Nuclear spin-lattice relaxation times for mixtures of ortho- and para-H$_2$. II. Low ortho-H$_2$ concentration

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We study the longitudinal relaxation time T_1 for the nuclear spins of ortho-hydrogen molecules in a para-hydrogen or a hydrogen deuteride (HD) matrix. Phonon-driven molecular reorientations give rise to both a temperature- and concentration-dependent modulation to the electric-quadrupole-quadrupole-induced electric-field-gradient couplings at ortho sites and provide an important mechanism of nuclear spin-lattice relaxation for experimentally accessible concentrations and temperatures. The well-known $c^{5/3}$ law for T_1 is recovered for the ortho-para system. We calculate explicit distributions of relaxation rates as a function of concentration, temperature, and magnetic field. These functions are then applied to ortho and para mixtures and HD. For both systems we find satisfactory agreement with experiment, including temperature and concentration dependence that has been previously unexplained.

I. INTRODUCTION

This is the second in a series of papers with which we intend to improve the theoretical understanding of the nuclear spin relaxation properties of mixtures of ortho and para hydrogen. Here we focus our attention on low concentrations of ortho-hydrogen (o-H$_2$) in a para-hydrogen (p-H$_2$) or hydrogen deuteride (HD) host. In the first paper of this series,[1] we calculated the infinite-temperature electric quadrupole-quadrupole (EQQ) correlation functions for o-H$_2$ concentrations above $c = 0.2$. In that paper, we demonstrated that it was sufficient to consider only the EQQ interaction between o-H$_2$molecules for high concentrations. For high enough ortho concentration, the local environment of all ortho molecules is fairly similar, and each o-H$_2$ interacts roughly equally with several neighbors. This strongly coupled many-body interaction leads to frequent, mutually induced transitions between the different states of the molecular angular momentum or "molecular spin." This state of affairs is usually called "homogeneous broadening." For low concentrations, however, the local environment changes dramatically[1] from one o-H$_2$ site to another, for $c < 0.1$. This spatial inhomogeneity is eventually enough to quench the homogeneous band formed by the EQQ interaction. It is the purpose of this paper to investigate this low-concentration regime, and to explain what mechanisms are responsible for the relaxation that is observed in experiments.[2-7]

Experiments measuring T_1 for mixtures of o-H$_2$ and p-H$_2$ have shown a rather surprising temperature and concentration dependence.[2] In studying low o-H$_2$ concentrations, Buzerak, Chan, and Meyer[2] have observed a temperature dependence in T_1 which is completely unexplained by theory. Hardy and Gaines[5] have seen a spectacular simultaneous temperature and concentration dependence for T_1 for o-H$_2$ in HD. For concentrations $c \approx 10^{-4}$ or less, T_1 can vary over an order of magnitude for the temperature in the range $1.2 < T < 4$ K while also depending heavily on c. In an attempt to explain their findings some researchers[6] have investigated a total relaxation rate Γ_{total} which tries to decouple the concentration and temperature dependence on T_1 and which takes the following form:

$$1/T_1 = \Gamma_{tot} = \Gamma_1(T) + \Gamma_2(c) , \tag{1}$$

where c denotes ortho concentration, and is valid if Γ_1 and Γ_2 are independent relaxation mechanisms. In Eq. (1), we assume that Γ_1 is due solely to phonons and Γ_2 is dependent upon the EQQ interaction, usually with the assumption that there is a homogeneous EQQ band. If the form of Eq. (1) was valid, we would anticipate the existence of two regimes with Γ_1 dominating for one and Γ_2 for another with a small crossover regime between. We would expect the crossover region to be small because of the very strong temperature dependence of $\Gamma_1 \sim T^7$. Yet this plausible picture is not borne out by the experimental data of Hardy and Gaines.

The failure of Eq. (1) suggests that the phonons drive a concentration-dependent relaxation mechanism. In this paper we develop a model which includes the effects of phonon-induced molecular reorientations and the resultant modulation of an electric-field gradient (EFG) experienced at o-H$_2$ sites and show this to be an important relaxation mechanism for low concentrations. Our basic physical picture is the following. Consider a particular reference o-H$_2$ molecule in a dilute lattice. This molecule experiences a time-dependent EFG due to the molecular reorientations of its ortho neighbors. For a variety of concentrations and temperaures this will involve *many* such neighbors. These reorientations are not due to a homogeneous band formed by the EQQ interaction, but are induced by phonons and thus the associated reorientation rate is strongly temperature dependent. In this paper we will work out the consequences of this phonon-driven modulation of electric-field gradients and gain in-

sight into the temperature dependence of the nuclear spin T_1 data for o-H_2 in p-H_2 and HD hosts.

Other approaches to the low-concentration limit have often involved the statistical theory of Harris[8] and Sung.[9] Here one starts with the assumption that each molecule is dominated by one or at most a few other molecules. One then takes the local or effective field at a given site to be additive, static, and dependent only upon the locations and configurations of the other o-H_2 molecules in the lattice. A given set of spin locations and orientations then implies a spectrum. This is averaged over all possible configurations and states to produce a spectral function which is supposed to be responsible for nuclear relaxation. There are difficulties with this picture. First, the statistical model is a theory based only on inhomogenous broadening, and thus, if taken literally, can never lead to the relaxation of the spins. That is, it is the transverse fluctuations of the H_2 molecular angular momentum or spin that induce the T_1 nuclear relaxation. An inhomogeneous broadening of the molecular correlation function with no real lifetime damping will not flip nuclear spins. Also, the method is temperature independent, and thus cannot explain the temperature dependence which has been observed[3,4] in H_2 and more spectacularly[5] in HD. Additionally, we will find that the assumption that "only a few spins matter" is not valid for a wide range of concentrations and temperatures.

Another approach to the ortho-para problem was that of Fujio, Hama, and Nakamura,[10] who recognized the importance of crystal-field effects on relaxation. These authors used moment methods for all concentrations, however dilute. This implicitly assumes the existence of homogeneous broadening due to the EQQ interaction, even for an isolated pair of molecular spins. But it is clear that such a pair does not flip unless a transition is induced by an external radiation field. Such a system is *not* homogeneously broadened and moment methods are not applicable.

Nakamura and Fujio also presented a paper about HD with o-H_2 impurity.[11] They compare their theory only to experimental data at a single temperature $T = 1.2$ K however, and do not treat the strong temperature dependence observed in the experiments at all. Also, the same remarks of the preceding paragraph concerning moments is applicable to this work as well.

The rest of this paper will be organized as follows. In Sec. II we introduce the model and its physical assumptions with an illustrative spin-$\frac{1}{2}$ analogy to the H_2 problem. Section III is concerned with formal issues: a mean-field-theoretic formulation of the problem, means of calculating T_1 and related points. In Sec. IV, we obtain explicit analytical expressions for the distribution of relaxation rates for H_2 and compare to experiment. Section V is an application of the results of Sec. IV to solid HD, where we compare our theory to the experiments of Hardy and Gaines.[5]

II. THE MODEL

There are four basic steps in the T_1 or longitudinal relaxation of the nuclear spins. First consider a reference

H_2 molecule. Molecules nearby the reference molecule are changing between states of different m_j. Second, since the electric-field gradient at the reference molecule due to another molecule depends on m_j of the other molecule, the reference molecule experiences a time-dependent EFG from other nearby molecules. This causes transverse (dephasing) fluctuations in the molecular spin or molecular angular momentum of the reference molecule. Third, these transverse fluctuations of the reference molecule can cause the nuclear spin of the refrence molecule to flip. Fourth, the nuclear magnetization may spread around by spin diffusion. Steps 1, 3, and to some degree 4 are well understood, so most of the exposition in this paper will be concerned with step 2.

A. Physical aspects

We began by considering a reference o-H_2 molecule embedded in a dilute para-H_2 or HD matrix. For some concentrations and temperatures the characteristic coupling frequency between the molecule and some other o-H_2 molecules is greater than the molecular correlation frequency γ, which characterizes the rate at the molecule is changing between states of different m_j. These fluctuations between m_j states are due to some mechanism such as phonons—not to the EQQ. Suppose that there are N such "strongly interacting" (compared to γ) o-H_2 neighbors. Then if each neighbor changes molecular orientation with a rate γ, the average time between major changes in the local EFG at the reference site is $1/N\gamma$. Thus in our model,

$$\gamma_M = N\gamma \tag{2}$$

is of great importance: it provides an important broadening mechanism for the spectral functions responsible for nuclear T_1 relaxation, and leads to a concentration and temperature dependence for T_1. We can easily form a simple estimate for N, the average number of neighbors of a given molecule for which the EQQ interaction is greater than γ,

$$N \approx 4\pi\sqrt{2}/3(\Gamma_d/\gamma)^{3/5} , \tag{3}$$

$$\Gamma_q = c^{5/3}\Gamma_{EQQ} . \tag{4}$$

Γ_{EQQ} is the EQQ coupling constant in the solid state; $\Gamma_{EQQ} \approx 0.83$ K.

Van Kranendonk and co-workers[12] have studied the spin-phonon interaction in some detail and have produced a functional form $\gamma(\Gamma)$ giving the molecular reorientation rate as a function of temperature T. On the experimental side, Conradi, Luszczynski, and Norberg[7] have studied isolated o-H_2 in p-H_2 and other nonmagnetic hosts and found that the Van Kranendonk model produces a satisfactory fit to their data. They evaluated the free parameters in the theory to specify for very dilute o-H_2 in p-H_2. We will use their fit in our analyses. Van Kranendonk finds that the temperature dependence is given by $\gamma = AT^7$ for $T \ll \Theta_D$ with Θ_D a Debye temperature for the solid. For higher temperatures a more detailed formula has been devised: for this we refer the reader to the literature.[12]

B. A spin-$\frac{1}{2}$ analogy

To clarify our model and to motivate certain approximations later, we introduce a spin-$\frac{1}{2}$ analogue very similar in principle, but simpler in detail than the H_2 version we will develop below. The simpler model has the advantage of possessing exact solutions in interesting limits. We consider a reference spin interacting with N "spins" which have the sole effect of introducing a fluctuating shift in the resonant frequency of the reference spin. We begin by considering the dephasing of a spin-$\frac{1}{2}$ particle due to a time-dependent local or effective field given by

$$\omega = \sum_{i=1}^{N} \omega_i \xi_i(t) , \qquad (5)$$

where ω_i denotes the positive coupling of a reference spin to another spin in a lattice, and $\xi_i(t)$ is a stochastic process with two values, ± 1, corresponding to the orientation of the ith spin being up or down. Of course, in this model $\omega(t)$ can only take on a discrete set of values. We further assume that the processes ξ_i are Markovian with a rate γ that one may think of as phonon induced. An immediate consequence of requiring $\xi(t)$ to be Markovian is that the time autocorrelation function for ξ is

$$G_\xi(t) = \exp(-\gamma t) . \qquad (6)$$

We note that the properties of correlation functions like G_ξ are well-studied objects in the literature of stochastic processes:[13] ξ is the well-known random telegraph signal.

As we show in detail elsewhere,[14] for the model [Eq. (5)] one can readily calculate the autocorrelation function for $S_+(t)$ (or in multipole language $A_{1,1}$). We have shown that for an arbitrary number interacting spins, N, there exists an exact solution for the limits $\omega_i \gg \gamma$, and the opposite limits. For the H_2 problem we will be concerned with the case $\omega_i \gg \gamma$, which we now assume to be the case for the rest of this section. Consider the time-dependent autocorrelation function which is defined by

$$G(t) = \Theta(t)\langle S_+(t)S_-(0)\rangle , \qquad (7)$$

where $\langle \ \rangle$ denotes a temporal average, Θ is the Heaviside step function and S_+ is a spin operator in the usual notation. We have shown[14] that the Fourier transform of $G(t)$ has the form

$$G(\omega) = \sum_{i=1}^{2^N} f(\omega - \Omega_i) . \qquad (8)$$

The function f is a Lorentzian with width $N\gamma/2$. We emphasize that this result is not merely a consequence of a scaling argument: we have demonstrated *rigorously* that $G(\omega)$ has the form indicated in Eq. (8), and that N is precisely given by Eq. (3), the number of spins with couplings larger than γ. The frequencies at which $G(\omega)$ has its maxima, Ω_i, are perhaps not unexpectedly just the set of possible values of $\omega(t)$ accounting for all possible values of the ξ_i (This result may be familiar to some readers as the NMR spectrum of a chemically exchanging nucleus in the slow exchange limit.)

Now consider the particularly simple example of identical couplings: $\omega_i = \omega_1$ for all i. Then,

$$\omega(t) = \omega_1 \sum_{i=1}^{N} \xi_i . \qquad (9)$$

The locations of the poles on the ω axis for G for this case are obviously binomially distributed, and consequently for $N \gg 1$ such a distribution is very well approximated by a Gaussian. This is also an immediate consequence of the central-limit theorem[13] in its weakest form. The Gaussian has width

$$\sigma = \left[\sum_{i=1}^{N} \omega_1^2 \right]^{1/2} . \qquad (10)$$

If we relax the rather stringent requirement of identical ω_i we see that a Gaussian is still a reasonable fit to $G(\omega)$. For example, we can calculate the second moment of the distribution of effective fields. By squaring Eq (1), averaging over spin configurations, and using the assumption that the motion is pairwise uncorrelated (from site to site), we recover the same width given in Eq. (6). Thus, even if the ω_i vary, the expected width is the same. If there are several couplings ω_i that are comparable, the distribution will be nearly centered at $\omega = 0$. If this condition does *not* hold, and one $\omega_i \gg \omega_j$ for $j \neq i$, the center of the spectral density will be shifted to the vicinity of $\omega = \omega_i$. Note that the shifted Lorentzian will retain its width $N\gamma/2$, however.

III. FORMALISM

A. Mean-field theory

To implement the ideas presented in Sec. II A, we find it convenient to construct a mean-field theory. Invoking the usual mean-field-theory rationale, we assume that the effects of neighboring o-H_2 spins can be well represented by an effective field or effective Hamiltonian. This reduction of the true bilinear coupling to a simplified "effective" form implies that correlations between pairs of spins must be fairly weak. For high levels of dilution this is a reasonable assumption. In this theory we will account for several interactions: (1) the static crystal field intrinsic to the hexagonal close-packed (hcp) structure; (2) electric-field gradients associated with defects (ortho molecules); (3) magnetic effects (dependence on the frequency of the experiment); and (4) molecular spin-phonon effects (phenomenologically). Ortho molecules feel an EFG from two sources: the axial crystal field and the EQQ interaction from o-H_2 neighbors. The latter EFG is in fact time dependent, since the molecular spin states are constantly changing at each site because of the spin-phonon process. In the dilute lattice it is reasonable to assume that the spin-phonon rate is site independent.

To set up a mean-field theory analogous to the spin-$\frac{1}{2}$ model, we first need to determine the eigenstates of an isolated o-H_2 molecule in an arbitrary EFG. In general, we may assume that the single-particle Hamiltonian takes the form[15]

$$H_s = V_c A_{20} - (\tfrac{2}{3})^{1/2}\omega_J A_{10} + \Delta A_{22} + \Delta^* A_{2-2} , \qquad (11)$$

where V_c denotes the axial crystal-field splitting, ω_J is the molecular Zeeman coupling,[15] and Δ is the transverse (complex) EFG coupling. For formal convenience we will always use the irreducible multipole operators A_α, the operator equivalents of the spherical harmonics, where α is the usual spherical harmonic index (l,m). For normalization conventions and a discussion of the use of the multipole operators, see Ref. 16. Our assumption that the axial crystalline field is much larger than typical EQQ interactions eliminates $m = \pm 1$ operators from Eq. (11) because for $V_c \gg \omega_J$, the doublet level is widely split off from the singlet level, and we therefore restrict ourselves to consider only transitions between the doublet levels, In other words, we have truncated the Hamiltonian to handle the crystal field for concentrations small enough that it dominates the other interactions in the problem. Diagonalizing Eq. (11) on the usual spin-1 basis we easily find the eigenvalues Ω and eigenvectors e_i:

$$\Omega_\pm = 2^{-1/2} V_c \pm \beta, \quad \Omega_0 = -2^{1/2} V_c ,$$

$$e_\pm = (1 + |\alpha_\pm|^2)^{-1/2} \begin{bmatrix} 1 \\ 0 \\ \alpha_\pm \end{bmatrix}, \quad e_0 = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}, \tag{12}$$

where

$$\alpha_\pm = 3^{-1/2}(\omega_J \pm \beta)/\Delta ,$$

and

$$\beta^2 = 3|\Delta|^2 + \omega_J^2 .$$

For comparison, we note that the bilinear EQQ Hamiltonian may be expressed as

$$H_{QQ} = \sum_{mn,ij} F_{mn}(ij) A_{2m}(i) A_{2n}(j) , \tag{13}$$

and the function F is fully discussed in Refs. 1 and 8. H_{QQ} is easily converted into an effective single-particle Hamiltonian for the site i:

$$H_{QQ}(i) = \sum_\alpha A_\alpha(i) W_\alpha , \tag{14}$$

where

$$W_\alpha = 2 \sum_{\beta j} F_{m_\alpha n_\beta} \langle A_\beta \rangle_j . \tag{15}$$

As discussed above, we shall be concerned only with the case of $\alpha = 2 \pm 2$, that part of the EFG which is time dependent because of molecular reorientation at other sites. By comparing Eq. (14) and Eq. (11) and using the eigenstates of H_s [Eq. (12)] to evaluate $\langle A_\beta \rangle_j$, the average of the multipole operator over the states of Eq. (12), we see that

TABLE I. Values of stochastic variables.

State label	ξ	β
+	$2^{-1/2}$	$(\frac{3}{2})^{1/2} e^{iK_j}$
−	$2^{-1/2}$	$(\frac{3}{2})^{1/2} e^{iK_j}$
0	$-2^{1/2}$	0

$$\Delta = W_{22} = 2 \sum_j [F_{20}(ij)\xi_j + F_{22}(ij)\beta_j$$

$$+ F_{2-2}(ij)\beta_j^*] \equiv \sum_j \Delta_j , \tag{16}$$

where ξ_j and β_j are complex stochastic variables specifying the molecular orientation at site j and their values are given in Table I. In obtaining the above equations we have assumed that ω_J can be neglected, which is true at all but the lowest concentrations. Even if it is not true it makes only a small difference since it is constant (independent of site) and is reasonably small compared to ω_0, the frequency of the experiment. We shall find that most of the physics depends on $|\Delta|$ and its distribution function.

B. Normal modes of the molecular spins

The simplest means of describing the nuclear relaxation of the system is to find the modes of the molecular motions, i.e, we seek linear combinations Φ of the Heisenberg representation multipole operators A_α such that by forming the Heisenberg equation of motion for Φ, one recovers a constant (depending on the local environment of the site) multiplied by Φ. We therefore seek Φ and Ω_Φ so that

$$i\frac{d\Phi}{dt} = [\Phi, H_s] = \Omega_\Phi \Phi \tag{17}$$

(we have set $\hbar = 1$ throughout this paper). Straightforward algebraic manipulations lead to three nontrivial modes X, $X^\dagger$, and Z where

$$X = 2^{-1/2}(A_{10} + 2^{-1/2}\Delta A_{22}/|\Delta| - 2^{-1/2}\Delta^* A_{2-2}/|\Delta|)$$

and

$$Z = 2^{-1/2}(\Delta A_{22} + \Delta^* A_{2-2})/|\Delta| . \tag{18}$$

These modes have frequencies $\Omega_X = 12^{1/2}|\Delta| = \Omega_{X^\dagger}$ and $\Omega_Z = 0$. We point out two properties of these modes. First, they have been calculated for the case of "no symmetry,"[7,15] meaning that a reference site experiences large axial and transverse field gradients. Also, the utility of working with the modes is that one avoids "interference" between different relaxation mechanisms. This leads to a simpler formula for T_1 and a more transparent treatment of the relaxation.

The modes X, $X^\dagger$ of Eq. (18) describe the effects of the intermolecular EQQ coupling, which in turn modulates the intramolecular nuclear dipole-dipole interaction to cause spin-lattice relaxation. The nuclear-molecular interaction may be expressed most elegantly in multipole-tensor form as

$$H_{mn} = \omega_d \sum_{m=-2}^{m=2} B_{2m} A_{2m}^\dagger - \frac{2}{3}\omega_c \sum_{m=-1}^{m=1} B_{1m} A_{1m}^\dagger . \tag{19}$$

A_α and B_α are multipole operators: A_α refers to molecular spins, B_α to nuclear spins. In this equation, $\omega_d = 3.62 \times 10^5$ sec^{-1} and $\omega_c = 7.15 \times 10^5$ sec^{-1} denote the dipolar and spin-rotation couplings, respectively. For the case of temperatures above about 1 K (where the

effects of the nuclear spins on the molecular spins may be neglected), T_1 is given by

$$T_1^{-1} = 6\omega_d^2 [G_X(2\omega_0) + G_Z(2\omega_0)] \ , \tag{20}$$

where G_Φ denotes the real part of the frequency autocorrelation function of the mode Φ, ω_0 is the frequency of the experiment (the Larmor frequency of the H nuclear spins), and the zero-frequency mode's correlation function G_Z is a Lorentzian of width γ. Another remark is in order concerning Eq. (20). We have calculated T_1 for a single crystal of H_2 rather than the powder sample that is usually studied. For a qualitative understanding of the c and T dependence that is reasonable. Physically, the mode X gives the relaxation due to intermolecular EQQ interactions driven by the phonons, while Z describes the relaxation of the nuclei only by phonons including changes in the molecular state at the nuclei's site only.

C. Spin dynamics of o-H_2 molecules

As we explained in Sec. III B, a calculation of T_1 requires the time evolution of the modes. In order to verify that the autocorrelation function of mode X has a two-component structure as we expect from our spin-$\frac{1}{2}$ analogy, we use the equation of motion for X to obtain a solution for $X(t)$:

$$X(t) = X(0)\exp\left[-i\int_0^t dt' \Omega_X(t')\right] \ . \tag{21}$$

Similar formulas in other contexts were developed long ago by Kubo.[17] It is a worthwhile pedagogic remark to note that $X(t)$ would be significantly more complicated if we had not chosen to work with the modes of H_s. We have calculated $X(t)$ using Eq. (21) for a computer simulated $\Omega_X(t)$ for o-H_2 spins diluted in a simulated hcp lattice at concentration c and molecular correlation frequency γ.[7,15] We obtain

$$G_X(t) = \Theta(t)e^{-\gamma t}\int_0^\infty dt' \cos\left[\int_t^{t+t'} dt'' \Omega_X(t'')\right] \ . \tag{22}$$

(The presence of the factor $e^{-\gamma t}$ can be traced to the effects of phonons directly on the reference site.) We find that the Fourier transform $G_X(\omega)$ of Eq. (22) has a structure similar to that depicted in Fig. 1. We note that there is, of course, a distribution of couplings in the hcp lattice due to the spatial disorder of dilution. For $c \ll 1$ there is a wide variety of such couplings and the distribution function for the couplings is therefore very broad. Still, the temporal and spatial average of the coupling Δ is zero, and those molecular spins which are not dominated by a single other spin can be expected to have most of their G_X spectral density centered about $\omega = 0$, by analogy with Sec. II B. While the average is zero, there may be considerable fluctuation about the mean. To quantify these notions we find that an analysis of a distribution function for couplings due to other o-H_2 is useful.

D. Distribution function for EFG couplings

In this section we calculate a distribution characterizing the EFG felt at a reference site due to other ortho
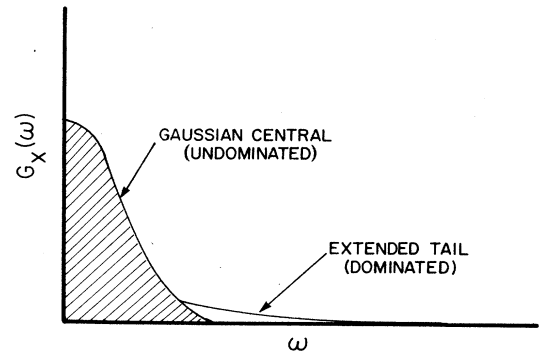

FIG. 1. Schematic representation of spectral function $G_X(\omega)$. Note the two-component structure. The central feature is due to undominated spins, the tail is due to spins with one dominant neighbor.

neighbors. This density is important for calculating T_1, and for obtaining distributions of relaxation rates for the nuclear spins. Throughout this section we will follow the procedure and nomenclature of Ref. 18 to estimate this distribution. From Eq. (16) we observe that

$$|\Delta|^2 = 4\left|\sum_j F_{20}(j)\xi_j + F_{22}(j)\beta_j + F_{2-2}(j)\beta_j^*(j)\right|^2 \ . \tag{23}$$

Expanding this into a double sum, using the assumed statistical independence of the stochastic variables ξ_i, β_j at sites $i \neq j$, and averaging over spin orientations, we obtain

$$x = 4\sum_j [|F_{20}(j)|^2 + |F_{22}(j)|^2 + |F_{2-2}(j)|^2] \ . \tag{24}$$

It is straightforward to use the method of Ref. 18 to calculate $p(x)dx$, the probability that frequency squared coupling x is in the range $[x, x + dx]$. Following Ref. 18, we see that an integral representation for $p(x)$ is

$$p(x) = -\frac{2}{\pi}\text{Im}\int_0^\infty dt \, e^{-xt - zt^{3/10}} \ , \tag{25}$$

where z is a complex constant. Expanding the second exponential in a Taylor series, integrating term by term, and simplifying, we see that

$$p(x) = -\frac{2}{\pi}x\sum_{l=1}^\infty (-\delta/y^{3/10})^l$$
$$\times \sin(l\psi)\Gamma(3l/10 + 1)/l! \tag{26}$$

with $\psi \approx 3\pi/20 + \tan^{-1}(0.510)$ and $\delta \approx 7.280$, and we have introduced a dimensionless variable $y = \Gamma_q^{-2}x$. Γ_q is defined in Eq. (4). Approximate results are given for δ and ψ because these involved a numerical quadrature.

We have numerically evaluated Eq. (26) and find that it provides an excellent approximation for $p(x)$ even quite near $x = 0$. Experience with the dipolar lattice and manipulations involving stationary phase (not rigorously applicable to our integral) suggest that $p(x)$ is not analytic at $x = 0$, with $p(x)$ decreasing faster than any power as

$x \rightarrow 0$. Numerical evaluation of Eq. (26) indicates that for any $c \ll 1$ the distribution function has the form shown in Fig. 2. We find empirically that x_{mp}, the most probable value of x satisfies $x_{mp} \approx 9\Gamma_q^2$. Also, $p(x_{mp}) \approx 1/16 x_{mp}$.

It is worthwhile at this point to interpret some of the formalism we have developed. As we indicated in Sec. III C, our correlation function $G_X(\omega)$ should have the general character illustrated in Fig. 1. We have performed numerical simulations based on Eqs. (21) and (22) to justify this, and have also developed the spin-$\frac{1}{2}$ analogue to make the physical origin of the two features of Fig. 1 comprehensible. Undominated spins contribute to the central part of $G_X(\omega)$; spins with a single neighbor (or small cluster) with a much larger than "typical" splitting (which we can interpret as being those spins with coupling near the most probable x) have their individual contributions to the total G_X shifted by an amount comparable to the dominant coupling. The distribution function $p(x)dx$ provides information concerning what fraction of spins are dominated and undominated. By analogy with the spin-$\frac{1}{2}$ case we assign a width of order

$$\sigma = \left[\sum_{i=1}^{N} |\Delta(i)|^2 \right]^{1/2} . \tag{27}$$

For configurations with a dominating $|\Delta(i)|^2 \gg x_{mp}$, corresponding to the tail of $p(x)$, we make the rather coarse assumption that for such a configuration $G_X(\omega)$ is approximately

$$G_X = 6\omega_d^2 \gamma_M / (\gamma_M^2 + u^2) , \tag{28}$$

where $u = (12x)^{1/2} - \omega$. Such a functional form is certainly not an exact representation of dominated contributions to G_X, but we believe that it retains essentially the right physics.
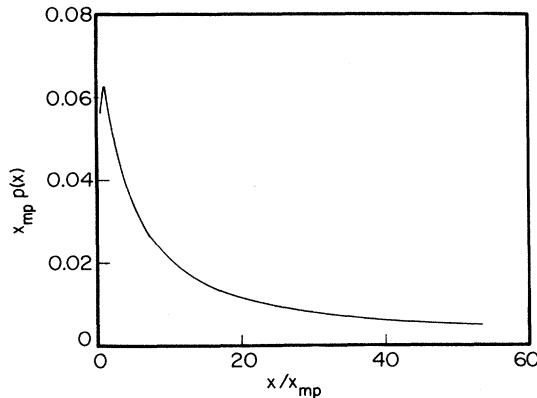

FIG. 2. Distribution function $p(x)$ for low concentrations. p is plotted in reduced units of $\bar{x} = x/x_{mp}$. x_{mp} is defined in Sec. III D.

IV. DISTRIBUTIONS OF RELAXATION RATES

Many workers have observed nonexponential recovery of the magnetization in experiments on H_2. Such effects can be explained by noting that any experiment measures a distribution of relaxation rates, a consequence of the dispersion in the characteristic recovery times for spins in different environments. In this section we will obtain explicit functional forms for the distribution of relaxations rates $\Gamma = T_1^{-1}$. We start with the observation that the dominated and undominated regimes lead to different kinds of relaxation.

A. Undominated regime

As we discussed in earlier sections, an appreciable fraction of the o-H_2 molecules in the lattice are not dominated by one other molecule, but feel the effects of many comparably. Such spins contribute a central component to the composite X autocorrelation function, with a width given by Eq. (27). Such spins have squared coupling x lying near x_{mp} (otherwise they would be dominated). The undominated central part of $G_X(\omega)$ is essentially temperature independent. To see why, consider a particular undominated reference spin. The center of the line for this spin is near $\omega = 0$. Now by analogy with the spin-$\frac{1}{2}$ problem [Eq. (8)] where $G(\omega)$ consists of 2^N spikes, $G_X(\omega)$ consists of a very large number (order 3^N) of spikes with width near $N\gamma$. In the spin-$\frac{1}{2}$ case it was possible to calculate exactly where in the line the spikes occurs. This is not easily done for the H_2 problem. However, in principle the features of $G_X(\omega)$ are similar to $G(\omega)$. Since each of the 3^N spikes has the same integrated intensity it is easy to see that the spikes overlap considerably to very low temperatures simply because there are so many of them and because of the additional broadening of the spike by the many-site process compared to consideration only of the direct phonon process. It is reasonable to assume a Gaussian representation for this central component from the analysis from the spin-$\frac{1}{2}$ case, and because in the absence of information other than a width, the Gaussian is the only functional form justified by information theory.[19] We give this Gaussian a width

$$\delta \sim [p(x_{mp})]^{-1/2} \sim 12\Gamma_q . \tag{29}$$

In the low-frequency limit, this produces [using Eq. (20)]

$$\Gamma = (\pi/8)^{1/2} \omega_d^2 / \Gamma_q , \tag{30}$$

which gives a T_1 close to experiment. This result is actually quite encouraging, since there is a factor of order unity uncertainty which enters into the choice of the width δ. In fact perfect agreement with experiment[4] is obtained if we take a width $f\delta$ instead of δ, with $f = 0.77$. This procedure is also consistent with our simulations explained in Sec. III C. Because of statistical noise, especially for $N \gg 1$, we found it difficult to extract quantitative results from the simulations, and the necessity of calculating numerical Fourier transforms made this even more difficult. Nevertheless, the existence of a central was clearly indicated even for low temperature. The

width of the simulated $G_X(\omega)$ was also qualitatively in accord with Eq. (29). We see, therefore, that our model is capable of explaining the well-known $c^{5/3}$ behavior of T_1, and that this temperature-independent mechanism is a manifestation of the undominated central part of $G_X(\omega)$.

We should make a few further remarks concerning the undominated regime. It is clear that the undominated regime cannot survive to arbitrarily low concentrations of o-H_2, since at some point phonons become more important than the intermolecular interaction, and we have essentially the case of an isolated spin, already treated in detail in Ref. 15. Since all of the spins in the undominated regime have similar spectral densities $G_X(\omega)$, they uniformly produce a T_1 near that derived above, and their contribution to $P(\Gamma)$, the distribution function of relaxation rates is temperature independent, and strongly dependent upon the concentration.

B. Domination by a single neighbor

For spins with their spectral densities centered in a frequency range corresponding to the tail of the distribution of couplings, we use the assumed functional form G_X of Eq. (28). The expression we derived for T_1 [Eq. (20)] provides a relation between the relaxation rate Γ and coupling x for which we know the distribution function. Thus to compute $P(\Gamma)d\Gamma$ for the dominated regime requires a transformation of $p(x)dx$ to $P(\Gamma)d\Gamma$. The dominant term of Eq. (20) is the Markovian (first) term: we neglect the molecular reorientations due to spin-phonon interaction acting directly at a reference site. This approximation is valid if the parameter $N \gg 1$. For isolated molecules (very dilute ortho concentration: $c < 5 \times 10^{-4}$) the second term $must$ be included. To obtain $P(\Gamma)$, we solve Eq. (20) for x. Using the standard procedure for changing variables in a probability density,[13] we obtain

$$P(\Gamma) = p(x_+)\left|\frac{dx_+}{d\Gamma}\right| + p(x_-)\left|\frac{dx_-}{d\Gamma}\right|, \qquad (31)$$

where

$$x_\pm = 12^{-1}(2\omega_0 \pm \omega_a)^2, \quad \omega_a = (6\omega_d^2\gamma_M\Gamma^{-1} - \gamma_M^2)^{1/2}, \qquad (32)$$

and p is given by Eq. (26). Note that this probability density has concentration, temperature, and field dependence. Also, for some values of these parameters the distribution can become very broad. For example, for any low concentration (where the undominated mechanism is not primarily responsible for relaxation) and high temperatures, $P(\Gamma)$ is so broad that it is difficult to give one meaningful number to characterize T_1. On the other hand, our theory clearly predicts a much better defined average rate for high fields and low temperatures. For large magnetic fields ($\omega_0 \gg \Gamma_q$) the distribution of rates can display additional structure: a peak near $6\omega_d^2\gamma_M/4\omega_0^2$ which is a manifestation of configurations with $(12x)^{1/2} \ll 2\omega_0$. We illustrate these points in more detail in Fig. 3. Inspection of Eqs. (31) and (32) shows that configurations for which $\omega_0^2/3 = x$ relax anomalously
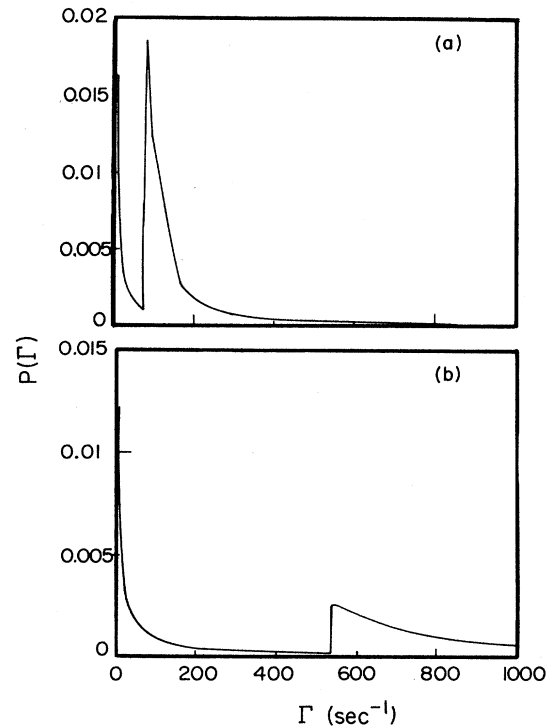

FIG. 3. Two illustrations of $P(\Gamma)$, both for $c = 5 \times 10^{-4}$, $\nu_p = 4.8$ MHz. (a) MCF $\gamma = 7.2 \times 10^3$ ($T \sim 2$ K), (b) MCF $\gamma = 10^6$ ($T \sim 4.4$ K). The principal peak is due to configurations with $(12x)^{1/2} \ll 2\omega_0$ (see text).

fast at a rate of order

$$\Gamma_{max} = 6\omega_d^2\Gamma_q^{-3/5}\gamma^{-2/5} . \qquad (33)$$

This may be traced to a resonant effect between the magnetic field and the coupling to the local environment. Such configurations are represented by a sharp "blip" in the remote tail of P. The naive calculation of an average over all rates Γ is rendered meaningless because the integral is completely dominated by the small, perhaps altogether negligible fraction of spins which decay at a very fast rate. In an experiment, such spins may not be detectable at all, or may appear as a rapidly decaying component of a free induction decay (FID). Thus to use Eq. (31) to calculate a T_1 to compare to experiment, one usually has to avoid the anomalous component. We have used Eq. (31) to calculate T_1 leaving out the anomalous part, and find satisfactory agreement with experiment for concentrations less than about 3×10^{-3} (see Fig. 4). Theory and experiment begin to disagree at this concentration, as the undominated regime becomes important, and produces a dominant temperature-independent mechanism of relaxation.

At this point we summarize the consequences of our model in various limits. The present theory contains two relevant dimensionless parameters, $p_1 = \gamma/\Gamma_p$ and $p_2 = \omega_0/\Gamma_q$. The first measures the importance of the molecular correlation frequency γ compared to typical
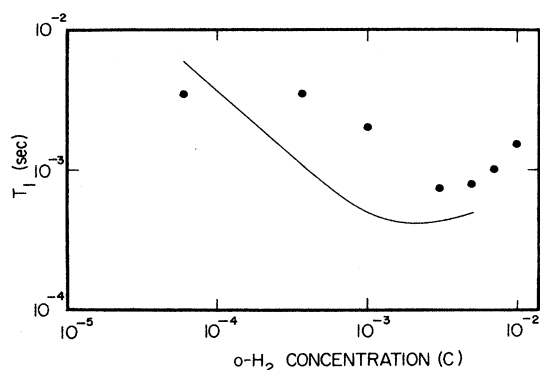
FIG. 4. Theory and experiment for mixtures of o-H_2 and p-H_2. Data are from Refs. 3 and 7. Theory, solid curve; data, solid circles.

EQQ couplings, the second sets the scale of the nuclear Larmor frequency compared to the EQQ.

For $p_1 \gg 1$ where the direct phonon process (phonons causing molecular reorientations at the reference site) dominates the Markoff process we have introduced, T_1 is given by consideration of completely isolated molecules as discussed in Ref. 15. For $p_1 \gg 1$ the discussion of the purely isolated molecule pertains for any p_2.

For the case $p_1 \ll 1$ the Markoff process dominates and parameter N introduced in Sec. III A is large compared to unity. For $p_2 \ll 1$ the undominated central produces a temperature-insensitive T_1 proportional to $c^{5/3}$. For $p_2 \gg 1$ experiments sample $G_\chi(\omega)$ in the "extended tail" in the terminology of Fig. 1. It is easy to calculate an approximate average Γ [average over $P(\Gamma)$]. The result is

$$\langle \Gamma \rangle \approx 88.08 \omega_d^2 \Gamma_q^{3/5} \omega_0^{-8/5} . \tag{34}$$

We note parenthetically that for ω_0 large enough $G_\chi(\omega) \sim \omega_0^{-2}$, but because the EQQ coupling for some configurations is much larger than any experimentally accessible fields, we do not expect this behavior to be observed. Note also that Eq. (34) provides a theoretical justification for the existence[20] of a $T_1 \sim c^{-1}$ regime which has been conjectured.

V. NUCLEAR RELAXATION OF HD

The distribution functions for Γ obtained in the preceding section can be used to lend insight into the persistently vexing problem of relaxation of HD with small concentrations of normal-H_2 impurity. Here, the only efficient means for the relaxation of the H nuclear spins to the lattice is through spin diffusion (between HD molecules) to a relaxation center (o-H_2) which is in good thermal contact with the lattice. One of us[21] has recently developed a detailed theory for such relaxation. To apply the distributions calculated above to HD, we first need to slightly generalize Ref. 21, where it is assumed that all relaxation centers have an identical magnetization relaxation rate to the lattice. The results are easily extended to

a distribution of rates $P(\Gamma)$. One finds that the thermalization is exponential with rate R and

$$R = c \int d\Gamma \, P(\Gamma)\Gamma/(1+\xi\Gamma/\nu) . \tag{35}$$

Here, ξ is the parameter of Ref. 21 (not a stochastic variable), and ν characterizes the hopping frequency (magnetization transfer rate) between the H nuclear spins of HD molecules. We have evaluated the integral of Eq. (35) numerically, using $P(\Gamma)$ from Eqs. (31) and (32), and have found rather good agreement with the temperature and concentration dependence of the data of Hardy and Gaines (HG) for concentrations below $c = 10^{-3}$ (see Fig. 5). We have found that our model provides best agreement with experiment if we subtract 5×10^{-5} from the normal H_2 concentrations reported by HG. We agree with Honig and co-workers[6] that these concentrations are a bit high, but we find less satisfactory agreement for the suggested reduction of 8.5×10^{-5} proposed in Ref. 6. Given the uncertainties in these estimates, our reduction is reasonable.

We observe that our model consistently overestimates T_1 for the higher two concentrations of Fig. 5. We attribute this to the importance of the temperature-independent EQQ central (see Fig. 1) for the higher con-
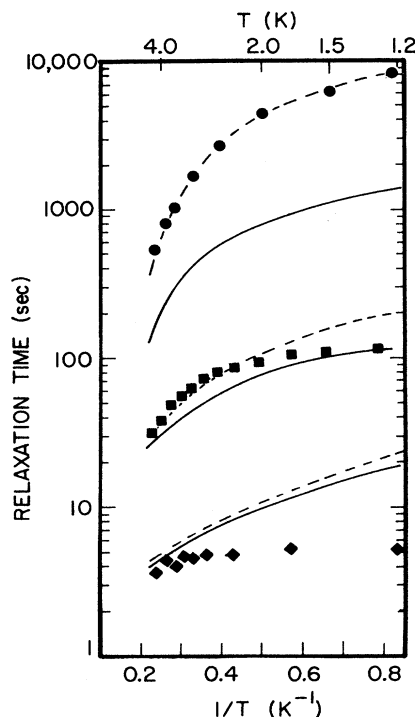

FIG. 5. Comparison of HD relaxation data with theory. Data are from Ref. 5. We illustrate experiment and theory with a subtraction of 5×10^{-5} from n-H_2 concentrations reported in Ref. 5 (dashed line), and the theoretical predictions using the concentrations originally given in Ref. 5 (solid lines). Circles, squares, and diamonds refer to normal concentrations $H_2 = 0.0001$, 0.000 28 and 0.0063, respectively, according to Hardy and Gaines.

centrations. In Fig. 5 we have included only the temperature-dependent part.

It is straightforward to obtain an asymptotic representation of Eq. (35) for low temperature if we assume that

$$\omega_0 \gg \Gamma_q \gg \gamma \ , \tag{36}$$

a condition which follows from requiring that the center of $G_\chi(\omega)$ be well separated from the region of x corresponding to the undominated spins. In that case, we approximately obtain

$$T_1^{-1} = 15.33 c^2 \omega_d (\nu \gamma_M)^{1/2} \Gamma_{EQQ}^{3/5} \omega_0^{-8/5} \ , \tag{37}$$

using an angular average value of $\xi = 5.5$. Thus for low temperatures and high fields, $T_1 \sim T^{-7/5}$. This behavior is relevant for the data which we examine in this paper. We note that the agreement between theory and experiment is particularly good for the lowest concentrations. This is not surprising: this model is essentially rigorous for the dilute limit. It is not unreasonable to regard the present work as the natural extension of the solution[15] given for isolated molecules. We also observe that all of the remarks of the preceding section concerning dimensionless parameters p_i hold for HD as well, provided that spin diffusion is taken into account.

We should also point out that, perhaps surprisingly, that it is somewhat easier to account for the HD data than the H_2 data, because the rapid spin diffusion encountered in HD makes averages over distributions of relaxation rates more meaningful than for H_2, where the very rapid component of distribution of rates is possibly altogether unobservable. In fact the temperature dependence in Eq. (37) arises because of Eq. (35). A simple average rate would be temperature independent.

A further point is that one must be careful in applying this model to very low temperatures where Pake doublet effects become important, i.e., where the nuclear spins have an important effect on the molecular spins.

VI. CONCLUSION

We hope that the present paper has helped to explain the NMR properties of different isotopic combinations of hydrogen. The theory presented has succeeded in explaining the temperature and concentration dependence of longitudinal relaxation without the introduction of free parameters.

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