}(\omega_0)+4J_2^{\,2}(2\omega_0)], \quad (3)$$

where $J_L^M(\omega)$ is the spectral density of the correlation function $\langle Y_L^M(\Omega_i)_t Y_L^M(\Omega_i)^*\rangle$, where the subscript t indicates a Heisenberg operator evaluated at time t, and the brackets indicate a statistical average. Actually T_1 is position-dependent since $J_L^M(\omega_0)$ is a function of the local environment. We may define an average relaxation time, which is given by Eq. (3) providing we interpret $J_L^M(\omega_0)$ as its average value:

$$J_L^M(\omega_0)\equiv\frac{1}{4\pi}\sum_i\int d\Omega_H J_L^M(\omega_0,\vec{R}_i,\Omega_H)/(\sum_i 1), \quad (4)$$

where Ω_H denotes the magnetic field orientation. For a powdered sample it is necessary to average $J_L^M(\omega_0,\vec{R}_i,\Omega_H)$ over magnetic field orientations.

Some years ago Tomita,[5] using the data of Hatton and Rollin,[10] derived estimates of the correlation times τ_L^M of these rotational correlation functions assuming (i) $J_L^M(\omega)=2\tau_L^M \times[1+\omega^2(\tau_L^M)^2]^{-1}$, (ii) $\tau_L^M=\tau$ independent of L and M, and (iii) τ increases as the temperature decreases. This last assumption was necessary to distinguish between the two possible roots for τ in terms of T_1. Although the resulting values of τ ($\sim10^{-4}$ sec) agreed qualitatively with the theoretical estimates of Reif and Purcell,[15] they were surprisingly long in comparison to the times corresponding to the splitting of the $J=1$ manifold.

The apparent paradox in the above analysis has been removed by our measurements of T_1 between the transition temperature and 4°K. We find T_1 to be frequency-independent and to decrease with decreasing temperature. Both these observations imply the choice of the other, much smaller, root for τ.

Furthermore, such a short correlation time ($\tau\sim10^{-12}$ sec) is to be expected theoretically, using the model we have described. Since h/τ is much less than the rotational energies, we can evaluate all the spectral densities in Eq. (3) for $\omega=0$. For the purpose of estimating $J_L^M(0)$, we assu $J_L^M(\omega)$ to be Gaussian:

$$J_L^M(\omega)=\frac{h}{\sigma_L^M(2\pi)^{1/2}}\exp[-\tfrac{1}{2}(\hbar\omega/\sigma_L^M)^2]. \quad (5)$$

However, $(\sigma_L^M)^2$ can be calculated by the diagonal-sum method of Van Vleck[16] in analogy with his calculations of the nmr linewidths:

$$(\sigma_L^M)^2=\frac{\sum_i\int\langle[T_L^M(J_i),\mathcal{H}_{\rm rot}][\mathcal{H}_{\rm rot},T_L^{-M}(J_i)]\rangle d\Omega_H}{\sum_i\int\langle T_L^M(J_i)T_L^{-M}(J_i)\rangle d\Omega_H}, \quad (6)$$

where $T_L^M(J_i)$ is the irreducible tensor operator which has the same matrix elements as $Y_L^M(\Omega_i)$ within the $J=1$ manifold.[14] We evaluate Eq. (6) as a high-temperature expansion in the parameter ϵ/kT so that using Eqs. (3) and (5)

$$T_1=A(1-B/T) \quad (7)$$

as is found experimentally (see Fig. 1). We have calculated A by setting the Boltzmann factor implicit in Eq. (6) equal to unity and have thus determined the proportionality constants ξ_L^M where $\sigma_L^M=\xi_L^M(1/\epsilon)$. In Table I we compare the theoretical and experimental values of A. The qualitative agreement obtained seems to indicate that the Gaussian approximation is a reasonable one.

From the Hamiltonian of Eq. (2), one also obtains terms which are off-diagonal in J, whose

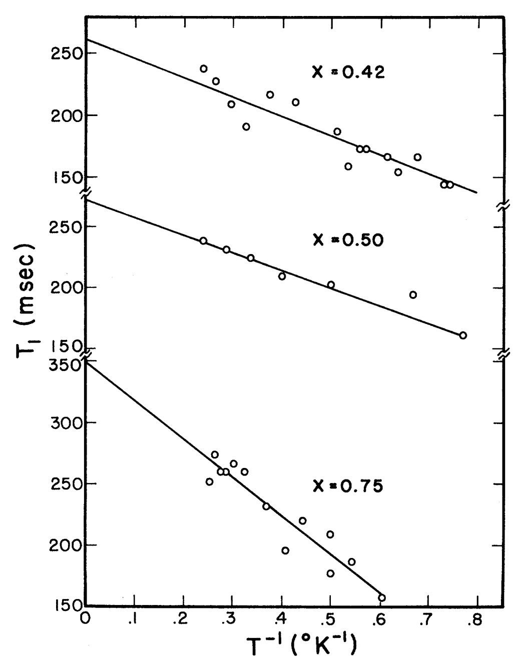

FIG. 1. Spin-lattice relaxation times as a function of inverse temperature for three ortho-hydrogen concentrations. The results at 4.2°K agree with those of J. Gaines and W. Hardy, private communication.

Table I. Some experimental and theoretical values of several parameters.

$J=1$ concentration, x	$A_{\rm exptl}$ (sec)	$A_{\rm calc}$ (sec)	$B_{\rm exptl}$ (°K)	$(\langle E^2\rangle_{\rm av})^{1/2}$, exptl (cm)
		H_2		
0.42 ± 0.03	0.26 ± 0.03	0.315	0.6 ± 0.1	
0.50 ± 0.03	0.27 ± 0.03	0.340	0.5 ± 0.1	0.18 ± 0.01
0.75 ± 0.03	0.35 ± 0.03	0.415	0.9 ± 0.1	0.22 ± 0.01
		D_2		
0.33				0.024 ± 0.002

effect in part is equivalent to a crystal-field Hamiltonian of the form

$$\mathcal{H}_c=\tfrac{1}{2}\sum_{\mu,\nu=x,y,z}A_{\mu\nu}(J_\mu J_\nu+J_\nu J_\mu-\tfrac{4}{3}\delta_{\mu\nu}). \tag{8}$$

The Hamiltonian (8) may also contain contributions from interactions not considered here, e.g., van der Waals forces,[6] so-called valence forces,[6] or the interactions between rotations and lattice vibrations.[8] The coefficients $A_{\mu\nu}$ are random variables corresponding to differing environments in a random mixture. Although these terms do not appreciably influence T_1, they are responsible for the temperature dependence of the nmr linewidth. Since the correlation times τ_L^M are much less than ω_0^{-1}, we can evaluate the second moment of the nmr absorption line, M_2, by replacing $[3\cos^2\theta-1]$ in Eq. (1) by its average over the rotational motion. Then we find

$$M_2^{\rm H}(T)=M_{2\,\rm inter}^{\rm H}+\left(\frac{15d_D^{\rm H}}{4}\right)^2[\langle1-3\cos^2\theta\rangle_{J=1}]^2, \tag{9a}$$

$$M_2^{\rm D}(T)=M_{2\,\rm inter}^{\rm D}+\left(\frac{15}{4}\right)^2\frac{1}{5-3x}\times\{2x[\langle1-3\cos^2\theta\rangle_{J=1}]^2(d_D^{\rm D}+d_Q^{\rm D})^2+(1-x)[\langle1-3\cos^2\theta\rangle_{J=0}]^2\times[5(d_Q^{\rm D})^2-2d_Q^{\rm D}d_D^{\rm D}+3(d_D^{\rm D})^2]\}, \tag{9b}$$

where x is the concentration of molecules with odd J, $\langle\,\rangle_{J=0}$ and $\langle\,\rangle_{J=1}$ indicate averages over the $J=0$ and $J=1$ manifolds, respectively, $M_{2\,\rm inter}$ is the usual contribution M_2 from intermolecular dipolar interactions, and the superscripts H and D refer to H_2 and D_2, respectively. We take

$$\langle3\cos^2\theta-1\rangle_{J=1}=-\tfrac{2}{5}\,{\rm Tr}[\exp(-\beta\mathcal{H}_c)](3J_z^2-2)/{\rm Tr}[\exp(-\beta\mathcal{H}_c)], \tag{10a}$$

$$\langle3\cos^2\theta-1\rangle_{J=0}=0, \tag{10b}$$

so that in the high-temperature limit

$$M_2^{\rm H}(T)=M_{2\,\rm inter}^{\rm H}+\frac{9}{10}\frac{\langle E^2\rangle_{\rm av}}{(kT)^2}, \tag{11a}$$

$$M_2^{\rm D}(T)=M_{2\,\rm inter}^{\rm D}+\frac{9x}{25-15x}\frac{\langle E^2\rangle_{\rm av}}{(kT)^2}\times(d_D^{\rm D}+d_Q^{\rm D})^2, \tag{11b}$$

where $\langle E^2\rangle_{\rm av}$, the mean-square splitting of the $J=1$ rotational states, is defined as[17]

$$\langle E^2\rangle_{\rm av}=\{{\rm Tr}\,\mathcal{H}_c^{\,2}/{\rm Tr}1\}_{\rm Av}, \tag{12}$$

where the subscript Av denotes an average over the random variables $A_{\mu\nu}$. Using the experimental data of Rorer and Meyer[18] for $M_2(T)$, we obtain the values of $(\langle E^2\rangle_{\rm av})^{1/2}$ given in Table I. These values of $(\langle E^2\rangle_{\rm av})^{1/2}$ are of the same order of magnitude as that estimated by Van Kranendonk and Sears[8] for low ortho concentration. We are currently studying the dependence of $(\langle E^2\rangle_{\rm av})^{1/2}$ on ortho concentration in order to make such a comparison more meaningful. Experimentally the temperature-independent contribution to $M_2^{\rm D}$ is found to be much larger than the calculated value of $M_{2\,\rm inter}^{\rm D}$. This can probably be explained by the inadequacy of the approximation (10b), since off-diagonal terms in $\mathcal{H}_{\rm rot}$ can deform the $J=0$ rotational state.

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[17]Note that if $\mathcal{H}_c = \Delta(J_z^2 - \frac{2}{3})$ then $E^2 = (2/9)\Delta^2$.

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NUCLEAR POLARIZATION OF NEGATIVE DEUTERIUM IONS PRODUCED BY CHARGE EXCHANGE*

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In 1950 Lamb and Retherford[1] pointed out that hydrogen atoms in the $2s$ (metastable) state could be polarized by passage through a magnetic field of 575 G crossed by a weak electric field. Since then there has been interest[2] in using this technique to produce a beam of polarized nuclei for injection into accelerators, and experiments along this line were carried out by Madansky and Owen.[3] However, in these experiments the beam of ions arising from metastable atoms was masked by a larger beam of ions arising from ground-state atoms.

Recently Donnally and Sawyer[4] have carried out an experiment in which it appears that this difficulty can be overcome. They produced a metastable beam by charge exchange in cesium vapor and converted it to negative ions in an argon gas cell. These negative ions are of particular value for injection into tandem Van de Graaff accelerators. They found that at a velocity of 3.1×10^7 cm/sec (500 eV for protons or 1000 eV for deuterons), the negative-ion current emerging from the argon gas cell decreased by a large factor ($\gg 10$) when the metastable atoms incident on the argon were quenched to the ground state by application of an electric field. However, no attempt was made in their experiment to measure the nuclear polarization obtainable.

In this Letter we wish to report a measurement of the tensor polarization of deuterons in D^- ions made by this method.

A schematic diagram of the apparatus is shown in Fig. 1. The 1-keV β ($m_J = -\frac{1}{2}$) metastable atoms were quenched to the ground state in the polarizing region P. The neutral beam leaving the polarizing region consisted of α ($m_J = +\frac{1}{2}$) metastables, together with ground-state atoms arising partially from charge exchange in the cesium and partially from quenching of the β's. The electronic polarization was transferred to the deuterons in a transition region T. The purpose of the transition region was to minimize nonadiabatic transitions among magnetic substates of the metastable atoms.

The neutral beam from the transition region then passed through the argon cell. Some of the metastables made charge-changing collisions with argon atoms to produce D^- ions in the electronic ground, ${}^1S_0$, state (any other states excited would presumably be short lived and decay before being detected). The tensor polarization P_{33} of the deuterons made by ionization of an α metastable was computed to equal -0.327.