Application of the Statistical Model to Nuclear Magnetic Relaxation in Solid Hydrogen

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The nuclear-spin relaxation of orthohydrogen molecules in solid H_2 is due to the intramolecular dipole-dipole interaction modulated by the quadrupole-quadrupole interaction between $J=1$ molecules. Using the statistical method developed by Margenau and Anderson, we calculate the angular momentum correlation functions. In contrast to Moriya and Motizuki's result, where the Gaussian mode is used and relaxation times are found to be proportional to $c^{1/2}$ (c is the concentration of orthohydrogen molecules in the solid), we obtain relaxation times proportional to $c^{5/3}$. Our result checks with the experimental data of Hardy and Gaines for $c<0.3$. In order to fit the experimental data for the entire range of concentration, a crystal field on the orthohydrogen molecules in the range 0.01–0.03°K must be assumed.

I. INTRODUCTION

THE properties of solid mixtures of orthohydrogen in parahydrogen molecules have been studied extensively after the first experiment was performed on the specific heat by Hill and Ricketson.[1] Nakamura[2] studied the possible molecular interactions and came to the conclusion that the interaction of two orthohydrogen molecules (with nuclear spin $I=1$ and orbital spin $J=1$) is dominated by the quadrupole-quadrupole interaction (QQ). All the other interactions, van der Waals and dispersive forces, contribute less than 10%. This conclusion is also supported by measuring the λ temperature,[3] which turns out to be proportional to (volume)$^{-n}$ where $n=\frac{5}{3}$.

The unsettled question is the interaction between ortho-H_2 (o-H_2) and para-H_2 (p-H_2) when averaged over the p-H_2 state $J=0$. The interaction is about zero, if the structure of the crystal of solid hydrogen is perfectly hcp. The large zero-point motion of H_2 makes all H_2 nonlocalized and thus produces the crystal field on o-H_2. This problem has been studied by Van Kranendonk and Sears.[4] There exists, however, a large discrepancy in the magnitude of the interaction required to fit the various experimental data on the specific heat[5] and on infrared absorption.[4]

Because no λ transition is observed for concentration of o-H_2 less than 33%, the thermodynamical properties of o-H_2 of low concentration seem not to be interesting. However, o-H_2 of various concentrations (especially for concentrations less than 10%) in nuclear-magnetic-resonance experiments can be very helpful in the determination of the crystal field on o-H_2, as will be shown later. Furthermore, we may consider the o-H_2 as magnetic impurities and compare our system with the usual paramagnetic-resonance situation, where the dipole-dipole interaction of two paramagnetic impurities is always much less than the Zeeman energy. Our system has the interesting feature that by changing the concentration of o-H_2 we may make the magnitude of the QQ interaction comparable to the Zeeman energy and the crystal field of o-H_2 in a p-H_2 lattice.

Moriya and Motizuki[6] have calculated the relaxation times for high o-H_2 concentration ($c>40\%$) in the high-temperature region. Their results are in good agreement with experimental data at high o-H_2 concentration.[7,8] In view of very recent experimental work by Hardy and Gaines,[8] their work has to be modified and extended at two points. First, the spin-lattice relaxation time, predicted on the basis of the Gaussian model where the correlation function is approximated by the Gaussian function, is proportional to $c^{1/2}$, which is not correct for $c<40\%$. It is well known that the Gaussian model is not correct for low concentration of impurities although the criteria for the validity of this approximation are open questions. The second point is that the Moriya and Motizuki calculation is limited to high concentrations where the QQ interaction is much greater than the interaction between o-H_2 and p-H_2 and the Zeeman energy. Harris and Hunt[9] have investigated the same problem in Ref. 6, but have taken the temperature dependence into account. A straightforward extension of either calculation to low concentration would lead to absurd results.

The mechanism of nuclear spin relaxation can be described as follows: The intramolecular dipole-dipole (DD) interaction causes the relaxation of the spins of the protons in o-H_2 molecules. The coupling of nuclear spin with orbital angular momentum, which is a rapidly varying function of time due to the QQ interaction, gives rise to the modulation of the DD interaction. Since the QQ interaction is much larger than the DD

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[2] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **14**, 135 (1955).
[3] G. Ahlers and W. H. Orrtung, Phys. Rev. **133**, A1642 (1964); G. Grenier and D. White, J. Chem. Phys. **40**, 3015 (1964).
[4] J. Van Kranendonk and V. J. Sears, Can. J. Phys. **44**, 313 (1966).
[5] W. H. Orrtung, J. Chem. Phys. **36**, 625 (1962).
[6] T. Moriya and K. Motizuki, Progr. Theoret. Phys. (Kyoto) **18**, 183 (1957).
[7] M. Bloom, Physica **23**, 767 (1957).
[8] W. Hardy and J. R. Gaines, invited paper by J. R. Gaines, Bull. Am. Phys. Soc. **12**, 1047 (1967); and (private communication).
[9] A. B. Harris and E. Hunt, Phys. Rev. Letters **16**, 845 (1966).

interaction, our main problem is to calculate the angular momentum correlation functions.

The purpose of the paper is to calculate the longitudinal and transverse relaxation times T_1 and T_2 for $0.4>c>10^{-3}$ by using the statistical theory[10,11] which has been developed by Margenau and Anderson and successfully applied to the paramagnetic resonance.[10]

We develop a formalism for this problem in Sec. II. T_1 and T_2 are expressed in terms of the correlation functions of the orbital angular momentum. Our equations differ from Ref. 6 by taking the crystal-field and magnetic field dependence into account. In Sec. III we calculate this correlation function by using the statistical theory. The computation is straightforward but tedious. In contrast to the usual application of the statistical theory, the secular part of the QQ interaction is as important as the nonsecular part, and this is the major difference between our work and many other applications of the theory. Finally, we compare our calculations with experimental data and find good agreement, if proper choice of the numical value of the crystal field is made. In the temperature range $T\approx 4°$K, where the experiments are carried out,[8] the temperature dependence can be ignored in the calculation. We discuss this problem in the Appendix.

II. RELAXATION OF SOLID ORTHOHYDROGEN MOLECULE

The Hamiltonian of a hydrogen molecule in an external magnetic field H_0 is[12,13]

$$H=H_1+H_2,$$

where

$$H_1=-aI_z-bJ_z,$$

$$H_2=-dJ^2I^2-(c'-3d/2)\mathbf{I}\cdot\mathbf{J}+3d(\mathbf{I}\cdot\mathbf{J})^2, \quad (1)$$

Here H_1 is the magnetic field energy; $I_z=I_z^1+I_z^2$ is the total nuclear spin of two protons in a hydrogen molecule; J is the rotational angular momentum; c' and d, respectively, are the magnetic coupling between $\mathbf{I}$ and $\mathbf{J}$ and the magnetic dipole-dipole interaction of two protons in a hydrogen molecule. The numerical values of a, b, c', and d in the external magnetic field H_0 are given as follows[6]:

$$a=4.3H_0\times 2\pi\times 10^3/\text{sec},$$

$$b=0.67H_0\times 2\pi\times 10^3/\text{sec},$$

$$c'=113.8\times 2\pi\times 10^3/\text{sec},$$

$$d=57.68\times 2\pi\times 10^3/\text{sec}.$$

The Hamiltonian of the intermolecular interaction can be written as H_J;

$$H_J=\sum_i H_i+\sum_{ik} H_{ik}. \quad (2)$$

Here H_i is the crystal field experienced by the ith o-H_2 molecule and is written as

$$H_i=\tfrac{1}{3}A[3J_z^2(i)-2]. \quad (3)$$

A is the separation of energy levels of $J_z=0$ and $J_z=\pm 1$.

Since H_i is obtained by summing over both para and ortho particles, in the nearest neighborhood of ith o-H_2,[2] it will be considered as a crystal field that each orthohydrogen particle experiences, independent of concentration of orthohydrogen. H_{ik} is the QQ interaction of two orthohydrogens given by[14]

$$H_{ik}=\tfrac{4}{5}\pi\epsilon\left(\frac{a}{|R_{ik}|}\right)^5\left(\frac{280\pi}{9}\right)^{1/2}\times\sum_{mn}C(224,m,n)\,Y_2^m(\Omega_i)\,Y_2^n(\Omega_k)\,Y_4^{m+n}(\Omega_{ik}).$$

Here $\epsilon=3.76\times 10^{-16}$ erg and a is the lattice distance. $C(223, mn)$ is the Clebsch-Gordan coefficient, and the angles Ω_i, Ω_j, and Ω_{ij} are the angular orientations of the axes of the ith and jth molecules and of $\mathbf{R}_i-\mathbf{R}_j(=\mathbf{R}_{ij})$, respectively, relative to the direction of the external magnetic field. We use the standard notation for spherical harmonics, Y_2^m and Y_4^{m+n}.

Among the interactions of two orthohydrogen molecules, we have neglected the dispersive force and the van der Waal force. The former is a short-range force and the latter is two orders smaller than H_{ik} and $\sim R_{ij}^{-6}$. Besides the relaxation mechanism which can be described by terms in Eq. (2), there is the intermolecular DD interaction, common to ortho-ortho and ortho-para pairs. The strength of this DD interaction is about $10^{-2}d$, which is modulated by diffusion processes. For the temperature range in which we are interested, this process can be neglected.

Using the identities between the angular momentum operator J and $Y_J^m(\Omega)$,[2,13] we obtain

$$H_{ik}=\epsilon\left(\frac{a}{|R_{ik}|}\right)^5\left(\frac{280\pi}{9}\right)^{1/2}\times\tfrac{3}{5}\sqrt{\tfrac{0}{}}\sum_{mm'}C(224,m-m')\,Y_4^{m-m'}(\Omega_{ik})\,a^m(\Omega_i)\,a^{-m'}(\Omega_k). \quad (4)$$

Here

$$a^0(\Omega_i)=(\sqrt{\tfrac{2}{3}})[3J_z^2(i)-2],$$

$$a^{\pm 1}(\Omega_i)=J_\pm(i)\,J_z(i)+J_z(i)\,J_\pm(i),$$

$$a^{\pm 2}(\Omega_i)=J_\pm^2(i). \quad (5)$$

We use the interaction representation to eliminate H_1; thus the operators I^+, I^-, J^+, and J^- are changed to $I^+e^{ia t}$, $I^{-ia t}$, J^+e^{ibt}, and J^-e^{-ibt}. The subsequent changes

[10] W. J. C. Grant and M. W. Strandburg, Phys. Rev. **135**, A717 (1964); the statistical theory is used to study the paramagnetic-magnetic resonance in this reference.

[11] A simple explanation of the statistical theory of line shape of nuclear magnetic resonance can be found in Ref. 12, p. 126.

[12] A. Abragam, *The Principle of Nuclear Magnetic Resonance* (Clarendon Press, Oxford, England, 1960).

[13] We use units such that $\hbar=K_B=1$.

[14] J. Van Kranendonk, Physica **25**, 1080 (1959).

in H_1 are obvious. T_1 and T_2 are given by[12]

$$T_1^{-1}(i)=\frac{1}{2}\int_{-\infty}^{\infty}dt \times\langle[I_z(i,t),H_2(t)]_-[I_z(i,0),H_2(0)]_-\rangle/\langle I_z^2(i,0)\rangle, \quad (6)$$

$$T_2^{-1}(i)=\frac{1}{2}\int_{-\infty}^{\infty}dt \times\langle[I_x(i,t),H_2(t)]_-[I_x(i,0),H_2(0)]_-\rangle/\langle I_x^2(i,0)\rangle. \quad (7)$$

Here $\langle\ \rangle$ is the thermodynamical ensemble average.

The longitudinal and transverse components of the magnitization are given by

$$M_z(t)=u\sum_i I_z(i,t)+u_L\sum_i J_z(i,t), \quad (8)$$

$$M_x(t)=u\sum_i I_x(i,t)+u_L\sum_i J_x(i,t). \quad (9)$$

Because the orbital magnetic moment is much smaller then nuclear-magnetic moment ($u_L/u\ll 1$), the orbital Zeeman energy is neglected in Eqs. (6) and (7).

Equations (6) and (7) are written to emphasize that our calculated $T_1(i)$ and $T_2(i)$ should be characterized by the position of each particle. The calculated $T(i)$ is to be compared with the experimental value after the average is taken over all the N particles

$$\langle T_1^{-1}\rangle=N^{-1}\sum_i T_1^{-1}(i), \quad (10)$$

where N is the total number of o-H_2 in the solid. This point is important when the concentration of o-H_2 is low, namely, T_1^{-1} will depend more on the configuration of the o-H_2. In other words, two o-H_2 close together will relax more effectively than two particles far away from each other. What we calculate later from Eqs. (8) and (9) is independent of positions R_i, since we will not assume an *a priori* distribution of the particles, as is usually done. Thus the calculated position-independent single-particle relaxation time for comparison with experimental data is taken to be the average value in in Eq. (10).

The complicated expression for T_1 in Ref. 6 can be simplified by the high-temperature approximation and the commutation relations for operators $J_\pm$ and J_z. Equations (6) and (7) are explicitly given by

$$T_1^{-1}(i)=\int_{-\infty}^{\infty}dt\{\tfrac{1}{4}(c'^2-\tfrac{9}{4}d^2) \times[f_1(i,t-t')e^{i(-a+b)t}+f_1^*(i,t-t')e^{i(a-b)t}] +\tfrac{9}{4}d^2[f_2(i,t-t')e^{i(-a+b)t}+f_2^*(i,t-t')e^{i(a-b)t}] +\tfrac{9}{4}d^2[(f_3(i,t-t')e^{2i(-a+b)t}+f_3^*(i,t-t')e^{2i(a-b)t}]\}, \quad (11)$$

$$T_2^{-1}(i)=\tfrac{1}{2}T_1^{-1}+\int_{-\infty}^{\infty}dt\{\tfrac{1}{4}(c'^2-(9/4)d^2)f_4(i,t-t') +\tfrac{9}{4}d^2[f_5(i,t-t')+f_6(i,t-t')]\}. \quad (12)$$

Here f_n is the correlation function obtained by taking thermodynamical ensemble averages of various operators[15]:

$$f_1(i,t-t')=\langle J_+(i,t),\ J_-(i,t')\rangle,$$
$$f_2(i,t-t')=\langle J_z(i,t)J_+(i,t),\ J_-(i,t')J_z(i,t')\rangle,$$
$$f_3(i,t-t')=\langle J_+^2(i,t),\ J_-^2(i,t')\rangle,$$
$$f_4(i,t-t')=\langle J_z(i,t),\ J_z(i,t')\rangle,$$
$$f(i,t-t')=\langle J_z^2(i,t),\ J_z^2(i,t')\rangle,$$
$$f_6(i,t-t')=\langle J_+(i,t)J_-(i,t),\ J_-(i,t')J_+(i,t')\rangle. \quad (13)$$

We notice that if all $f_n(i,\ t-t')$ are the same (isotropic), then $T_1=T_2$ from Eq. (11).

III. STATISTICAL THEORY

There are several ways to calculate $f_n(t-t')$ in the theory of nuclear magnetic resonance. It seems that there is no basic principle to decide which method is the most appropriate one. When the number of magnetic impurities is large, $f_n(t-t')$ is usually approximated by the Gaussian function, whereas the Lorentz function is assumed for low concentration of impurities. It is well known that both methods are not substantially different as far as the contribution to the relaxation time from the branch of frequency close to the Larmor frequency is concerned. Thus in most problems, the two approximations do not make too much difference. There are, however, indications that the statistical theory developed by Margenau and Anderson[10,11] works better than other methods when the concentration of paramagnetic impurities is low. In most cases the statistical theory yields for the tail of the line shape a function in between the Gaussian form and Lorentz form.

The statistical method assumes that the impurities are in random positions and each configuration of all impurities contributes to $f_n(i,\ t-t')$ in a statistically independent way. In other words, the correlation length which is defined by the zero of the two-particle correlation function is zero.[16]

In one important aspect our computation of $f_n(t-t')$ from the statistical theory differs from the usual application of theory in the DD interaction, namely, we will include all terms in Eq. (4). The reason for using a "truncated Hamiltonian"[10] where only terms with a^0 are kept in Eq. (4) is due to the adiabatic principle.[17] It is applicable when the Zeeman energy is much greater than the DD interaction. In our problem, this criterion is that b in Eq. (1) is much greater than the QQ interaction. Since the QQ interaction is larger than 10 MHz when $c\approx 3\times 10^{-3}$, the secular and nonsecular parts are of equal importance. The second point is that we need to compute the functions of various types in Eqs. (11) and (12). We treat all the functions independently.

In the statistical method of evaluating the relaxation function $f_n(t-t')$, the assumption is made that each

[15] We sometimes write $f(t-t')$ instead of $f(i,\ t-t')$ later.
[16] M. V. Klein and R. Brout, Phys. Rev. **132**, 2412 (1963).
[17] See Ref. 12, p. 103, for a discussion.

term of the Hamiltonian H_{ik} commutes, i.e.,

$$\exp(it\sum_{ij}H_{ij}) \equiv \exp[it(\sum_{ij}\sum_{m=-2}^{2}H_m(ij))] = \prod_{m=0}^{2}\prod_{ij}\exp[it(H_m(ij)+H_{-m}(ij))]. \tag{14}$$

The approximation is equivalent to neglecting the correlation of all the particles completely, and is very similar to the method of taking the first-order correction term in the linked cluster expansion of the free energy.

A further approximation used in Ref. 6 is to write

$$f_1(t) = f_1(0)\prod_{m,j}\exp(-\omega_m^2(j)t^2/2). \tag{15}$$

Here

$$\omega_m^2(j) = \frac{\langle[H_{ij}(m)+H_{ij}(-m),\ J_+][H_{ij}(m)+H_{ij}(-m),\ J_-]\rangle}{\langle J_+J_-\rangle}. \tag{16}$$

In contrast to the Gaussian approximation in Eq. (15), we write, on the basis of Eq. (14),

$$f_1(t) = f_1(0)\prod_j \cos\{t[\sum_m \omega_m^2(j)]^{1/2}\}. \tag{17}$$

Here $\omega_m(j)$ is defined by Eq. (15).

It is clear that these two approximations differ mainly through the assumptions in Eqs. (15) and (17) about the time dependence of $f_1(t-t')$ as $|t-t'|\to\infty$. We are not aware of any detailed discussions on the justification of the approximations in different conditions, although this problem is discussed in a simple model.[18]

We want to emphasize that the correlation functions $f_n(t-t')$ in both Eqs. (15) and (17) yield the same second moment, and only give rise to some numerical difference in the relaxation times. However, in Eq. (15) the product over j is taken over the nearest neighbors in Ref. 6, while we will assume equal *a priori* probability of all particles in evaluating Eq. (17). This difference in taking the average over j in Eqs. (15) and (17) causes a very different concentration dependence of T_1 and T_2.

We write Eq. (13) as follows:

$$f_n(i,\ t-t') \equiv \langle O_n^{\dagger},\ O_n\rangle = f_n(0)\prod_j \cos[\omega_n(i,j)(t-t')]\exp[-i\omega_m'(t-t')]. \tag{18}$$

Here

$$f_1(0)=\tfrac{4}{3},\quad f_2(0)=\tfrac{2}{3},\quad f_3(0)=\tfrac{4}{3},\quad f_4(0)=\tfrac{2}{3},\quad f_5(0)=\tfrac{2}{3},\quad f_6(0)=\tfrac{4}{3}, \tag{19}$$

$$\omega_n(i,j) = \epsilon'\left(\frac{a}{|R_{ij}|}\right)^5\left[\frac{4\pi}{9}\sum_{mm'}\frac{\langle[a^m,\ O_n^{\dagger}][a^{-m'},\ O_n]\rangle}{\langle O_n^{\dagger},\ O_n\rangle}C(224,\ m-m')^2 Y_4^{m-m'}(\Omega_{ij})\,Y_4^{-m+m'}(\Omega_{ij})\right] \tag{20}$$

$$= \epsilon'(a/|R_{ij}|)^5 S_n(\Omega_{ij}),$$

$$\omega_1'=A,\quad \omega_2'=A,\quad \omega_3'=0,$$

$$\omega_4'=0,\quad \omega_5'=0,\quad \omega_6'=0,$$

and $\epsilon' = (3/50)(\sqrt{70})\epsilon = 1.887\times10^{-16}$ erg.[19,20]

Next we perform the product in Eq. (18) by assuming that all terms are independent of j and averaging $\omega(i,j)$ over all lattice sites N_0.

$$f_n(t-t') = f(0)\prod_j \cos[\omega_n(i,j)(t-t')]\exp[-i\omega'_n(t-t')]$$

$$= f_n(0)\left\{1-\frac{1}{N_0a^3}\int d^3r_j[1-\cos\omega_n(i,j)(t-t')]\right\}^N \exp[-i\omega_n'(t-t')]$$

$$= f_n(0)\exp[-cQ_n(t-t')]\exp[-i\omega_n'(t-t')]. \tag{21}$$

[18] T. Matsubara, Progr. Theoret. Phys. (Kyoto) **32**, 50 (1964).

[19] The numerical values of a, b, c', and d are obtained from N. F. Ramsey, *Molecular Beams* (Clarenden Press, Oxford, England, 1956). The value of ϵ used here is calculated in Ref. 2 by taking quadrupole moment ($\approx$0.11 Å^2). Recently, C. Karl and J. D. Poll have calculated the quadrupole moment [J. Chem. Phys. **46**, 2944, (1967)] and the new value will raise ϵ about 50%. However, this electrostatic interaction ϵ of two o-H_2 must be screened by p-H_2 when the concentration of o-H_2 is low. If we take the new value of ϵ divided by the dielectric constant ($\approx$1.3) as the quadrupole-quadrupole interaction in our calculation, the calculated T_1 and T_2 will be about 10% greater than the experimental data instead of 10% smaller than experimental data as shown in Fig. 1.

[20] We have neglected a few terms in our writing of H_1 in Eq. (3). The neglected terms will not contribute to ω_n', although they can change the value of the second moments. Since the strength of the crystal field is much less than the QQ interaction, Eq. (3) is justified.

Here $c=N/N_0$ and

$$Q_n(t-t')=\int \frac{d^3r_j}{a^3}\,[1-\cos(\omega_n(i,j)\,(t-t')\,)]. \quad (22)$$

In the evaluation of $\omega_n(i,j)$ in Eq. (19), we have assumed $H_J/T\ll 1$ and have replaced $\exp(-H_J/T)$ by unity in taking the trace over $J(i,t)$. Furthermore, we assume equal population of all J_z states, and our results are temperature-independent. Using Eqs. (20) and (22), we may evaluate $Q_n(t-t')$ explicitly;

$$Q_n(t)=\tfrac{4}{5}\pi\int_0^\infty du(1-\cos u)\,u^{-8/5}$$

$$\times\int_0^{\pi/2} S_n(\theta)\,d\theta\,\sin\theta(|\,t\,|\,\epsilon')^{3/5}$$

$$=4.93\beta_n(|\,t\,|\,\epsilon')^{3/5}.$$

Here

$$\beta_1=1.53,\quad \beta_2=1.44,\quad \beta_3=1.25,$$

$$\beta_4=1.34,\quad \beta_5=0.94,\quad \beta_6=1.04.$$

The Fourier transform of relaxation functions in Eq. (18) is of the form

$$f_n(\omega)=f_n(0)\int_{-\infty}^{\infty} dt\,\exp[-4.93c\beta_n(\epsilon'\,|\,t\,|)^{5/3}-i\omega t]$$

$$=\frac{f_n(0)\,2\cdot 5/3}{\epsilon'(4.93\cdot c\cdot\beta_n)^{3/5}}\int_0^\infty duu^{2/3}e^{-u}\cos\left[\frac{\omega u^{5/3}}{\epsilon'(4.93c\beta_n)^{5/3}}\right]. \quad (23)$$

For ω much less than $\epsilon'\,(4.93c\beta_n)^{5/3}$, $f_n(\omega)$ is independent of ω and equal to $0.11\,(c\beta_n)^{-5/3}$. This result shows $T_1\sim c^{5/3}$ for $0.1<c<0.3$ when $\omega<\epsilon'\,(4.93c\beta_n)^{5/3}$: $f_n(\omega)$ can be evaluated by the method of steepest descent for $\omega\gg\epsilon'\,(4.93c\beta_n)^{5/3}$.

$$f_n(\omega)\sim f_n(0)\,\cos\tfrac{3}{8}\pi\cdot c^{5/4}\omega^{-7/4}. \quad (24)$$

The asymptotic region is not reached in our problem, since $A\,(10^{-2}\,^\circ\mathrm{K})$ is about equal to $\epsilon'\,(4.93c\beta_n)^{5/3}$ at the lowest concentration in the experiment. However, we find (24) useful to explain the fast increase of T_1 of HD+o-H_2 as a function of concentration.[21]

IV. DISCUSSION OF EXPERIMENTAL DATA

The relaxation of the transverse and longitudinal components of the magnetizations $M_x(t)$ and $M_z(t)$ in the experiments can not be characterized by a single exponential function of time at low o-H_2 concentration because of distribution of o-H_2.[8] There are two ways of obtaining T_1 and T_2 from experimental data in this circumstance. We might define the relaxation times from $M_z(T_1)M_z^{-1}(0)=e^{-1}$ and $M_z(T_2)M_x^{-1}(0)=e^{-1}$. Alternatively, we may take the slope $[dM_z(t)/dt]_{t=0}M_z^{-1}(0)$ as the experimental T_1^{-1} (with a corersponding definition for T_2). This particular value of T_1^{-1} is taken to be $\langle 1/T_1\rangle$ in Eq. (10), when there exists a distribution of relaxation times. If there exists a unique relaxation time, T_1 defined in these two ways will coincide. We will compare our calculation with experimental values from the second definition by arguing that the nonexponential behavior of $M_z(t)$ and $M_x(t)$ is due to the distribution of o-H_2 which we do not consider in the calculation. Thus our calculated values must be identified as the initial slope of the magnetization.

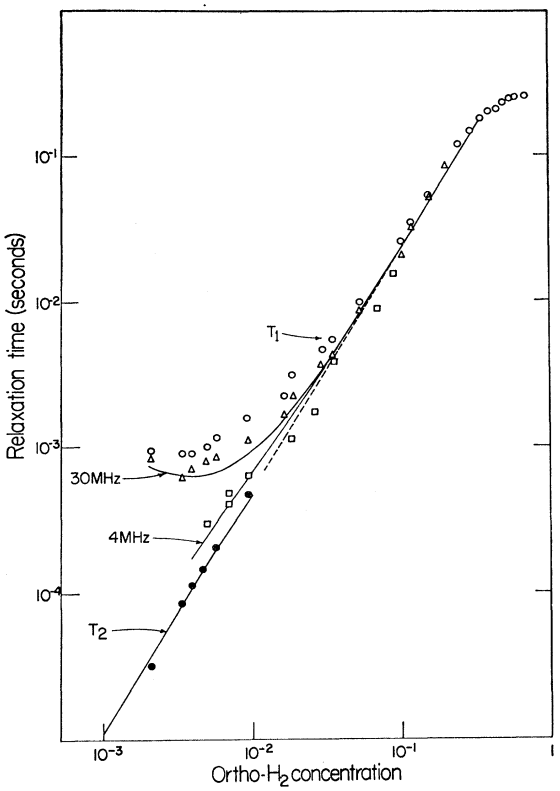

FIG. 1. Relaxation times T_1 at the external field 30 and 4 MHz and T_2 at 30 MHz. The crystal field A is taken to be 0.2°K. Triangles and closed circles are the experimental points of T_1 and T_2 taken as the initial slope of the magnetizations in the external magnetic field. Open circles are the experimental T_1 defined by $M_z(t)$ at e^{-1} of its initial value. The solid curves are the calulated values and the dashed line is T_1 with zero crystal field and magnetic field.

Our calculated results from Eqs. (11) and (21) are given in Figs. 1 and 2, and the following conclusions can be drawn:

(1) The statistical method works out very well in general.[19] It is surprising that even at $c\approx 0.3$, $T_1\sim c^{5/3}$. This is a consequence of the statistical model. Thus the method seems to apply to a higher concentration than one would expect.

(2) The magnetic field dependence of T_1 can also be explained very well. T_1 is dominated by $f_3(t-t')$ at

[21] W. Hardy and J. R. Gaines, Phys. Rev. Letters **17**, 1278 (1966); C. C. Sung, Solid State Commun. (to be published).

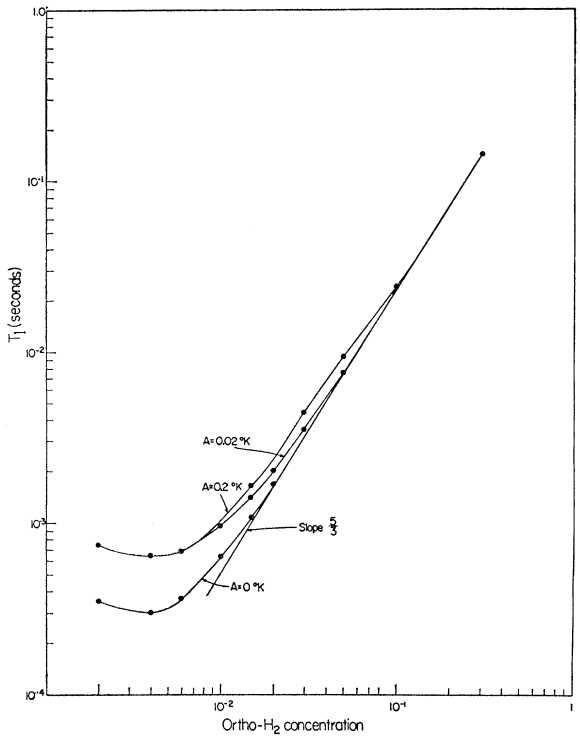

FIG. 2. Calculated T_1 at 30 MHz for three values of the crystal field.

small c in Eq. (11), which depends on the external magnetic field, not on A. The strong field dependence of T_1 at low c, where f_1 and f_2 are suppressed because of A, is entirely a property of $f_3(t-t')$.

(3) We wish to be able to determine A precisely from data fitting. Unfortunately, the calculated values of T_1 seem to be not very sensitive to the magnitude of A. The calculated curves would not change substantially if we choose A between 0.01 and 0.04°K. Any value of A larger than 0.05, however, would not fit the data at high concentration, whereas a small A fails to explain the magnetic field dependence. This point is clearly shown in Fig. 2. It is interesting to note that our estimated value of A is in reasonable agreement with those deduced from experimental data on nuclear magnetic resonance,[8] infrared absorption,[4] and direct theoretical calculation.[4] On the other hand, to fit the specific-heat data, a much larger value of A ($\sim$1°K) is always needed.[2,5]

(4) T_2 in the experiments is measured for a restricted region of concentration[8] and is given in Fig. 1 at $c\sim 10^{-2}$. In this region T_2 is dominated by f_4, f_5, and f_6, which are independent of the crystal field and the external magnetic field.

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APPENDIX

Our calculation is limited to the high-temperature region such that the ensemble average over $\exp(H_J/T)$ can be replaced by unity. Since in our treatment a uniform distribution of o-H_2 is assumed. The temperature region that satisfies the high-temperature approximation is

$$T\gg c^{5/3}\times(\text{QQ interaction}). \qquad \text{(A1)}$$

Furthermore, T must be larger than A [the crystal field in Eq. (3)] in order to justify our calculation in Eq. (22).

On the other hand, we want the temperature sufficiently low so that the contribution from diffusion processes can be neglected completely. The diffusion of o-H_2 can modulate the intermolecular DD interaction. According to the Kubo-Tomita theory, T_1 is given by[6]

$$T_1^{-1}=(5/3\ \ln 2)\,(T_2'')^{-2}\Gamma. \qquad \text{(A2)}$$

Here $T_2''=10^{-2}d$, the relaxation time for a rigid lattice. The factor 10^{-2} is from the difference of intramolecular distance and intermolecular distance. Γ in (A2) can be inferred from experimental data[6];

$$\Gamma=6.82\times 10^{-14}e^{-176/T}\ \text{sec}.$$

Since it is hard to estimate theoretically the relaxation times when the two mechanisms—modulation caused by diffusion and QQ interaction—are both present; our calculation applies only when T_1 given by (A2) is much greater than 1 sec in our in our problem, so that the contribution from the diffusion processes can be ignored. On the basis of (A1) and (A2), we conclude that the temperature range to which our calculation is applicable is $2<T<7$°K.