

Nuclear-spin-lattice relaxation times for H₂ in solid nonmagnetic hosts

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(Received 8 May 1979)

We calculate the nuclear-spin relaxation times T_1 and T_2 for isolated ortho ($J=1$) H₂ molecules in solid nonmagnetic hosts located at sites with various crystal fields. The mechanism considered for the relaxation of a nuclear spin to lattice equilibrium proceeds via the molecular angular momentum and is valid in the limit where molecular spin-lattice decay rates are much greater than molecular-nuclear-spin coupling frequencies. We find that many relaxation properties, including the value of T_1 at the T_1 minimum and the product of $T_1 T_2$ at temperatures well below the temperature of the T_1 minimum, depend crucially on the crystal field at the H₂ molecular site. Thus measurements of T_1 and T_2 can yield definite information about the environment of H₂ molecules in a host lattice.

I. INTRODUCTION

Recent observations^{1,2} of nuclear-spin relaxation times T_1 and T_2 for low concentrations of ortho-H₂ ($J=1$) in solid rare gases and in para-H₂ show several puzzling anomalies. In particular, observed values of T_1 at the T_1 minimum are larger by factors of about 2 or 4 than what one would expect from theory or from experiments on H₂ gas.³ Further, the transverse (T_2) decay can be drastically nonexponential at low temperatures in contrast to the exponential behavior at higher temperatures or in the gas. Similar effects have been observed by others⁴⁻⁶ in solid H₂ but either at ortho concentrations that are too large to unequivocally separate out ortho-H₂ pair interactions from the spin-lattice relaxation or at temperatures so low that our results are either not valid or are only marginally valid.

Motivated by these results,¹ we have calculated the nuclear-spin relaxation times for low concentrations of isolated ortho ($J=1$) H₂ molecules in nonmagnetic solid hosts. Since the nuclear spins relax via the molecular angular momentum, T_1 and T_2 can depend crucially on the crystal fields experienced by the H₂ molecules. We calculate the appropriate molecular-spin-correlation functions in various limiting cases of electric-field-gradient configurations in order to obtain the nuclear-spin relaxation times. The results explain most of the observed anomalies.² The calculations are valid only if the spin-lattice decay rates for the rotational angular momentum of the molecules are much greater than the coupling frequencies between the molecular- and nuclear-spin systems. Since these spin-lattice decay rates decrease rapidly with decreasing temperature, our results are applicable only at temperatures above a few degrees K.²

In the rest of this section we explain the model more fully and present a simple physical picture for the values of T_1 at the T_1 minimum. Section II con-

tains the details of the calculation. In Sec. III we display and discuss T_1 and T_2 for a variety of limiting cases of electric-field-gradient configurations.

In this paper we are considering only ortho-H₂ in the $J=I=1$ state. Since the rotational angular momentum of a single H₂ molecule can be described by a $J=1$ spin formalism, we shall refer to the molecular angular momentum as a molecular spin. This is not only a more convenient wording but it also emphasizes the fact that the molecule (in the $J=1$ state) acts like a spin in every way including interactions with the lattice, magnetic fields, electric field gradients, and other spins. Similarly, the two protons will be referred to as a single nuclear spin with $I=1$. Further, the gyromagnetic ratios for the molecular- and nuclear-spin systems are $\gamma_m = 0.3876 \times 10^4$ sec/G and $\gamma_n = 2.675 \times 10^4$ sec/G, respectively. Thus γ_n is the same as γ for a free proton while γ_m is several orders of magnitude smaller than γ 's for typical electron-spin systems. The Hamiltonian connecting the nuclear- and molecular-spin systems for a single H₂ molecule, H_{m-n} , can be written⁷

$$H_{m-n} = \hbar \omega_d [3(\vec{I} \cdot \vec{J})^2 - 4] + \hbar \left(\frac{3}{2} \omega_d - \omega_c \right) (\vec{I} \cdot \vec{J}) \quad (1)$$

where \vec{I} and \vec{J} are the vector spin operators for the nuclear and molecular spins, respectively, and

$$\omega_c = 7.15 \times 10^5 \text{ sec}^{-1}$$

and

$$\omega_d = 3.62 \times 10^5 \text{ sec}^{-1}$$

For our purposes, however, it is more convenient to write the Hamiltonian as⁸

$$H_{m-n} = \hbar \omega_d \sum_{m=-2}^{m=+2} B_{2,m} A_{2,m}^\dagger - \frac{2}{3} \hbar \omega_c \sum_{m=-1}^{m=+1} B_{1,m} A_{1,m}^\dagger \quad (2)$$

where the $A_{l,m}$ and $B_{l,m}$ are the irreducible multipole operators for the molecular and nuclear spins, respectively. It will be our approximation that the effects of the lattice (phonons) on the molecular spins are much greater than are the effects of nuclear spins. This approximation is valid if typical molecular-spin-phonon decay rates are much larger than ω_c and ω_d and, in this limit, the calculation is quite straightforward. Using Eq. (2) the nuclear relaxation times can be expressed in terms of the molecular-spin-correlation functions. Further, the necessary molecular-spin-correlation functions can be calculated as a function of the molecular-spin-phonon interaction and the electric field gradients V_{ij} at the molecular site. 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.

Part of our results can be anticipated by regarding Eq. (2) as describing the coupling of the eight non-trivial molecular-spin modes to the nuclear-spin system. In the multipole language these modes correspond to the A_{lm} with $(l=1, m=0, \pm 1)$ and $(l=2, m=0, \pm 1, \pm 2)$. Further, the coupling strengths for these modes are roughly equal since $\omega_d = \frac{2}{3}\omega_c$ to within 30%. First consider the effect of a strong axial electronic field gradient. This will push the resonant frequencies of four of the molecular modes (those with $m = \pm 1$) to very high values. These modes are now ineffective in relaxing the nuclear spins because they have little spectral weight at nuclear resonance frequencies. Thus we expect T_1 to be increased by roughly a factor of 2. Finally, consider the effect of many strong electric-field-gradient components. Now, in general, the splittings between all pairs of molecular states are large and only two of the eight molecular modes have appreciable spectral weight at nuclear resonance frequencies. Thus we expect T_1 to be increased by a factor of 4. There is no way to increase T_1 further because $2J$ modes of a spin J system describe relative level populations and thus have their spectral weight centered about zero (like M_z). Thus T_1 (and T_2) depend on the magnitudes of the components of the electric field gradients at the H₂ sites. However, as will be seen, T_1 and T_2 measurements cannot determine values for the electric field gradients but can only determine whether the gradients are large or small with respect to certain other parameters to be discussed.

II. CALCULATIONS

Since we have assumed that the nuclear spins have a negligible effect on the molecular spins, the effects of H_{m-n} on the nuclear spins can easily be obtained.

In our notation T_1 and T_2 are given by the equations

$$(T_1)^{-1} = \frac{3}{2}\omega_d^2 \sum_{m=-2}^{m=+2} m^2 F_{2,m}(m\omega_0) + \frac{2}{3}\omega_c^2 \sum_{m=-1}^{m=+1} m^2 F_{1,m}(m\omega_0) , \quad (3a)$$

$$(T_2)^{-1} = \frac{3}{2}\omega_d^2 [2F_{2,-1}(-\omega_0) + 3F_{2,0}(0) + 3F_{2,1}(\omega_0) + 2F_{2,2}(2\omega_0)] + \frac{2}{3}\omega_c^2 [F_{1,0}(0) + F_{1,1}(\omega_0)] , \quad (3b)$$

where $\omega_0 = \gamma_I H_0$, γ_I is the gyromagnetic ratio of the H₂ ($I=1$) nuclear spin, and H_0 is the magnitude of an external magnetic field \vec{H}_0 that defines the z axis. In these equations $F_{l,m}(\omega)$ is the normalized spectral function for the molecular-spin operators $A_{l,m}$,

$$F_{l,m}(\omega) = \text{Re} \int_{-\infty}^{\infty} dt F_{l,m}(t) e^{-\omega t} , \quad (4)$$

$$F_{l,m}(t) = \langle A_{l,m}(t) A_{l,m}^\dagger(0) \rangle \Theta(t) ,$$

where $\Theta(t)$ is the step function, the brackets $\langle x \rangle$ denote the thermal average of x , and $\text{Re}(f)$ denotes the real part of f . Formulas like these have been derived by numerous authors⁹ and their derivation will not be repeated here.

The next step is to calculate the molecular-spin-correlation functions $F_{l,m}(\omega)$. Since we will ultimately be dealing with H₂ molecules in highly anisotropic crystal fields, this becomes rather messy. First it is convenient to find the transformation between the $A_{l,m}$ and $\bar{A}_{l,m}$ where unbarred quantities refer to the laboratory coordinates and barred quantities refer to the crystal coordinates. We consider the crystal to have a definite z axis and the laboratory z axis, defined by an external magnetic field \vec{H}_0 , lies in the x - z plane of the crystal making an angle $-\theta$ with respect to the crystal z axis. The y axes of the two systems coincide and the transformation is

$$A_{l,m} = \sum_{m'=-l}^{m'=+l} a(l,m,m') \bar{A}_{l,m'} , \quad (5)$$

where

$$\begin{aligned} a(l,m,m') &= (-1)^{m+m'} a(l,m',m) , \\ a(1,0,0) &= \cos\theta , \\ a(1,\pm 1,\pm 1) &= \frac{1}{2}(1 + \cos\theta) , \\ a(1,0,\pm 1) &= \pm \sin\theta/2^{1/2} , \\ a(1,1,-1) &= \frac{1}{2}(1 - \cos\theta) , \\ a(2,2,2) &= \frac{1}{4}(\cos\theta + 1)^2 , \\ a(2,\pm 1,\pm 1) &= \frac{1}{2}(\cos^2\theta - \sin^2\theta + \cos\theta) , \end{aligned}$$

$$\begin{aligned}
a(2, 0, \pm 2) &= \left(\frac{3}{8}\right)^{1/2} \sin^2 \theta, \\
a(2, 0, \pm 1) &= \pm \left(\frac{3}{2}\right)^{1/2} \sin \theta \cos \theta, \\
a(2, 2, -2) &= \frac{1}{4} (\cos \theta - 1)^2, \\
a(2, 2, \pm 1) &= \frac{1}{2} \sin \theta (\mp \cos \theta - 1), \\
a(2, -2, \pm 1) &= \frac{1}{2} \sin \theta (\mp \cos \theta + 1), \\
a(2, 1, -1) &= \frac{1}{2} (\sin^2 \theta - \cos^2 \theta + \cos \theta), \\
a(2, 0, 0) &= \frac{1}{2} (3 \cos^2 \theta - 1). \quad (6)
\end{aligned}$$

These transformation coefficients are rotation matrices that are easy (but tedious) to derive using the representation of the $A_{l,m}$'s in terms of the vector spin operators.^{8,10} The correlation functions $F_{l,m}(\omega)$ in the laboratory coordinates can be expressed in terms of the crystal coordinates as

$$F_{l,m}(\omega) = \sum_{m',m''} a(l,m,m') a(l,m,m'') \bar{F}_{l,m',m''}(\omega), \quad (7)$$

where

$$\bar{F}_{l,m',m''}(t) = \langle \bar{A}_{l,m'}(t) \bar{A}_{l,m''}^\dagger(0) \rangle \Theta(t). \quad (8)$$

Further, the molecular Zeeman Hamiltonian in the crystal coordinate system is

$$H_{zm} = -\hbar \omega_J (\bar{J}_z \cos \theta - \bar{J}_x \sin \theta), \quad (9)$$

$$\omega_J = \gamma_m H_0,$$

where γ_m is the gyromagnetic ratio of the molecular spins.

The other two elements left to consider are the molecular-spin-phonon interaction and the possibility of static electric field gradients interacting with the molecular spins via their quadrupole moments. We shall characterize the effects of the molecular-spin-phonon interaction on the molecular spins by two decay rates (inverse correlation times). These decay rates are Γ_1 which is the decay rate appropriate for the dipole ($l=1$) correlation functions $F_{l,m}(\omega)$ and Γ_2 which is the decay rate appropriate for the quadrupole ($l=2$) correlation functions $F_{2,m}(\omega)$. For a wide variety of spin-phonon regimes one obtains exponential decay independent of magnetic field and the condition

$$\Gamma_2/\Gamma_1 = \frac{3}{5}, \quad (10)$$

if the spin-phonon interaction is spherically symmetric.^{10,11} Although this condition of spherical symmetry will not obtain exactly in most crystal lattices, most spin-phonon decay rates are only weakly angular dependent indicating that spherical symmetry is not too bad an approximation.

Finally we consider the effects of static electric

field gradients on the molecular-spin-correlation functions. In general there are five independent components of the electric-field-gradient tensor V_{ij} at a given H_2 site. However, it is neither practical nor especially desirable to consider an arbitrary set of such field gradients. Instead we shall consider some likely limiting cases. First consider the case where the only nonzero component is V_{zz} ($V_{xx} = V_{yy}, V_{xy} = V_{yz} = V_{zx} = 0$). The "single-particle" part of the H_2 molecular-spin Hamiltonian (the Hamiltonian excluding molecular-spin-phonon interactions) is

$$H_0 = -\hbar \omega_J (\bar{J}_z \cos \theta - \bar{J}_x \sin \theta) + \hbar \omega_{Q1} \bar{A}_{2,0}, \quad (11)$$

where ω_{Q1} is a (real) frequency proportional to the axial electric field gradient V_{zz} and the electronic quadrupole moment of the H_2 molecule. Equations of motion can be written down for the $\bar{A}_{l,m}$ using the prescription⁸

$$\left(\frac{d \bar{A}_{l,m}}{dt} \right) = \left(\frac{[\bar{A}_{l,m}, H_0]}{i \hbar} \right) - \Gamma_l \bar{A}_{l,m}. \quad (12)$$

Since the set of equations are linear in the $\bar{A}_{l,m}$ they can easily be diagonalized to obtain the $\bar{F}_{l,m',m''}(\omega)$. In this paper, however, we are primarily interested in the limit of large field gradients, $\omega_{Q1} \gg \omega_0, \omega_J, \Gamma_l$. In this case correlation functions with m or $m' = \pm 1$ vanish as Γ_l/ω_{Q1}^2 and

$$\bar{F}_{l,m,m'}(\omega) = \frac{\delta_{m,m'} \Gamma_l}{[\omega - m \omega_J(\theta)]^2 + \Gamma_l^2}, \quad (13)$$

for $l=2, m=m'=0, \pm 2$ and $l=1, m=m'=0$, where

$$\omega_J(\theta) = \omega_J \cos \theta. \quad (14)$$

Finally consider the additional electric field gradients in the x - y plane of the crystal. Since the multipole operators with $m = \pm 1$ have been eliminated in the preceding paragraph, we simply ignore them here. Thus the effective single-particle Hamiltonian for the \bar{A}_{lm} with $m \neq \pm 1$ is

$$H_0 = -\hbar \omega_J(\theta) \bar{J}_z + \hbar (\omega_{Q2} \bar{A}_{2,2} + \omega_{Q2}^* \bar{A}_{2,-2}), \quad (15)$$

where ω_{Q2} is complex frequency whose real part is proportional to $V_{xx} - V_{yy}$ and whose imaginary part is proportional to V_{xy} . By using Eq. (12) with Eq. (15) and ignoring the $A_{l,\pm 1}$, we obtain the following equations of motion:

$$\begin{aligned}
(\omega + i \Gamma_1) \bar{A}_{1,0} &= \sqrt{6} (\omega_{Q2} \bar{A}_{2,2} + \omega_{Q2}^* \bar{A}_{2,-2}), \\
(\omega + i \Gamma_2) \bar{A}_{2,0} &= 0, \quad (16)
\end{aligned}$$

$$[\omega - 2\omega_J(\theta) + i \Gamma_2] \bar{A}_{2,2} = \sqrt{6} \omega_{Q2}^* \bar{A}_{10},$$

$$[\omega + 2\omega_J(\theta) + i \Gamma_2] \bar{A}_{2,-2} = -\sqrt{6} \omega_{Q2} \bar{A}_{10}.$$

Again we are primarily interested in the limit of strong electric field gradients, $|\omega_{Q2}| \gg \omega, \omega_J(\theta), \Gamma_l$. In this limit the only finite correlation functions are

$$\begin{aligned}\bar{F}_{2,0,0}(\omega) &= F_2(\omega) = \Gamma_2/(\omega^2 + \Gamma_2^2) , \\ \bar{F}_{2,\pm 2,\pm 2}(\omega) &= \frac{1}{2}F_2(\omega) , \\ \bar{F}_{2,\pm 2,\mp 2}(\omega) &= \frac{1}{2}F_2(\omega)r ,\end{aligned}\quad (17)$$

where

$$r = [\text{Re}(\omega_{Q2}/|\omega_{Q2}|)]^2 = [(V_{xx} - V_{yy})^2 - V_{xz}^2]/[(V_{xx} - V_{yy})^2 + V_{xz}^2] . \quad (18)$$

In this section we have ignored the possibility that the molecular-spin decay rates may be altered by the presence of the large electric field gradients. Except for relaxation by the direct spin-phonon process, the molecular decay rates should not depend on the ω_Q 's unless $\hbar\omega_Q$ becomes comparable to kT . Thus we shall now explicitly assume that both $|\omega_{Q1}|$ and $|\omega_{Q2}|$ are much less than kT/\hbar , which eliminates any possibility of Pake doublet effects.¹² Finally, it would seem impossible that direct molecular-spin-lattice relaxation could dominate within the assumed limit $\Gamma_l \gg \omega_c, \omega_d$.

III. RESULTS

In this section we will discuss T_1 and T_2 in detail for several limiting cases of large crystal fields. Since most experiments are done on polycrystalline samples, the results will be averaged over all angles where appropriate.

A. Cubic symmetry

First we consider an H₂ molecule at a site possessing cubic symmetry. In this case there are no electric field gradients and thus no angular dependence. The results in this case are the same as those obtained by Hardy³ and are useful primarily as a standard with

which to compare other cases. The results are conveniently written

$$T_1^{-1} = 3\omega_d^2[4F_2(2\omega_0 - 2\omega_J) + F_2(\omega_0 - \omega_J)] + \frac{4}{3}\omega_c^2F_1(\omega_0 - \omega_J) , \quad (19a)$$

$$T_2^{-1} = \frac{3}{2}\omega_d^2[2F_2(2\omega_0 - 2\omega_J) + 5F_2(\omega_0 - \omega_J) + 3F_2(0)] + \frac{2}{3}\omega_c^2[F_1(\omega_0 - \omega_J) + F_1(0)] , \quad (19b)$$

where

$$F_l(\omega) = \Gamma_l/(\omega^2 + \Gamma_l^2) , \quad (20)$$

and $\omega_0 = \gamma_n H_0$ is the resonant frequency of the nuclear spins. For numerical evaluations we shall use $\Gamma_2 = 0.6\Gamma_1$, $\omega_c = 1.97\omega_d$, and $\omega_J = 0.145\omega_0$. By evaluating these equations over a range of frequencies we find that $(T_1)_m$, the value of T_1 at the T_1 minimum, is given by

$$(T_1)_m = 0.138(\omega_0/\omega_d^2) , \quad (21a)$$

and that $(T_2)_m$, the value of T_2 at the T_1 minimum, is given by

$$T_{2m} = 0.0785(\omega_0/\omega_d^2) . \quad (21b)$$

The value of $(T_1 T_2)_0$, the asymptotic value of $T_1 T_2$ for $\Gamma_l \ll \omega_0$, is given by

$$(T_1 T_2)_0 = 0.00826(\omega_0/\omega_d^2)^2 . \quad (21c)$$

B. Axial symmetry

We next consider a crystal site with only an axial electric field gradient, V_{zz} , along the crystal z axis. As discussed in Sec. II, we assume that the frequency characterizing the magnitude of this field gradient is much greater than ω_0 or Γ_l . By combining Eqs. (3), (6), (7), and (13), we obtain T_1 and T_2 as a function of θ , the angle between \bar{H}_0 and the crystal z axis.

$$\begin{aligned}T_1(\theta)^{-1} &= \frac{3}{2}[\omega_d^2 3(1-z^2)^2 F_2(2\omega_0) + \frac{1}{2}(z+1)^4 F_2(2\omega_0 - 2\omega_J z) + \frac{1}{2}(z-1)^4 F_2(2\omega_0 + 2\omega_J z) \\ &\quad + 3z^2(1-z^2) F_2(\omega_0) + \frac{1}{2}(1-z^2)(1+z)^2 F_2(\omega_0 - 2\omega_J z) + \frac{1}{2}(1-z^2)(1-z)^2 F_2(\omega_0 + 2\omega_J z)] \\ &\quad + \frac{2}{3}\omega_c^2(1-z^2) F_1(\omega_0) ,\end{aligned}\quad (22a)$$

$$\begin{aligned}T_2^{-1}(\theta) &= \frac{3}{8}\omega_d^2[3(1-z^2)^2 F_2(2\omega_0) + \frac{1}{2}(z+1)^4 F_2(2\omega_0 - 2\omega_J z) + \frac{1}{2}(z-1)^4 F_2(2\omega_0 + 2\omega_J z) \\ &\quad + 30z^2(1-z^2) F_2(\omega_0) + 5(1-z^2)(1+z)^2 F_2(2\omega_0 - 2\omega_J z) \\ &\quad + 5(1-z^2)(1-z)^2 F_2(\omega_0 + 2\omega_J z) + 3(3z^2 - 1)^2 F_2(0) + 9(1-z^2)^2 F_2(-2\omega_J z)] \\ &\quad + \frac{1}{3}\omega_c^2[2z^2 F_1(0) + (1-z^2) F_1(\omega_0 - \omega_J z)] ,\end{aligned}\quad (22b)$$

where $z = \cos\theta$ and $F_l(\omega)$ is given by Eq. (20).

If Eqs. (22a) and (22b) are averaged over all solid angles one obtains the angular averages

$$T_{ia}^{-1} = \frac{1}{2} \int_0^\pi T_i^{-1}(\theta) \sin\theta d\theta, \quad (23)$$

where $i = 1$ or 2 .

$$T_{1a}^{-1} = \left(\frac{9}{5}\right) \omega_d^2 \{4F_2(2\omega_0)[1 + 32\omega_0\omega_J F_2(2\omega_0)/9\Gamma_2] + F_2(\omega_0)[1 + 8\omega_0\omega_J F_2(\omega_0)/9\Gamma_2]\} + \left(\frac{4}{9}\right) \omega_c^2 F_1(\omega_0), \quad (24a)$$

$$T_{2a}^{-1} = \left(\frac{3}{10}\right) \omega_d^2 \{6F_2(2\omega_0)[1 + 32\omega_0\omega_J F_2(2\omega_0)/9\Gamma_2] + 15F_2(\omega_0)[1 + 8\omega_0\omega_J F_2(\omega_0)/9\Gamma_2] \\ + 3F_2(0) + (45/4\Gamma_2)[- \frac{5}{3}a^2 - a^4 + a(1+a^2)^2 \tan^{-1}(a^{-1})]\} \\ + \left(\frac{2}{9}\right) \omega_c^2 [F_1(0) + F_1(\omega_0)], \quad (24b)$$

where

$$a = \Gamma_2/2\omega_J. \quad (25)$$

In obtaining Eqs. (24a) and (24b) we have neglected terms of order $(\omega_J/2\omega_0)^2$ with respect to one. These terms contribute less than 1% to T_1 and T_2 for any value of Γ_2 .

Equations (24) are quite complex but the resulting behavior is relatively simple. T_{2a} still is a monotonic function of Γ_2 and T_{1a} has a simple minimum as a function of Γ_2 . Using the same notation as in Eqs. (21), we obtain values at the T_1 minimum and as $\Gamma_2 \rightarrow 0$ of

$$(T_{1a})_m = 0.297(\omega_0/\omega_d^2), \quad (26a)$$

$$(T_{2a})_m = 0.177(\omega_0/\omega_d^2), \quad (26b)$$

$$(T_{1a}T_{2a})_0 = 0.102(\omega_0/\omega_d^2)^2. \quad (26c)$$

These equations should be compared with Eqs. (21) for the case of cubic symmetry. As argued in Sec. I, T_{1a} and T_{2a} are increased by roughly a factor of 2.

In addition to the increase in T_1 and T_2 , the decay signals in pulsed experiments on powdered samples will exhibit some nonexponential character. This will occur because the signal $S(t)$ observed is not $\exp(-t/T_{ia})$ but rather

$$S(t) = \frac{1}{2} \int_0^\pi \sin\theta d\theta \exp[-t/T_i(\theta)]. \quad (27)$$

Thus Eqs. (24) are only useful for the short-time part of a decay. This nonexponential decay is more pronounced for T_2 than for T_1 and is more pronounced for $\Gamma_2 < \omega_0$ than for $\Gamma_2 > \omega_0$.

C. No symmetry

Finally we consider crystal sites with large electric field gradients $V_{xx} - V_{yy}$ and V_{xy} in addition to the large axial field gradient V_{zz} . As discussed in Sec. II, the magnitude of the frequency associated these additional field gradients must be much greater than ω_0 or Γ_i . By combining Eqs. (3), (6), (7), and (17) we obtain T_1 and T_2 as a function of θ .

$$T_1^{-1}(\theta) = \frac{3}{4} \omega_d^2 \{ [6z^2(1-z^2) + z^2(1-z^2)(1+r) + (1-z^2)(1-r)] F_2(\omega_0) \\ + [6(1-z^2)^2 + (z^2+1)^2(1+r) + 4z^2(1-r)] F_2(2\omega_0) \}, \quad (28a)$$

$$T_2^{-1}(\theta) = \frac{3}{16} \omega_d^2 \{ [6z^4 + (z^2+1)^2(1+r) + 4z^2(1-r)] F_2(2\omega_0) \\ + [60z^2(1-z^2) + 10z^2(1-z^2)(1+r) + 10(1-z^2)(1-r)] F_2(\omega_0) \\ + [6(3z^2-1)^2 + 9(1-z^2)^2(1+r)] F_2(0) \}, \quad (28b)$$

where $z = \cos\theta$, r is given by Eq. (18), and $F_i(\omega)$ is given by Eq. (20). When Eqs. (28) are averaged over all angles as described by Eq. (23), we obtain

$$T_{1a}^{-1} = \frac{2}{5} \omega_d^2 [(3-r)F_2(\omega_0) + (12+r)F_2(2\omega_0)], \quad (29a)$$

$$T_{2a}^{-1} = \frac{1}{10} \omega_d^2 [(12+r)F_2(2\omega_0) + (30-10r)F_2(\omega_0) + (18+9r)F_2(0)]. \quad (29b)$$

The quantity r , $-1 \leq r \leq 1$, is a measure of the strength of $V_{xx} - V_{yy}$ vs V_{xy} , $r = 1$ when $|V_{xx} - V_{yy}| \gg V_{xy}$ and

$r = -1$ when $|V_{xy}| \gg |V_{xx} - V_{yy}|$. By numerical evaluation of Eqs. (29) we obtain,

$$(T_{1a})_m|_{r=-1} = 0.612(\omega_0/\omega_d^2) , \quad (30a)$$

$$(T_{1a})_m|_{r=-1} = 0.557(\omega_0/\omega_d^2) ,$$

$$(T_{2a})_m|_{r=-1} = 0.367(\omega_0/\omega_d^2) , \quad (30b)$$

$$(T_{2a})_m|_{r=-1} = 0.370(\omega_0/\omega_d^2) ,$$

$$(T_1 T_2)_0 = 100(\omega_0/\omega_d^2)^2 / (24 - 3r)(18 + 9r) . \quad (30c)$$

As expected from the discussion in Sec. I, $(T_1)_m$ for the case of no symmetry is roughly twice as large as in the case of axial symmetry and roughly four times as large as in the case of cubic symmetry. The quantities $(T_{1a})_m$ and $(T_{2a})_m$ depend only weakly on r and as functions of r are well approximated by lines of constant slope. $(T_1 T_2)_0$, on the other hand, depends strongly on r . The nonexponential character of T_1 and T_2 in pulsed experiments on powders is more pronounced in this case than in the case of axial symmetry. This is especially true of T_2 when $\omega_0 \gg \Gamma_2$. In fact, an examination of Eq. (28a) shows that $T_2(\theta)$ is infinite when $\cos\theta = \frac{1}{3}$ if $r = -1$. Thus at low tem-

peratures when $r = -1$, the T_2 decay will be drastically nonexponential.

D. Conclusion

Although we have explicitly calculated T_1 and T_2 for only a few specific configurations of electric field gradients, our results can be used to at least semi-quantitatively describe any relevant experiment on powders. For example, a single strong electric field gradient V_{ij} with $i \neq j$ will produce effects very close to the effects described in Sec. III B. Further, if V_{zz} dominates all other electric field gradients, V_{xx} and V_{yz} will have essentially no effect.

ACKNOWLEDGMENTS

This work was supported in part by the NSF under Grant No. DMR 77-06719. The author would like to thank Dr. R. E. Norberg and Dr. M. Conradi for many interesting discussions and for helpful comments on this manuscript.

¹M. S. Conradi, K. Luszczynski, and R. E. Norberg, Bull. Am. Phys. Soc. **21**, 238 (1976).

²M. S. Conradi, K. Luszczynski, and R. E. Norberg, Phys. Rev. B **20**, 2594 (1979) (following paper).

³W. N. Hardy, Can. J. Phys. **44**, 265 (1965).

⁴R. F. Buzarak, M. Chan, and H. Meyer, Solid State Commun. **18**, 685 (1976); J. Low Temp. Phys. **28**, 415 (1977).

⁵J. R. Gaines, Y. C. Shi, and J. H. Constable, Phys. Rev. B **17**, 1028 (1978).

⁶J. R. Gaines, A. Mukherjee, and Yan-Chi Shi, Phys. Rev. B **17**, 4188 (1978).

⁷C. C. Sung, Phys. Rev. **167**, 271 (1968).

⁸For a brief description of the use of the irreducible spin

multiple operators see P. A. Fedders, Phys. Rev. B **11**, 995 (1975), and references therein.

⁹See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University, London, 1961) or M. Bloom and I. Oppenheim, Can. J. Phys. **41**, 1580 (1963). The derivation in terms of the irreducible multipole operators is very close to the derivation of similar quantities in Ref. 8.

¹⁰P. A. Fedders, Phys. Rev. B **10**, 4510 (1974).

¹¹M. Bloom, I. Oppenheim, M. Lipsicas, C. G. Wade, and C. F. Yarnell, J. Chem. Phys. **43**, 1036 (1965).

¹²W. J. Hardy and J. R. Gaines, Phys. Rev. Lett. **19**, 1417 (1967).