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Effects of higher-J states on nuclear-spin relaxation times for H_2 in solid nonmagnetic hosts

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We calculate the effects of $J>1$ states on nuclear-spin relaxation times for isolated H_2 or D_2 molecules located at sites with various crystal fields in solid nonmagnetic hosts. This extends similar earlier work to temperatures higher than about 100 K. In this warm regime we find that the relaxation times depend quantitatively and even qualitatively on the environment of the molecules in or on a host lattice.

I. INTRODUCTION

In an earlier paper[1] we calculated nuclear-spin relaxation times T_1 and T_2 for isolated orthohydrogen ($J=1$) [o-H_2] molecules in solid nonmagnetic hosts. This work showed that the relaxation times depend crucially on the magnitude and symmetry of the crystal fields experienced by the H_2 molecules and explained several puzzling anomalies.[2–5] However, since the calculation was restricted to $J=1$, it is valid only for temperatures less than about 100 K because the occupation of higher J states significantly alters the relaxation times at higher temperatures.

Recently NMR measurements[6–9] have been made on amorphous Si:H that relate to the relaxation of H_2 at temperatures well above 100 K. Furthermore, there is considerable interest about where the H_2 in amorphous Si:H resides, and a knowledge of the crystal-field environment of the H_2 should be useful in determining this. Thus in this paper we extend our previous calculation to all J states (and thus to all temperatures) for o-H_2, o-D_2, and p-D_2 (paradeuterium). As will be seen, different crystal-field symmetries and magnitudes lead to quantitative and even qualitative differences in relaxation times.

In the rest of this section we briefly explain our model and basic approximations. Section II contains the details of the calculations for molecules in a specific state J. The results, including averaging over J, are displayed and discussed in Sec. III.

As in Ref. 1, we refer to the molecular angular momentum as molecular spin of magnitude J in order to emphasize the fact that the molecule acts like a spin in every way. Similarly, the two protons (or deuterons) will be referred to as a single nuclear spin of magnitude I. For o-H_2 or p-D_2 the Hamiltonian H_{int} connecting the nuclear and molecular spin systems of a single molecule can be written as[1,10]

$$H_{\text{int}}(J)=\hbar\omega_1\sum_{m=-1}^{+1}B_{1m}A_{1m}^{\dagger}+\hbar\omega_2\sum_{m=-2}^{+2}B_{2m}A_{2m}^{\dagger}\ , \tag{1}$$

where the A_{lm} and B_{lm} are the irreducible multipole operators for the molecular spin J and the nuclear spin I, respectively. The coupling constants ω_1 and ω_2 depend upon the molecular state J and are conveniently written as

$$\omega_1=[I(I+1)J(J+1)/9]^{1/2}\omega'\ , \tag{2a}$$

$$\omega_2=[I(I+1)J(J+1)/5(2J-1)(2J+3)]^{1/2}\omega''\ , \tag{2b}$$

where ω' and ω'' are independent of J. For H_2, ω' and ω'' are often denoted by ω_c and ω_d, respectively. For o-D_2 the Hamiltonian is very similar and will be discussed in Sec. II along with formulas for ω' and ω'' in more familiar terms. Most of the language and approximations used in Ref. 1 will be used in the present paper. This includes the consideration of the dynamics of the molecular spin system as molecular spin modes described by the multipole operators A_{lm}.

For our purposes the H_2 and D_2 molecules can be characterized by two sets of properties that reflect their environment. The static environment of the molecules is characterized by a set of electric field gradients V_{ij} at the molecular sites. Although our formalism is valid for electric field gradients of any magnitude, detailed calculations will be limited to cases where each V_{ij} is either very large or very small. Very large field gradients will push the resonant frequencies of some of the spin-normal modes so high that they will cease to be effective in relaxing the nuclear spins.

Dynamically the molecules are characterized by a set of molecular spin-phonon decay rates $\Gamma_l(J)$ that depend on the state J of the molecule and the multipole operator or mode l that is being considered. In practice only the $l=1$ and 2 modes will be needed, and the ratio between the relevant molecular relaxation rates[11,12] is

$$\Gamma_2(J)/\Gamma_1(J)=3(4J^2+4J-7)/(4J^2+4J-3)\ . \tag{3}$$

It is assumed that these relaxation rates are much greater than ω_1 or ω_2 so that the effects of the nuclear spins on the molecular spins can be ignored.

II. CALCULATIONS

A. Cubic symmetry

Since we have assumed that the nuclear spins have a negligible effect on the molecular spins, the effects of H_{int} on the nuclear spins can easily be obtained. The relaxation time of the z component of the nuclear magnetization when the molecule is in the state J is given by[13]

$$[T_1(J)]^{-1}=[J(J+1)/3](\omega')^2\sum_{m=-1}^{+1}m^2F_{1m}(m\omega_0)+[3J(J+1)/5(2J-1)(2J+3)](\omega'')^2\times\sum_{m=-2}^{+2}F_{2m}(m\omega_0)\,, \tag{4}$$

where $\omega_0=\gamma_I H_0$, γ_I is the gyromagnetic ratio of the nuclear spins, and H_0 is the magnitude of an external magnetic field $\vec{H}_0$ that defines the z axis. $F_{lm}(\omega)$ is the normalized spectral function for the molecular spin operator A_{lm} as defined in Ref. 1 and can be written as

$$F_{lm}(\omega)=\Gamma_l/[(\omega-\omega_{lm})^2+\Gamma_l^2]\,. \tag{5}$$

In this equation ω_{lm} is the frequency of the (l,m) normal mode described by A_{lm} and Γ_l is its decay rate.

For molecules in sites of cubic symmetry the A_{lm} represent the normal modes of the system[14] and $\omega_{lm}=m\omega_J$, where $\omega_J=\gamma_m H_0$ and γ_m is the gyromagnetic ratio of the molecular spin. Since we are concerned with reasonably high temperatures in this paper, we shall assume that Γ_l is much greater than ω_J and ω_0. In this case Eq. (4) can be written as

$$[T_1(J)]^{-1}=[2J(J+1)(\omega')^2/3\Gamma_1(J)]\times[1+3r/(3J^2+4J-7)]\,,\quad r=(\omega'/\omega'')^2\,. \tag{6}$$

B. Axial symmetry H_2

We next consider a crystal site with an axial electric field gradient V_{zz} that defines a new z axis. By using the transformation given in Ref. 1, T_1 can be written in terms of the F_{lm} in the new coordinate system and this expression includes F_{lm} with $l=1$, $m=0,\pm1$, and $l=2$, $m=0,\pm1,\pm2$. If we assume that the frequency that characterizes this field gradient is much greater than $\Gamma_l(J)$, then a number of normal modes of the system will have their frequencies pushed so high that the modes will be ineffective in relaxing the nuclear spin. That is, the resulting spectral functions will have virtually no weight at nuclear resonance frequencies. Thus we wish to identify those modes whose frequencies do and do not scale as V_{zz}.

With a strong axial field the mode (l,m) is coupled to the modes $(l\pm1,m)$ so that m remains a good quantum number but l does not.[14] However, the modes with $m=0$ do not couple to any other modes. At this point it is useful to introduce the projection operator $B(n,k)$ which changes a spin in the state k to the state n. The frequency associated with $B(n,k)$ is $\omega(n,k)$, where

$$\omega(n,k)=(E_n-E_k)/\hbar \tag{7}$$

and A_{lm} is proportional to a sum over n of $B(n,n-m)$. The change in the energy level E_n arising from V_{zz} is proportional to $V_{zz}n^2$. Since all $\omega(n,n\pm1)$ are proportional to V_{zz}, none of the F_{lm} with $m=\pm1$ in the new coordinate system contribute to T_1. The only $\omega(n,n\pm2)$ that are not proportional to V_{zz} are $\omega(\pm1,\mp1)$. Thus we need only compute the projection of $B(\pm1,\mp1)$ on $A_{2,\pm2}$ in order to complete the calculation. For molecular spin J the projection $R(J)$ is easily computed to be

$$R(J)=\sum_m\langle m[B(\pm1,\mp1)A^\dagger_{2\pm2}\,|\,m\rangle]/(2I+1)=[15J(J+1)/2(2J-1)(2J+1)(2J+3)]^{1/2}\,. \tag{8}$$

Then, after averaging over orientations as in Ref. 1, we obtain

$$[T_1(J)]^{-1}=[2J(J+1)(\omega')^2/9\Gamma_1(J)]\{1+[9r/5(4J^2+4J-7)][1+15J(J+1)/(2J-1)(2J+1)(2J+3)]\}\,. \tag{9}$$

C. No symmetry

Finally we consider crystal sites with large electric field gradients $V_{xx}-V_{yy}$ and/or V_{xy} in addition to V_{zz}. The multipole operators with $m=\pm1$ have already been eliminated and we ignore them here. As in Ref. 1, an additional effective Hamiltonian H' acts on the system,

$$H'=\hbar(\omega_Q I_+^2+\omega_Q^* I_-^2)\,, \tag{10}$$

where ω_Q is a complex frequency whose real part is proportional to $V_{xx}-V_{yy}$ and whose imaginary part is proportional to V_{xy}.

In addition to the operators $B(n,k)$ introduced in Sec. II C, we introduce the projection operator $N(k)$, where

$$N(k)\,|\,n\rangle=\delta_{n,k}\,|\,n\rangle\,. \tag{11}$$

From the discussion of the last section it is clear that the modes whose frequencies are not proportional to V_{zz} must be constructed from the $B(m,-m)$ and $N(k)$. That is, all of the $B(m,k)$ with $k\neq-m$ have frequencies proportional to V_{zz} and can be ignored. Within this restricted set of operators, the only ones whose commutators with H' are nonzero are $B(\pm1,\mp1)$ and $N(\pm1)$, and those commutators are

$$\begin{aligned}&[B(1,-1),H']=\omega_Q^*J(J+1)[N(1)-N(-1)]\,,\\&[B(-1,1),H'']=\omega_QJ(J+1)[N(-1)-N(1)]\,,\\&[N(\pm1),H']=J(J+1)\{\pm\omega_QB(1,-1)\mp\omega_Q^*B(-1,1)\}\,.\end{aligned} \tag{12}$$

From the above equations one can find the modes whose frequencies do not scale as V_{zz} or ω_Q and then find the projections of these modes onto the relevant A_{lm}. When this is done and the appropriate angular average is performed, one obtains

$$[T_1(J)]^{-1}=[2J(J+1)/5\Gamma_1(J)(4J^2+4J-7)](\omega'')^2[1+15J(J+1)/2(2J-1)(2J+1)(2J+3)]\,. \tag{13}$$

D. Coupling constants

The first term in Eq. (1) describes the spin-rotational magnetic interaction which, using Eq. (2a), can be written as

$$H_{\rm sr}=\omega'\vec{\rm I}\cdot\vec{\rm J}\ . \tag{14}$$

As mentioned earlier, ω' is often denoted as ω_c. The second term in Eq. (1) is due to the dipolar interaction in H_2 and due to a combination of the dipolar interaction and the quadrupolar interaction[10] in D_2. Using Ref. 10 one can easily verify that for o-H_2, p-D_2, and o-$(I=2)$ D_2, respectively,

$$\omega''=\omega_m/2\ , \tag{15a}$$

$$\omega''=\omega_m+eqQ/4\ , \tag{15b}$$

$$\omega''=(7/15)^{1/2}(\omega_m-eqQ/4)\ , \tag{15c}$$

where

$$\omega_m=\gamma^2\hbar/R^3\ , \tag{16}$$

and q and Q refer to the nuclear quadrupolar interaction of D_2.

In addition, there is a term in the magnetic dipolar Hamiltonian for o-D_2 that connects the $I=0$ and 2 subspaces.[15] It is rather easily seen that this term makes a small additional correction to T_1 to account for the loss of magnetization by transfer from the $I=2$ to $I=0$ state. This term can be taken into account by using an effective ω_e'' given by

$$\omega_e''=[(8/15)\omega_m^2+(\omega'')^2]^{1/2}\ . \tag{17}$$

In practice, this correction term is quite small.

III. RESULTS

In the preceding section we derived results for the relaxation time $T_1(J)$ for o-H_2, p-D_2, or o-D_2 in a state of given J under crystal fields of various symmetries. These results are valid in the high-temperature or low-frequency regime where the molecular relaxation rate $\Gamma_1(J)$ is much greater than ω_0. The crystal fields considered in detail are three limiting cases. The results for cubic symmetry, where the frequencies associated with all electric field gradients are much less than $\Gamma_1(J)$, are given by Eq. (6). The results for axial symmetry, where there is a very large axial field gradient which defines the z direction, are given by Eq. (9). The results for the case of no symmetry, where there are large additional electric field gradients in the x-y plane, are given by Eq. (13).

At temperatures high enough so that more than the lowest J state can be appreciably occupied, we average the relaxation rate over different J states with the appropriate weighting factor for each state,

$$\begin{aligned} T_1^{-1}&=\sum_J P(J)[T_1(J)]^{-1} \\ P(J)&=\frac{(2J+1)(\exp[-J(J+1)\Theta/T]}{\sum_J(2J+1)\exp[-J(J+1)\Theta/T]}\ . \end{aligned} \tag{18}$$

In these equations the summation is over odd J for o-H_2 and p-D_2 and over even J for o-D_2. This averaging is appropriate[16,17] if the transition rate between states of different J is much greater than T_1^{-1} but much less than the relevant $\Gamma_1(J)$. We note that if the transition rate between states of different J is less than T_1^{-1}, the molecules in different J states will have different T_1's and a very nonexponential signal will be observed.

For the purposes of illustration we shall now assume that the molecular spin-phonon relaxation mechanism is the standard one where the quadrupole moment of the molecule interacts with the time-dependent electric field gradients that are set up by phonons. The Hamiltonian can be written as[18]

$$\begin{aligned} H&=\sum_{i,j}Q_{ij}V_{ij}\ , \\ Q_{ij}&=[eQ/12J(2J-1)]\times[3\{J_i,J_j\}-2\delta_{ij}I(J+1)]\ , \end{aligned} \tag{19}$$

where V_{ij} are the electric field gradients. From this equation one can easily determine that the J dependence of $\Gamma_1(J)$ will be $(2J+3)/J^2(2I-1)$. Thus we assume a $\Gamma_1(J)$ of

$$\Gamma_1(J)=AT^2(2J+3)/J^2(2J-1)\ , \tag{20}$$

where T^2 is the expected high-temperature behavior,[8] and A is a constant.

From Eqs. (18) and (20), along with the previous equation for $T_1(J)$, one can get the asymptotical forms for T_1 in the limit $T\gg\Theta$. They are

$$T_1^{-1}=(4/3A)(\omega'/\Theta)^2[1-(9\pi^{1/2}/8)(\Theta/T)^{1/2}+(\Theta/T)(2.25+0.375r)\cdots] \tag{21a}$$

for cubic symmetry,

$$T_1^{-1}=(4/9A)(\omega'/\Theta)^2[1-9\pi^{1/2}/8)(\Theta/T)^{1/2}+(\Theta/T)(2.25+0.45r)\cdots] \tag{21b}$$

for axial symmetry, and

$$T_1^{-1}=[(\omega'')^2/10A\Theta T][1-(33\pi^{1/2}/32)(\Theta/T)^{1/2}+(23\Theta/16T)+\cdots] \tag{21c}$$

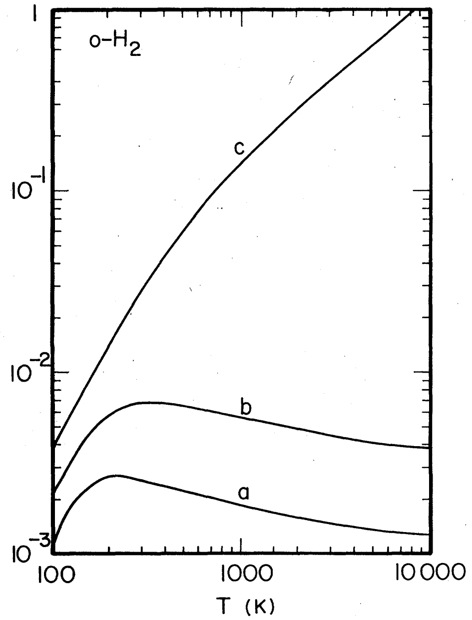

FIG. 1. T_1 versus T for o-H_2 for the cases of (a) cubic symmetry, (b) axial symmetry, and (c) no symmetry. Values of the parameters used are discussed in the text.

for no symmetry.

In Figs. 1—3 we have plotted T_1 versus temperature for o-H_2, p-D_2, and o-D_2, respectively. In these figures we have used $\Theta=86$ K, $\omega'=7.15\times10^5$ sec^{-1}, $\omega_m=1.81\times10^6$ sec^{-1} for H_2 and $\Theta=43$ K, $\omega'=5.52\times10^4$ sec^{-1}, $\omega_m=4.28\times10^4$ sec^{-1}, $eqQ=1.41\times10^6$ sec^{-1} for D_2. A typical value of $A=10^5$ sec^{-1} K^{-2} was used for all three.

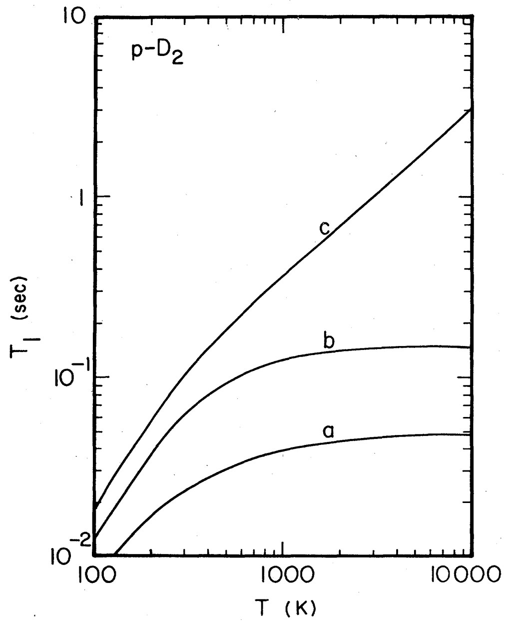

FIG. 2. T_1 versus T for p-D_2 for the cases of (a) cubic symmetry, (b) axial symmetry, and (c) no symmetry. Values of the parameters used are discussed in the text.

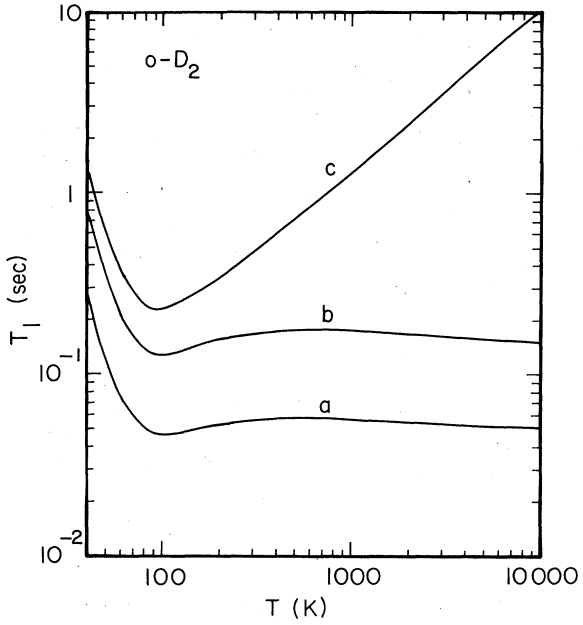

FIG. 3. T_1 versus T for o-D_2 for the cases of (a) cubic symmetry, (b) axial symmetry, and (c) no symmetry. Values of the parameters used are discussed in the text.

From Eqs. (21) or from the figures one can see that the high-temperature behavior in the case of no symmetry is different than the cases of cubic or axial symmetry. The reason for this is that the spin-rotation (IJ) term in the Hamiltonian usually dominates the relaxation rate at high temperatures because its J dependence is stronger than the dipolar-quadrupolar term. However, in the case of no symmetry, the spin-rotation relaxation cannot come into play because of the lack of symmetry. A word of caution should be added to this point. The various limiting cases considered here were for the quadrupole splitting to be large or small with respect to Γ_1. However, because Γ_1 is temperature dependent, this condition can depend on temperature even if everything else is temperature independent. Thus, as the temperature increases, it is possible to go from no symmetry to axial symmetry to cubic symmetry.

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