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Properties of Solid Hydrogen. II. Theory of Nuclear Magnetic Resonance and Relaxation*

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Various NMR properties of solid H_2 and D_2 are studied, and the following results are obtained. The leading terms in the high-temperature expansion of the second moment $M_2(T)$ for H_2 are $M_2(T) = M_2(\infty) + \frac{125}{3} d^2 x(1-x)\ (\beta\Gamma)^4\ (1 - 2\beta\Gamma - \frac{415}{64}\beta\Gamma x)$, where $M_2(\infty)$ is the Van Vleck term, Γ is the electric quadrupole-quadrupole coupling constant, $\beta \equiv 1/kT$, and x is the concentration of $(J=1)$ molecules. For H_2, this expression fits the data qualitatively for $T \geq 5\ {}^\circ\mathrm{K}$. For D_2, the observed second moment agrees with our calculations only for very small or very large values of x. For intermediate values of x, the observed second moment is much smaller than expected, which leads us to propose that the resonance of the $(J=1)$ molecules is too broad to be observable. Under this assumption, we find a temperature-dependent contribution at 5 °K about 100 times smaller than that given above, in rough agreement with experiment. For H_2, a reasonable fit to the fourth moment M_4 is obtained by the relation

$$M_4(T) - M_4(\infty) \approx \tfrac{16}{3} M_2(\infty)\ [M_2(T) - M_2(\infty)],$$

which is derived by decoupling certain averages required in the otherwise rigorous moment calculation at high temperatures. The spin-lattice relaxation time T_1 is calculated by extending the Gaussian approximation for the spectral functions to finite temperatures. The high-temperature result is $T_1 = 0.780\ (\Gamma/hc_0)\ x^{1/2}(1 - \frac{9}{14}\beta\Gamma - \frac{1857}{1792}\beta\Gamma x)^{1/2}$ for H_2, and $T_1 = 5.12\ (\Gamma/hc_0) \times x^{1/2}(1 - \frac{9}{14}\beta\Gamma - \frac{1857}{1792}\beta\Gamma x)^{1/2}$ for $(J=1)$ molecules in D_2. At low concentrations we modify the results of Sung and find $T_1 = 2.53\, x^{5/3}\Gamma^{-1}$ for H_2, and $T_1 = 18.7\, x^{5/3}\Gamma^{-1}$ for $(J=1)$ molecules in D_2, if T_1 is in seconds and Γ in cm^{-1}. These formulas reproduce the concentration dependence of T_1 in H_2 and D_2 very consistently over the entire concentration range $x \geq 0.005$. For a quantitative fit to experiment one must take Γ/Γ_0 between 0.6 and 0.65 for both H_2 and D_2, values which are slightly smaller than obtained from other experiments. Here Γ_0 is the rigid-lattice value of Γ. Both the resonance and the relaxation data tend to confirm that in the solid all interactions must be renormalized to take account of lattice vibrations. We also obtain explicit analytic results for T_1 in the ordered phases of H_2 and D_2 due to libron scattering, making use of the libron density of states calculated by Mertens *et al.* At present the data are too scanty for a meaningful comparison with theory. Finally, we calculate the Pake splitting of $(J=0)$ D_2 molecules in the ordered phase to be $8.8x$ kHz. This prediction has recently been confirmed by experiment.

I. INTRODUCTION

This paper is the second in a series of detailed treatments of the properties of solid hydrogen.[1] In the first of these[2] we discussed the various interactions between molecules. In particular, we showed that the electric quadrupole-quadrupole (EQQ) interactions were renormalized by static and dynamic phonon modulation in the solid. The present paper is devoted to a discussion of nuclear-magnetic-resonance (NMR) properties of solid hydrogen. Other papers in this series deal with the analysis of the high-temperature orientational specific heat of solid hydrogen and the interpretation of Raman and infrared spectra of nearly pure para H_2. The ultimate objective of this program is to show that the orientational properties of solid hydrogen can be understood on the basis of interactions between molecules which are derived from first principles. Beyond this objective one might hope to arrive at a complete first-principles understanding of the properties of solid hydrogen.

This paper is organized as follows. In Sec. II we review the interactions between molecules in solid hydrogen. We quote some results for the renormalized interactions between molecules in the solid. Here we also discuss the interactions between nuclear spins and molecular rotations based on the Hamiltonian given by Ramsey.[3] In Secs. III and IV we present a calculation of the second and fourth moments of the NMR absorption spectrum as a function of temperature. Intermolecular dipolar interactions lead to temperature-independent moments, as has been discussed by Van Vleck[4] some time ago, and these are in agreement with experiment. The intramolecular interactions are shown to give temperature-dependent contributions to the moments, which can be evaluated using a high-temperature expansion. The two leading terms in this series are evaluated and for H_2 reasonable agreement with experiment[5] is obtained considering the fact that such high-temperature expansions converge slowly at the temperature in question.[6] For D_2, agreement between theory and experiment[7] is only obtained at very high or very low $(J=1)$ concentration. As an explanation we suggest that at intermediate concentration perhaps only the ortho $(J=0)$ molecules effectively contribute to the moments. A calculation of the temperature dependence of the second moment based on this assumption is in qualitative agreement with experiment.

In Sec. V we study the dynamical behavior of a pair of $(J=1)$ molecules subject to EQQ interactions. We compute exactly the spectral weight functions of all the independent correlation functions. These calculations are of constant use in later sections.

Sections VI–VIII deal with the spin-lattice relaxation time T_1. In Sec. VI we extend the Gaussian approximation[8] to the spectral functions which determine T_1. The fact that the two leading terms in the high-temperature expansion lead to values of T_1 in reasonable agreement with experiment may be slightly fortuitous. This point is being studied at present by extending the number of terms in the series. Here we show that the fourth moment at infinite temperature is consistent with a Gaussian shape for the spectral functions. From our study we conclude that the dependence of T_1 on the orientation of the magnetic field is too small to be observed at present.

In Sec. VII we study T_1 in the regime of low concentrations of $(J=1)$ molecules. We show that the agreement with experiment[9,10] achieved by Sung's theory[10] is fortuitous, although his physical mechanism is undoubtedly correct. We use an improved approximation in the statistical model[11] which appears to be rigorous in the low-concentration limit. Accordingly, it is surprising that although the concentration dependence is correctly reproduced, the absolute magnitudes of the theoretical values of T_1 are 50% larger than the experimental values.

In Sec. VIII we calculate the spin-lattice relaxation time for $(J=1)$ molecules in the orientationally ordered phase. Our analytic results are based on the density of states for libron excitations given by Mertens *et al.*[12] While the qualitative features of the experimental results[13–15] agree with the calculations, a detailed comparison of theory with experiment cannot be made until more extensive experimental data are available.

In Sec. IX we calculate the NMR spectrum of $(J=0)$ molecules in the orientationally ordered phase. We point out that $(J=0)$ D_2 molecules should display a Pake splitting similar to, but smaller than that of $(J=1)$ molecules.[5,16,17] This splitting is caused by partial ordering of $(J=0)$ molecules via EQQ interactions which cause distortions in the $(J=0)$ state. This Pake splitting is calculated to be $8.8x$ kHz, where x is the concentration of $(J=1)$ molecules. The magnitude and concentration dependence agree rather well with experiment.[7] This Pake splitting also explains the anomalous width in the $(J=0)$ resonance seen by Gaines *et al.*[17] previously.

Finally, in Sec. X we summarize briefly the conclusions reached on the basis of the various calculations presented here. On the whole, we conclude that our calculations provide a reasonable understanding of the NMR behavior of solid hydrogen.

For completeness we should note certain NMR phenomena which we have not discussed. For example, we do not consider nuclear spin-lattice relaxation in the diffusion-dominated regime. This phenomenon has been studied experimentally by Bloom[18] and others.[19] The experimental results are in good agreement with the calculations of Moriya[20] and Moriya and Motizuki.[8] Also, we do not discuss the observation of pair interactions via the characteristic line shape of isolated pairs of $(J=1)$ molecules in otherwise pure $(J=0)$ hydrogen. From the temperature dependence of the Pake splitting, Harris *et al.*[21] were able to determine the effective EQQ coupling constant for nearest neighbors. Lastly, we do not discuss the temperature dependence of the Pake splitting either for H_2[5,16] or for D_2[7,17] in the ordered phase. We note that the treatment of Raich and Etters[22] using the random-phase approximation does not accurately reproduce the temperature dependence of these splittings.[5,7]

II. INTERACTIONS INVOLVING MOLECULES AND NUCLEI

A. Orientational Interactions between Molecules

The purpose of this section is first to review the interactions between molecules in solid hydrogen, and secondly to obtain a few simple results which will be useful in the course of this work. As Nakamura[23] first showed, the orientationally dependent part of the intermolecular potential is dominated by the EQQ interaction. The EQQ Hamiltonian can be written as[24]

$$\mathcal{H}_{\mathrm{EQQ}} = \tfrac{20}{9}\pi\Gamma_0\,(70\pi)^{1/2}\sum_{mn} C(2,2,4;m,n)\,Y_2^m(\omega_1)\,Y_2^n(\omega_2) \times Y_4^{m+n}(\Omega_{12})^* . \qquad (2.1)$$

In Table I we give the values of the EQQ coupling constant Γ_0, defined by

$$\Gamma_0 \equiv \Gamma_0(R_0) = (6e^2Q^2/25R_0^5) , \qquad (2.2)$$

where eQ is the quadrupole moment of the molecule[25,26] and R_0 is the equilibrium intermolecular separation.[27–30] Also $C(2,2,4;m,n)$ is a Clebsch-Gordan coefficient,[31] $Y_L^M(\omega)$ is a spherical harmonic using the phase convention of Rose,[31] where ω_i and Ω_{12} specify the orientations of the axis of molecule i and the vector $\vec{r}_{12}=\vec{r}_1-\vec{r}_2$, connecting the centers of gravity of the two molecules, respectively. In Eq. (2.1) the quantization axis is arbitrary. If

TABLE I. Molecular and intermolecular constants for hydrogen.

Symbol	Eq.	H_2	D_2	Ref.
a (kHz)	(2.15)	$4.258H_0$ [a]	$0.6536H_0$	39
b (kHz)	(2.15)	$0.6717H_0$	$0.3368H_0$	39
c (kHz)	(2.15)	113.9	8.773	39
d_M (kHz)	(2.16c)	57.67	2.74	39
d_Q (kHz)	(2.16d)	0	22.50	39
d (kHz)	(3.8)	57.67	25.24	39
B (cm^{-1})	(9.3)	59.34	29.91	40
Q (a.u.)	(2.2)	0.4883	0.4783	26
Γ_0 (cm^{-1})	(2.2)	0.698	0.842	See 2
K_0 (Hz)	(2.18)	2278	61.12	39, 27–31
Q_N (cm^2)	(2.15)		2.74×10^{-27}	39

[a] Here H_0 is the applied magnetic field.

we specialize to the case when the quantization axis is taken parallel to $\vec{r}_{12}$, we obtain

$$\mathcal{H}_{\mathrm{EQQ}} = \tfrac{10}{3}\pi\Gamma_0(70)^{1/2}\sum_m C(2, 2, 4; m, -m)\, Y_2^m(\omega_1) \times Y_2^{-m}(\omega_2)\ . \tag{2.3}$$

It will often be convenient to use the operator equivalents, i.e., the irreducible tensor operators $\mathcal{T}_L^M(J)$ within the manifold $J=1$,

$$Y_L^M(\omega) = \alpha_L \mathcal{T}_L^M(J)\ , \tag{2.4}$$

where

$$\alpha_2 = -\tfrac{2}{5}, \quad \alpha_1 = 0, \quad \alpha_0 = 1, \tag{2.5}$$

and the tensor operators are given in Table II. Also, within $J=1$ these operators obey

$$[\mathcal{T}_L^M(J), \mathcal{T}_{L'}^{M'}(J)] = \sum_{L''} \alpha(L, L', L'')\, C(L, L', L''; M, M')\, \mathcal{T}_{L''}^{M+M'}(J), \tag{2.6a}$$

$$\tfrac{1}{2}\{\mathcal{T}_L^M(J), \mathcal{T}_{L'}^{M'}(J)\}_+ = \sum_{L''} \beta(L, L', L'')\, C(L, L', L''; M, M')\, \mathcal{T}_{L''}^{M+M'}(J), \tag{2.6b}$$

$$\mathcal{T}_L^M(J)\, \mathcal{T}_{L'}^{M'}(J) = \sum_{L''} \gamma(L, L', L'')\, C(L, L', L''; M, M')\, \mathcal{T}_{L''}^{M+M'}(J)\ , \tag{2.6c}$$

where obviously

$$\gamma(L, L', L'') = \tfrac{1}{2}\alpha(L, L', L'') + \beta(L\ , L', L''). \tag{2.7}$$

TABLE II. Irreducible tensor operators.

L	2	1	0
$\mathcal{T}_L^0(J)$	$(5/16\pi)^{1/2}(3J_z^2-2)$	$(3/4\pi)^{1/2}J_z$	$(1/4\pi)^{1/2}$
$\mathcal{T}_L^{\pm1}(J)$	$\mp(15/32\pi)^{1/2}(J_zJ_\pm + J_\pm J_z)$	$\mp(3/8\pi)^{1/2}J_\pm$	0
$\mathcal{T}_L^{\pm2}(J)$	$(15/32\pi)^{1/2}J_\pm^2$	0	0

Note that α vanishes when $L+L'+L''$ is even and β vanishes when $L+L'+L''$ is odd. The coefficients $\alpha(L_1, L_2, L_3)$ and $\beta(L_1, L_2, L_3)$ are given in Table III. With the normalization of the $\mathcal{T}_L^M(J)$ taken in analogy with the $Y_L^M(\omega)$ as indicated by Eq. (2.4) one has the convenient relation within a manifold of constant J,

$$(2J+1)^{-1}\,\mathrm{Tr}[\mathcal{T}_L^M(J)\,\mathcal{T}_L^{-M}(J)\,(-1)^M] = (4\pi)^{-1}\prod_{m=0}^{L-1}[X - \tfrac{1}{4}m(m+2)]\ , \tag{2.8}$$

where $X = J(J+1)$.

In terms of these tensor operators the analogs of Eqs. (2.1) and (2.3) are

$$\mathcal{H}_{\mathrm{EQQ}} = \tfrac{16}{45}\pi\Gamma_0(70\pi)^{1/2}\sum_{mn} C(2, 2, 4; m, n)\, \mathcal{T}_2^m(J_1) \times \mathcal{T}_2^n(J_2)\, Y_4^{m+n}(\Omega_{12})^*, \tag{2.9a}$$

$$\mathcal{H}_{\mathrm{EQQ}} = \tfrac{8}{15}\pi\Gamma_0(70)^{1/2}\sum_m C(2, 2, 4; m, -m)\, \mathcal{T}_2^m(J_1) \times \mathcal{T}_2^{-m}(J_2). \tag{2.9b}$$

In I we discussed various types of interactions and how these interactions were modified in the solid by lattice vibrations and dielectric screening. Although the calculation can be improved,[32] the main trends are already apparent. We concluded that the EQQ coupling constant Γ_0 should be replaced by an effective renormalized constant Γ_{eff}. In that calculation we included not only the static effect, i.e., averaging the orientational interaction over the phonon motion, but also the dynamical effects caused by collisions between the phonons and the molecular rotations. Thus, for fcc-ordered hydrogen we found the values

$$\Gamma_{\mathrm{eff}}/\Gamma_0 = 0.84 \ \text{ for } H_2\ , \tag{2.10a}$$

$$\Gamma_{\mathrm{eff}}/\Gamma_0 = 0.84 \ \text{ for } D_2\ , \tag{2.10b}$$

whereas for nearest-neighbor pair interactions in nearly pure ($J=0$) hydrogen we found the renormalized coupling constant to be

$$\Gamma_{\mathrm{eff}}^{\mathrm{pairs}}/\Gamma_0 = 0.94 \ \text{ for } H_2\ , \tag{2.11a}$$

$$\Gamma_{\mathrm{eff}}^{\mathrm{pairs}}/\Gamma_0 = 0.92 \ \text{ for } D_2\ . \tag{2.11b}$$

The dynamical effects for concentrated ($J=1$) hydrogen in the disordered hcp phase were not calculated

TABLE III. Values of $\alpha(L_1, L_2, L_3)$ and $\beta(L_1, L_2, L_3)$. For typographical convenience the table gives values of $\pi^{1/2}\alpha$ and $\pi^{1/2}\beta$, e.g., $\alpha(2, 2, 1) = \frac{5}{8}(30/\pi)^{1/2}$.

$\alpha(2, 2, 1) = \frac{5}{8}\sqrt{30}$	$\alpha(2, 1, 2) = -\frac{3}{2}\sqrt{2}$	$\alpha(1, 2, 2) = -\frac{3}{2}\sqrt{2}$
$\alpha(1, 1, 1) = \frac{1}{2}\sqrt{6}$	$\beta(1, 1, 2) = \frac{1}{10}\sqrt{30}$	$\beta(2, 2, 2) = \frac{1}{8}\sqrt{70}$
$\beta(2, 2, 0) = \frac{5}{4}\sqrt{5}$	$\beta(2, 1, 1) = -\frac{5}{8}\sqrt{2}$	$\beta(1, 1, 0) = -\sqrt{3}$
$\beta(1, 2, 1) = \frac{5}{8}\sqrt{2}$	$\beta(2, 0, 2) = \frac{1}{2}$	$\beta(0, 2, 2) = \frac{1}{2}$
$\beta(1, 0, 1) = \frac{1}{2}$	$\beta(0, 1, 1) = \frac{1}{2}$	$\beta(0, 0, 0) = \frac{1}{2}$

explicitly. However, it was argued that these effects were scaled by the parameter $E^2/(k\theta_D)$, where E is proportional to the orientational energy and θ_D is the Debye temperature. Accordingly, at high temperatures ($kT \gg \Gamma$) where the orientational energy is small, the dynamical effects can be neglected, and only static effects and dielectric screening need to be considered. Denoting this limit by the superscript HT, we thus have

$$\Gamma_{\text{eff}}^{\text{HT}}/\Gamma_0 = 0.87 \quad \text{for } H_2 , \tag{2.12a}$$

$$\Gamma_{\text{eff}}^{\text{HT}}/\Gamma_0 = 0.88 \quad \text{for } D_2 . \tag{2.12b}$$

Also note that distant neighbors should not be renormalized by lattice vibrations since the relative vibrations of distant molecules affect these interactions in a negligible way. We will neglect this refinement and will renormalize all interactions by the same factor. Actually, this turns out to be quite a satisfactory procedure, because although the further-neighbor interactions are reduced less than the nearest-neighbor interactions by phonon renormalization, the dielectric screening becomes more effective for more distant neighbors.[2] Since these two dependences on separation tend to cancel, they can safely be neglected, which justifies renormalizing all interactions in the same way.

From I it is apparent that for nearest neighbors other pairwise and three-body interactions are negligible in comparison to the EQQ interactions and, accordingly, we can neglect them for the purposes of this paper. For widely separated molecules we must consider other interactions, as for instance, the single-molecule crystal-field Hamiltonian

$$\mathcal{H}_c = V_c(J_z^2 - \tfrac{2}{3}) , \tag{2.13}$$

where $|V_c|$ was determined by Hardy and Gaines[33] and by Gaines *et al.*[34] to be about 0.006 cm^{-1}. Also in I we showed that at sufficiently large separations the indirect interaction caused by the virtual emission and absorption of a phonon (the analog of the Suhl-Nakamura[35, 36] interaction in magnetic materials) becomes dominant. The form of this interaction was given in I. Here we need only the result for the root mean square interaction energy ΔE,

$$\Delta E = C_{\text{SN}}\, x , \tag{2.14}$$

assuming the separation at ($J=1$) concentration x is approximately $R_0 x^{-1/3}$. Here C_{SN} is a constant depending critically on the renormalized orientationally dependent intermolecular potential. Using the most reliable estimates of the bare potentials and using a renormalization procedure based on the theory of quantum crystals,[37, 38] we obtained the value $C_{\text{SN}} = 0.022$ cm^{-1}. Since the EQQ energy per molecule is about $2\Gamma x^{5/3}$, we see that there are two regimes. In regime A, for $x \geq 0.003$, the interaction energy is primarily due to EQQ interactions, whereas in regime B, for $x \leq 0.003$, the interaction energy is mainly due to the indirect interactions via phonons. Here we shall mainly be concerned with regime A, and, hence, the indirect interactions will not play a role in our calculations.

B. Interactions Involving Nuclear Spins

Next, let us consider the interactions involving the nuclear spins. We use the spin-rotation Hamiltonian $\mathcal{H}_{\text{SR}}$ given by Ramsey[39] for noninteracting D_2 or H_2 molecules in their electronic ground states:

$$\begin{aligned} h^{-1}\mathcal{H}_{\text{SR}} = {} & - aI_z - bJ_z - c\,\vec{I}\cdot\vec{J} \\ & + (\mu/i)^2\langle r^{-3}\rangle[\vec{i}^{(1)}\cdot\vec{i}^{(2)} - 3(\vec{i}^{(1)}\cdot\hat{n})(\vec{i}^{(2)}\cdot\hat{n})] \\ & + eQ_N\frac{\partial^2 V_e}{\partial z_0^2}\,[3(\vec{i}^{(1)}\cdot\hat{n})^2 \\ & + 3(\vec{i}^{(2)}\cdot\hat{n})^2 - 2i(i+1)] . \end{aligned} \tag{2.15}$$

Here the first two terms represent the Zeeman energy of the nuclear spins and the Zeeman energy of the magnetic moment associated with molecular rotation, respectively, where I is the total nuclear spin, $I = i^{(1)} + i^{(2)}$, and $i^{(1)}$ and $i^{(2)}$ are the nuclear spins, each of magnitude i, the superscripts being used to distinguish the two nuclei. The third term represents the interaction of the nuclear spins with the magnetic field caused by the molecular rotation currents. The fourth term is the internuclear dipolar interaction, where μ is the magnetic moment of the nuclei, $\hat{n}$ is the orientation of the molecular axis, and $\langle r^{-3}\rangle$ is the average of r^{-3} over the electronic ground state, where r is the internuclear separation. The last term in Eq. (2.15) represents the interaction of the quadrupole moments of the nuclei with the electric field gradients caused by the charge distribution in the molecule, where $\partial^2 V_e/\partial z_0^2$ is the electric field gradient along the internuclear axis due to the molecular charge distribution and Q_n is the deuteron quadrupole moment. One defines

$$d_M = \tfrac{4}{5}\,\mu^2\langle r^{-3}\rangle \quad \text{for } H_2 , \tag{2.16a}$$

$$d_M = \tfrac{2}{5}\,\mu^2\langle r^{-3}\rangle \quad \text{for } D_2 . \tag{2.16b}$$

Since $i = \frac{1}{2}$ for H_2 and $i = 1$ for D_2,[40] one can write this as

$$d_M = (2\mu^2/5i)\langle r^{-3}\rangle \quad \text{for } H_2,\ D_2 . \tag{2.16c}$$

Also, we define

$$d_Q = \tfrac{2}{5}\, eQ_N\frac{\partial^2 V_e}{\partial z_0^2} \quad \text{for } D_2 , \tag{2.16d}$$

$$d_Q = 0 \qquad \text{for } H_2 . \tag{2.16e}$$

The constants[39, 40] appearing in Eqs. (2.15) and (2.16) are listed in Table I.

Finally, we take account of the dipolar interaction between nuclear spins in different molecules through the term $\mathcal{H}_{\mathrm{Dip}}$, where

$$\mathcal{H}_{\mathrm{Dip}}=g^2\beta^2\sum_{i<j}R_{ij}^{-3}[\vec{\mathrm{I}}_i\cdot\vec{\mathrm{I}}_j-3(\vec{\mathrm{I}}_i\cdot\hat{R}_{ij})(\vec{\mathrm{I}}_j\cdot\hat{R}_{ij})] \quad . \tag{2.17}$$

For nearest neighbors we found in I a renormalization due to phonon interactions which indicated that we should replace the intermolecular dipolar-interaction constant for a rigid lattice K_0, defined as

$$K_0=g^2\beta^2/R_0^3h, \tag{2.18}$$

by a renormalized interaction constant $K_{\mathrm{eff}}=\xi_{32}K_0$, where

$$\xi_{32}\approx 0.97 \tag{2.19}$$

for both H_2 and D_2. Further-neighbor interactions should not be renormalized.

C. Summary

To summarize: The model of solid hydrogen that we consider is the following. The nuclear spins are described by the Hamiltonians of Eqs. (2.15) and (2.17) and the molecular rotations are described by the Hamiltonian of Eq. (2.9), the coupling constants being renormalized in each case as discussed above.

III. MOMENTS OF NMR ABSORPTION LINE IN H_2

A. Formulation

In this section we derive expressions for the second and fourth moments, M_2 and M_4, of the NMR absorption spectrum in solid H_2. In various subsections these expressions are evaluated using high-temperature expansions. The NMR line shapes at low temperatures in the disordered phase involve rather complicated calculations and will be treated in a separate publication. Except for the absorption spectrum of isolated pairs of $(J=1)$ molecules,[21] little progress has been made towards interpreting the line shapes in that regime. The line shape in the ordered phase is essentially dependent on a calculation of the order parameter. In order to reproduce quantitatively the temperature dependence of the order parameter implied by the temperature dependence of the Pake splitting in the cubic phase it would be necessary to make some modifications to the existing libron-wave theories.[12,22,41,42] Such calculations are beyond the scope of the present work and will not be considered further.

Our discussion will be based on the Hamiltonians of Eqs. (2.15) and (2.17). First we note that the EQQ interaction energy is much larger than the nuclear-spin energies. This comparison implies that the rotational-correlation times are short in comparison to the times corresponding to the various nuclear-spin energies. Consequently, the rotational variables appearing in Eq. (2.15) can be replaced by their thermodynamic averages. The contribution to the second moment which we lose by discarding the fluctuation terms can be estimated[43] to be of order $T_1^{-1}\,M_2^{1/2}$, where T_1 is the nuclear spin-lattice relaxation time. Since normally one has

$$M_2^{1/2}\,T_1\gg 1\ , \tag{3.1}$$

the fluctuation terms can be neglected. We also confine our attention to sufficiently low temperatures ($T<9$ °K for H_2 and $T<14$ °K for D_2) that the effects of thermally activated diffusion[44] can be neglected. These effects have been considered by Moriya[20] and Moriya and Motizuki[8] and their calculations agree reasonably well with the experimental data of Bloom.[18] We will further assume that the magnetic energies ha, hb, and hc are negligible in comparison to kT, as is normally the case, so that

$$\langle\,\vec{\mathrm{J}}_i\rangle_T=0\ . \tag{3.2}$$

Here the bracket $\langle\;\rangle_T$ indicates a thermodynamic average at temperature T. Also we confine ourselves to the high-field limit $a\gg d$, in which case one calculates the moments of the NMR spectrum near $\nu_0\equiv a$ from the truncated Hamiltonian[45]

$$h^{-1}\mathcal{H}'=\textstyle\sum_i(\mathcal{H}_{Z\,i}+\mathcal{H}_{D\,i})+\mathcal{H}_{DD}\ , \tag{3.3}$$

where

$$\mathcal{H}_{Z\,i}=-aI_{iz}\ , \tag{3.4a}$$

$$\mathcal{H}_{Di}=-(d_MA_i/3i)\,(3i_{zi}^{(1)}\,i_{zi}^{(2)}-\vec{\mathrm{i}}_i^{(1)}\cdot\vec{\mathrm{i}}_i^{(2)})\ , \tag{3.4b}$$

$$\mathcal{H}_{DD}=\sum_{i<j}B_{ij}(\vec{\mathrm{I}}_i\cdot\vec{\mathrm{I}}_j-3I_{iz}I_{jz})\ . \tag{3.4c}$$

Here the subscripts label the molecules and the superscripts the nuclei, and we set

$$B_{ij}=\tfrac{1}{2}K_{\mathrm{eff}}(3\cos^2\theta_{ij}-1)\ ,\quad i,j\ \text{nearest neighbors} \tag{3.5a}$$

$$=0\ ,\qquad i=j \tag{3.5b}$$

$$=\tfrac{1}{2}K_0(R_0/R_{ij})^3\,(3\cos^2\theta_{ij}-1)\ ,\quad\text{otherwise} \tag{3.5c}$$

$$A_i\equiv\tfrac{15}{4}\langle\,3\cos^2\theta_i-1\rangle_T\ , \tag{3.5d}$$

where θ_{ij} is the angle between the vectors $\vec{\mathrm{R}}_{ij}$ and $\vec{\mathrm{H}}_0$ and θ_i is the angle between the vectors $\hat{n}_i$ and $\vec{\mathrm{H}}_0$.

Still, there are two possible cases depending on the relative sizes of $\mathcal{H}_{DD}$ and $\mathcal{H}_{Di}$. If the former dominates, then the moments can be calculated from the truncated Hamiltonian of Eq. (3.3). In the reverse case one must further truncate the intermolecular interaction. As we shall see, $\mathcal{H}_{DD}$ is responsible for the temperature-independent contribution to M_2, whereas the temperature-dependent contributions to M_2 can be attributed to $\mathcal{H}_{Di}$. Accordingly, the condition that Eq. (3.3) be the correct truncated Hamiltonian is

$$[M_2(T)-M_2(\infty)]\ll M_2(\infty)\ . \tag{3.6}$$

Even if this condition is not strictly fulfilled, use of Eq. (3.3) probably does not lead to a great error.[46] This conclusion follows from the result of Ishiguro *et al.*[47] that the second moment of one peak of the fully split Pake doublet is $\frac{5}{6}$ that of the unsplit line. Hence, in the interest of simplicity we will use Eq. (3.3).

For H_2 this truncated Hamiltonian can be written in terms of the total nuclear spins as follows:

$$h^{-1}\mathcal{H}' = -a\sum_i I_{iz} - \tfrac{1}{3}d\sum_i A_i[3I_{zi}^2 - I_i(I_i+1)] + \tfrac{1}{2}\sum_{ij} B_{ij}(\vec{\mathrm{I}}_i\cdot\vec{\mathrm{I}}_j - 3I_{zi}I_{zj}) \,, \tag{3.7}$$

where by convention one writes (for both H_2 and D_2)

$$d = d_M + d_Q \,. \tag{3.8}$$

In Eq. (3.7) the sums are restricted to $I=1$, i.e., odd J molecules. As is evident from Ref. 45, the moments M_2 and M_4 are given by

$$I_0M_2 = \langle (\textstyle\sum_i D_i^+)(\sum_j I_j^-)\rangle_T \,, \tag{3.9a}$$

$$I_0M_4 = \langle (\textstyle\sum_i D_i^+)(\sum_j D_j^-)\rangle_T \,, \tag{3.9b}$$

where

$$I_0 = \sum_{ij}\langle I_i^+ I_j^-\rangle_T \tag{3.10a}$$

$$\approx \tfrac{4}{3}Nx \,, \tag{3.10b}$$

Here N is the total number of molecules, x is the fraction of $(J=1)$ molecules, and

$$D_i^{\pm} = [\mathcal{H}', [\mathcal{H}', I_i^{\pm}]\,] \,. \tag{3.11}$$

After a tedious calculation one obtains

$$\begin{aligned} h^{-2}\sum_i D_i^+ = {} & \sum_{ijk\neq}[I_i^+I_j^+I_k^-\tfrac{3}{4}(B_{ij}B_{ik}+B_{ij}B_{jk}-2B_{ik}B_{jk}) \\ & + I_i^+I_{jz}I_{kz}(6B_{ij}B_{ik}+\tfrac{3}{2}B_{ik}B_{jk}+\tfrac{3}{2}B_{ij}B_{jk})] \\ & + \sum_{ij}\{(I_i^+)^2I_j^-(-\tfrac{3}{2}B_{ij}^2+dA_iB_{ij}) \\ & + I_{jz}(I_i^+I_{iz}+I_{iz}I_i^+)(\tfrac{3}{2}B_{ij}^2+5dA_iB_{ij}) \\ & + I_i^+[3I_j(I_j+1)B_{ij}^2+(3I_{jz}^2-I_j(I_j+1)) \\ & \times(\tfrac{3}{2}B_{ij}^2+dA_iB_{ij})]\} \\ & + \sum_i d^2A_i^2I_i^+(1+2I_{iz})^2 \,, \end{aligned} \tag{3.12}$$

where $\neq$ means i, j, and k are all distinct.

B. Van Vleck Moments

Substituting Eq. (3.12) into Eq. (3.9a) we find

$$M_2 = \frac{\sum_i X_i(d^2A_i^2 + 3\sum_j B_{ij}^2X_j)}{\sum_i X_i} \,, \tag{3.13}$$

where

$$X_i = I_i(I_i+1) \,. \tag{3.14}$$

Instead of restricting the sums in Eq. (3.12) to $(I=1)$ molecules, we can define $A_i=0$ for $I_i=0$. We need to take the powder and alloy averages of the quantities in Eq. (3.13). We will indicate these averages by double brackets, $\langle\langle\ \rangle\rangle_{pa}$, with the subscripts p and a, respectively. To take the powder average we express the spherical harmonics with respect to the crystal axis rather than to the magnetic field:

$$(3\cos^2\theta_{ij}-1) = (\tfrac{16}{5}\pi)^{1/2}Y_2^0(\hat{r}_{ij})_{\hat{H}} \tag{3.15a}$$

$$= (\tfrac{16}{5}\pi)^{1/2}\textstyle\sum_\rho D_{\rho 0}^{(2)}(\chi_{\hat{c}\hat{H}})\,Y_2^\rho(\hat{r}_{ij})_{\hat{c}} \tag{3.15b}$$

$$= (\tfrac{8}{5}\pi)\textstyle\sum_\rho Y_2^\rho(\hat{H})_{\hat{c}}^*\,Y_2^\rho(\hat{r}_{ij})_{\hat{c}} \,. \tag{3.15c}$$

Here the outermost unit-vector subscript indicates the quantization axis, $D_{mn}^{(J)}(\chi_{uv})$ is the rotation matrix[31] and χ_{uv} is the triad of Euler angles which take the u coordinate system into the v coordinate system.[31] Thus,

$$\langle\langle B_{ij}^2\rangle\rangle_p = \tfrac{1}{5}K_{\mathrm{eff}}^2 \,, \quad i,j \text{ nearest neighbors} \tag{3.16a}$$

$$= 0, \qquad i=j \tag{3.16b}$$

$$= \tfrac{1}{5}K_0^2(R_0/R_{ij})^6, \quad \text{otherwise} \tag{3.16c}$$

$$\langle\langle A_i^2\rangle\rangle_p = 45\pi\textstyle\sum_\rho |\langle Y_2^\rho(\omega_i)\rangle_T|^2 \,, \tag{3.16d}$$

where the quantization axis in Eq. (3.16d) is arbitrary. Assuming a random configuration of even- and odd-J molecules, one has the alloy average

$$\langle\langle X_i\rangle\rangle_a \equiv \langle\langle X\rangle\rangle = 2x \,. \tag{3.17}$$

In this way one obtains from Eq. (3.13) the result

$$M_2 = M_2^{\mathrm{inter}} + M_2^{\mathrm{intra}} \,, \tag{3.18}$$

where the contributions M_2^{inter} and M_2^{intra} are due, respectively, to inter- and intramolecular interactions of the nuclear spins and are given as

$$M_2^{\mathrm{inter}} = \tfrac{6}{5}x[(S_0-12)K_0^2 + 12K_{\mathrm{eff}}^2] \,, \tag{3.19a}$$

$$M_2^{\mathrm{intra}} = 9d^2\pi\langle\langle\textstyle\sum_l|\langle Y_2^l(\omega_i)\rangle_T|^2\rangle\rangle_a \,, \tag{3.19b}$$

where the alloy average over $(I=1)$ molecules is understood in Eq. (3.19b), and where S_0 in Eq. (3.19a) is

$$S_0 = \textstyle\sum_j (R_0/R_{ij})^6 \,. \tag{3.20}$$

The sum has been evaluated numerically for an hcp lattice by Kihara and Koba,[48] who give $S_0 = 14.445$.

Since we discuss the evaluation of M_2^{intra} via a high-temperature expansion in Sec. III C, we only make a few general remarks here about the form of Eq. (3.19). Note that M_2^{inter} is temperature independent, whereas M_2^{intra} is strongly temperature dependent and vanishes at infinite temperature.[49] The approximation of a random alloy is probably reasonable except at low temperature and low $(J=1)$ concentration where clustering[50,51] of $(J=1)$ molecules can be significant. Also, we note that Eq. (3.19b) is invariant with respect to the choice of quantization axis, so we can make whatever choice is convenient.

Similarly, we obtain from Eq. (3.9b) and (3.12) the following expression for M_4:

$$M_4 = (\sum_i \tfrac{2}{3}X_i)^{-1}[\sum_i \tfrac{8}{105}X_i(X_i - \tfrac{3}{4})\,(7X_i - 12)\,d^4A_i^4 + \tfrac{4}{15}\sum_{ij} X_i(X_i - \tfrac{3}{4})X_j(9B_{ij}^4 + 12dA_iB_{ij}^3 + 32d^2A_i^2B_{ij}^2) + 6\sum_{ij} X_iX_j^2B_{ij}^4 + \sum_{ijk\neq} X_iX_jX_k \times (14B_{ij}^2B_{ik}^2 + 4B_{ij}^2B_{jk}B_{ki})]\,. \tag{3.21}$$

For $A_i = 0$ this expression agrees with that of Van Vleck.[4] We write this result as

$$M_4 = M_4^{\text{inter}} + M_4^{\text{intra}} + M_4^{\text{cross}}, \tag{3.22}$$

where the terms on the right-hand side of this equation are, respectively, the contributions to M_4 from the intermolecular interactions, intramolecular interactions, and cross terms involving both types of interactions. We shall give results for the temperature-independent Van Vleck term M_4^{inter} here. The other terms will be treated in a later subsection. By repeated use of Eq. (3.15) the powder average of Eq. (3.22) can be evaluated. Also, to evaluate the alloy average one needs to use

$$\langle\langle X_i^2\rangle\rangle_a \equiv \langle\langle X^2\rangle\rangle = 4x\,. \tag{3.23}$$

Thus we find for a rigid lattice

$$M_4^{\text{inter}} = K_0^4[\tfrac{27}{7}xS_1 + \tfrac{18}{35}x^2(7S_2 + S_3)]\,, \tag{3.24}$$

where

$$S_1 = R_0^{12}\sum_j R_{ij}^{-12}\,, \tag{3.25a}$$

$$S_2 = R_0^{12}\sum_{jk\neq} R_{ij}^{-6}R_{ik}^{-6}(3\cos^4\theta_1 - 2\cos^2\theta_1 + 1)\,, \tag{3.25b}$$

$$S_3 = R_0^{12}\sum_{jk\neq} R_{ij}^{-6}R_{ik}^{-3}R_{jk}^{-3}[\sin^2\theta_1\sin^2\theta_2 - \sin 2\theta_1\sin 2\theta_2 + (3\cos^2\theta_1 - 1)(3\cos^2\theta_2 - 1)]\,, \tag{3.25c}$$

where θ_1 is the angle between R_{ij} and R_{ik}, and θ_2 is the angle between R_{ij} and R_{jk}. These lattice sums were evaluated for an hcp lattice by Priest,[52] who obtained

$$S_1 = 12.13, \tag{3.26a}$$

$$S_2 = 171.1, \tag{3.26b}$$

$$S_3 = 42.94. \tag{3.26c}$$

We may summarize the results of this subsection by giving the results for the second and fourth moments and also the resulting value of the ratio ρ, where ρ is defined as

$$\rho = M_4^{\text{inter}}/(M_2^{\text{inter}})^2\,.$$

We have found

$$M_2^{\text{inter}} = [0.17 + 0.83(K_{\text{eff}}/K_0)^2] \times 90.0\ \text{kHz}^2, \tag{3.27}$$

and for a rigid lattice

$$M_4^{\text{inter}} = (1.26x + 17.18x^2) \times 10^3\ \text{kHz}^4\,, \tag{3.28a}$$

$$\rho = 2.12 + 0.156x^{-1} \equiv \rho_{\text{rigid}}\,. \tag{3.28b}$$

Crudely, we can take account of phonon renormalizations by neglecting their effect on the NMR line shape or, equivalently, by using the value ρ_{rigid} from Eq. (3.28b). Thus, we write

$$M_4^{\text{inter}} = \rho_{\text{rigid}}(M_2^{\text{inter}})^2\,, \tag{3.29}$$

where we use Eq. (3.19a) for M_2^{inter}.

C. High-Temperature Expansion for M_2^{intra}

This subsection will be devoted to a calculation of the leading terms in the high-temperature expansion for M_2^{intra} as given by Eq. (3.19b).

The high-temperature expansion for M_2^{intra} is generated by substituting for the thermodynamic averages their high-temperature expansions,

$$\langle Y_2^l(\omega_0)\rangle_T \equiv \langle Y_2^l(\omega_0)\,e^{-\beta\mathcal{H}_{\text{EQQ}}}\rangle_\infty / \langle e^{-\beta\mathcal{H}_{\text{EQQ}}}\rangle_\infty \tag{3.30a}$$

$$= \langle Y_2^l(\omega_0)\textstyle\sum_s(-\beta\mathcal{H}_{\text{EQQ}})^s(s\,!)^{-1}\rangle_\infty / \langle \textstyle\sum_s(-\beta\mathcal{H}_{\text{EQQ}})^s(s\,!)^{-1}\rangle_\infty \tag{3.30b}$$

$$= \tfrac{1}{2}\beta^2\langle Y_2^l(\omega_0)\,[\mathcal{H}_{\text{EQQ}}^2 - \tfrac{1}{3}\beta\mathcal{H}_{\text{EQQ}}^3\cdots]\rangle_\infty\,. \tag{3.30c}$$

To obtain Eq. (3.30c) we have used the fact that the two leading terms in the expansion of $e^{-\beta\mathcal{H}_{\text{EQQ}}}$ in the numerator give no contribution. Also since $\langle\mathcal{H}_{\text{EQQ}}\rangle_\infty = 0$, the temperature dependence of the denominator has no effect to the order considered in Eq. (3.30c). First we evaluate $\langle Y_2^l(\omega_0)\mathcal{H}_{0\vec{\delta}}^2\rangle_\infty$, where $\mathcal{H}_{0\vec{\delta}}$ is the EQQ Hamiltonian describing interactions between molecules at $r = 0$ and $\vec{r} = \vec{\delta}$ and for the moment the quantization axis $\hat{n}$ is arbitrary.[53] Using the operator equivalents and the transformation properties of these operators we find

$$\langle Y_2^l(\omega_0)_{\hat{n}}\mathcal{H}_{0\vec{\delta}}^2\rangle_\infty = -\tfrac{2}{5}\langle \mathcal{T}_2^l(J_0)_{\hat{n}}\mathcal{H}_{0\vec{\delta}}^2\rangle_\infty \tag{3.31a}$$

$$= \sum_{l'} D_{ll'}^{(2)}(\chi_{\hat{n}\hat{\delta}})^*\langle \mathcal{T}_2^{l'}(J_0)_{\hat{\delta}}\mathcal{H}_{0\vec{\delta}}^2\rangle_\infty\,. \tag{3.31b}$$

Using the eigenfunctions for a pair of $(J = 1)$ molecules as given in Table IV we obtain

$$\langle \mathcal{T}_2^l(J_0)_{\hat{\delta}}\mathcal{H}_{0\vec{\delta}}^2\rangle_\infty = -\tfrac{25}{18}\,\Delta_{l0}(5/\pi)^{1/2}\Gamma^2\,, \tag{3.32}$$

where Δ_{mn} is the Kronecker delta. Combining this

TABLE IV. Rotational states of a pair of $(J = 1)$ molecules.

State	E/Γ
$\psi_1 = 6^{-1/2}(\mid 1, -1> + 2\mid 0, 0> + \mid -1, 1>)$	6
$\psi_2 = \mid 1, 1>$	1
$\psi_3 = \mid -1, -1>$	1
$\psi_4 = 2^{-1/2}(\mid 1, 0> - \mid 0, 1>)$	0
$\psi_5 = 2^{-1/2}(\mid -1, 0> - \mid 0, -1>)$	0
$\psi_6 = 2^{-1/2}(\mid 1, -1> - \mid -1, 1>)$	0
$\psi_7 = 3^{-1/2}(\mid 1, -1> - \mid 0, 0> + \mid -1, 1>)$	0
$\psi_8 = 2^{-1/2}(\mid 1, 0> + \mid 0, 1>)$	-4
$\psi_9 = 2^{-1/2}(\mid -1, 0> + \mid 0, -1>)$	-4

result with Eq. (3.31b) we find

$$\langle Y_2^l(\omega_0)_{\hat{n}} \mathcal{H}^2_{0\vec{\delta}} \rangle_\infty = \tfrac{10}{9}\Gamma^2 Y_2^l(\hat{\delta})_{\hat{n}} = \tfrac{10}{9} Y_2^l(\beta', \alpha') \;, \qquad (3.33)$$

where β' and α' are the polar and azimuthal angles of $\hat{\delta}$ with respect to the $\hat{n}$ coordinate system. Thus, according to Eq. (3.30c) we have to lowest order in β

$$\langle Y_2^l(\omega_0)_{\hat{n}} \rangle_T \approx \tfrac{5}{9}\beta^2\Gamma^2 \sum_{\vec{\delta}, J_{\vec{\delta}}=1} Y_2^l(\hat{\delta})_{\hat{n}} \;. \qquad (3.34)$$

This result leads to a lowest-order evaluation of Eq. (3.19b):

$$M_2^{\text{intra}} = \tfrac{25}{9}\pi d^2 \beta^4 \Gamma^4 \langle\langle \sum_{l, \vec{\delta}, \vec{\delta}'; J=1} (-1)^l Y_2^l(\hat{\delta}) Y_2^{-l}(\hat{\delta}') \rangle\rangle_a \;, \qquad (3.35)$$

where it only remains to take the alloy average. Since the sum is only over $(J=1)$ molecules, we can take the alloy average by including the probability factor $f_2(\vec{\delta}, \vec{\delta}')$ describing the probability that $(J=1)$ molecules are at nearest-neighbor lattice sites $\vec{\delta}$ and $\vec{\delta}'$:

$$f_2(\vec{\delta}, \vec{\delta}') = x^2 + x(1-x)\Delta_{\vec{\delta}, \vec{\delta}'} \;. \qquad (3.36)$$

Then Eq. (3.35) becomes

$$M_2^{\text{intra}} = \tfrac{125}{3} d^2 (\beta\Gamma)^4 x(1-x) \;, \qquad (3.37)$$

since the term which does not involve the Kronecker delta vanishes when use is made of the relation

$$\textstyle\sum_{\vec{\delta}} Y_2^l(\vec{\delta}) = 0 \;, \qquad (3.38)$$

which is valid when the sum runs over nearest neighbors in an hcp lattice.

The next term in the high-temperature expansion for M_2^{intra} is found by collecting the various terms of order β^5 which occur when Eq. (3.30c) is substituted into Eq. (3.19b). The details of this calculation are rather complicated and are given in Appendix A. Collecting the various calculations we find the second moment correct to order β^5 to be

$$M_2^{\text{intra}} = \tfrac{125}{3} d^2 (\beta\Gamma)^4 x(1-x) \left[1 - \beta\Gamma(2 + \tfrac{415}{64}x)\right] \;. \qquad (3.39)$$

Note that M_2^{intra} vanishes for $x=1$ within our approximation. We may understand this result in the following simple way. For $x=1$ in a cubic structure where each site possesses cubic symmetry (this is *not* true for the Pa_3 structure) one has that

$$\langle n_x^2 \rangle = \langle n_y^2 \rangle = \langle n_z^2 \rangle = \tfrac{1}{3} \;, \qquad (3.40)$$

where $\hat{n}$ is the orientation of the molecular axis at position R. In other words, one has

$$\langle Y_2^l(\omega_i) \rangle_T = 0 \;, \qquad (3.41)$$

and by Eq. (3.19b) one sees that for $x=1$ it follows that

$$M_2^{\text{intra}} = 0 \;. \qquad (3.42)$$

It is well known that the hcp and fcc structure are quite similar, and so we may expect that the number of high-temperature graphs is nearly the same for both structures.[54] Thus, this argument, which invokes local cubic symmetry, is nearly applicable to the hcp structure. As a result we expect M_2^{intra} to be very small for $x=1$ over the entire temperature range above the order-disorder transition. From the data in Ref. 5 one sees that this is indeed the case.

D. Evaluation of $M_4(T)$

The evaluation of the leading terms in $M_4(T)$ at high temperature is similar, but more involved than that for $M_2(T)$ and consequently the details have been relegated to Appendix C. There we estimate the various types of terms one finds at high temperature. Our results may be written in the form

$$M_4(T) - M_4(\infty) \sim M_4^{(1)} + M_4^{(2)} + M_4^{(4)} \;, \qquad (3.43)$$

with

$$M_4^{(r)} \sim (d\beta^2\Gamma^2)^r (K_{\text{eff}})^{4-r} \;, \qquad (3.44)$$

where $d\beta^2\Gamma^2$ is a measure of the intramolecular interactions and K_{eff} scales the intermolecular interactions. We find

$$M_4^{(1)} = \tfrac{360}{7} K_{\text{eff}}{}^3 d\beta^2\Gamma^2 x(1-x) \;, \qquad (3.45\text{a})$$

$$M_4^{(2)} = 384x(1-x)(\tfrac{25}{24} dK_{\text{eff}}\beta^2\Gamma^2)^2 \times \left[\tfrac{16}{25} x S_0 + \tfrac{48}{35}(1-2x)\right] \;, \qquad (3.45\text{b})$$

$$M_4^{(4)} = (d\beta^2\Gamma^2)^4 x(1-x)\left[177 + 1913x(1-x)\right] . \qquad (3.45\text{c})$$

It turns out that $M_4^{(2)}$ is the dominant contribution in Eq. (3.43), and for this term we derive an empirical relation, which is probably not restricted to the extreme high-temperature limit, viz.,

$$M_4^{(2)} = \tfrac{16}{3}\left[M_2(T) - M_2(\infty)\right] M_2(\infty) \;. \qquad (3.45\text{d})$$

E. Comparison with Experiment

In this subsection we compare the results of our calculations with the experimental data of Amstutz *et al.*[5] From their data it is apparent that $M_2(\infty)$, the value of M_2 extrapolated to infinite temperature, is approximately a linear function of x as indicated by Eq. (3.27). Experimentally, Amstutz *et al.* find for $x > 0.5$ that $K_{\text{eff}}/K_0 \approx 0.94$ compared to the theoretical estimate[2] $K_{\text{eff}}/K_0 = 0.97$. This slight discrepancy is possibly due to inaccuracies in the static-phonon renormalization. In that calculation only short-range calculations were taken into account, which probably leads to underestimates of the reduction in both coupling constants K_{eff} and Γ_{eff}.[55] At low concentrations x of $(J=1)$ molecules Amstutz *et al.* find $K_{\text{eff}}/K_0 \approx 1.00$. Such a concentration dependence of K_{eff}/K_0 is rather easy to understand since it is completely analogous to that predicted for $\Gamma_{\text{eff}}/\Gamma_0$, cf. Eqs. (2.11) and (2.12). At low concentrations x the extra attraction between $(J=1)$

molecules decreases their separation thus increasing K_{eff}. In the limit $x \to 1$, nonuniform strains are precluded by symmetry.

Next we compare the experimental values of $M_4(\infty)$ with the theoretical values given in Eq. (3.28) (see Fig. 1). We see roughly the same features here as for M_2: K_{eff}/K_0 is essentially unity at low concentrations and is about 0.94 at high concentrations. Again the anomalous behavior near $x = 0.5$ is not understood at present. The scatter in the experimental data is a little too large to obtain useful results by analyzing the data according to Eq. (3.29).

Let us now compare experimental and theoretical values of $M_2(T) - M_2(\infty)$. The problem encountered in making such a comparison is that only at high temperatures is the theoretical formula valid because only there does it suffice to keep only the first two terms in the high-temperature series for $M_2(T)$. To get an estimate of when our two-term formula might be reasonably accurate we may look at the convergence of the high-temperature expansion for the specific heat.[6] There a two-term expansion gives 10% accuracy only for $kT/\Gamma > 15$ for moderate concentrations. However, from the data of Amstutz *et al.* it is apparent that $M_2(T) - M_2(\infty)$ rapidly becomes small in comparison to $M_2(\infty)$ for $kT/\Gamma > 10$, in which limit it is essentially unobservable. Hence, there is really no regime where both the present theory and experiment are accurate enough to be meaningfully compared.

Nevertheless, we will attempt a crude comparison by analyzing data for $T = 5$ and $T = 6$ °K, at which temperatures the combined experimental and theoretical uncertainty is the smallest. To do this we plot in Fig. 2 the quantity

$$m(x) \equiv [M_2(T) - M_2(\infty)]/[x(1-x)]$$

versus x for these two temperatures. We see that $m(x)$ behaves in qualitative agreement with Eq. (3.39) in that it is a linearly decreasing function of x. The slope and intercept of a linear fit to the experimental values of $m(x)$ do not quantitatively agree with Eq. (3.39), i.e., if we write $m(x) = \alpha_0 - \alpha_1 x$, then from Eq. (3.39) we should expect (taking $\Gamma_{\mathrm{eff}} = 0.77\,\Gamma_0 = 0.55\ \mathrm{cm}^{-1}$)

$$\alpha_0 = 54\ \mathrm{kHz}, \quad \alpha_1 = 78\ \mathrm{kHz}, \quad T = 5\ {}^\circ\mathrm{K}, \tag{3.46a}$$

$$\alpha_0 = 28\ \mathrm{kHz}, \quad \alpha_1 = 31\ \mathrm{kHz}, \quad T = 6\ {}^\circ\mathrm{K}, \tag{3.46b}$$

whereas the experimental values are

$$\alpha_0 = 88\ \mathrm{kHz}, \quad \alpha_1 = 78\ \mathrm{kHz}, \quad T = 5\ {}^\circ\mathrm{K}, \tag{3.47a}$$

$$\alpha_0 = 44\ \mathrm{kHz}, \quad \alpha_1 = 30\ \mathrm{kHz}, \quad T = 6\ {}^\circ\mathrm{K}. \tag{3.47b}$$

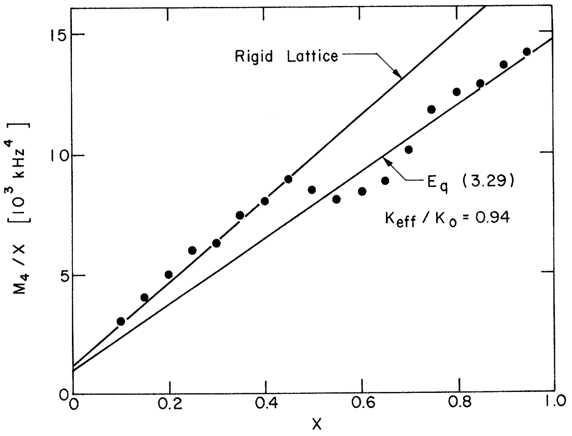

FIG. 1. $M_4(\infty)$ versus concentration. We plot M_4 extrapolated to infinite temperature versus x. The rigid-lattice theory fits the low-concentration data, whereas the high-concentration data imply a renormalized dipolar interaction.

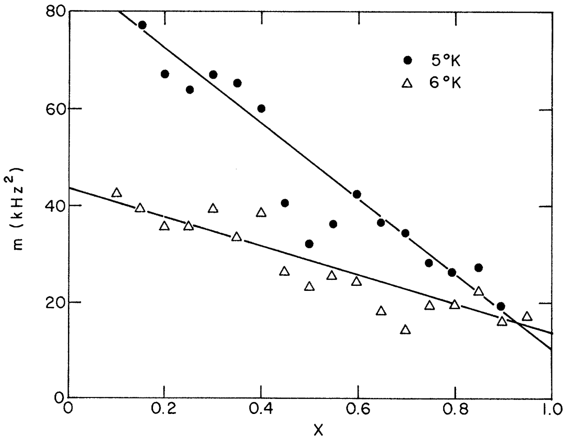

FIG. 2. Temperature dependence of M_2. We plot experimental values of $m(x) \equiv [M_2(T) - M_2(\infty)]/[x(1-x)]$ versus x at 5 and 6 °K. The solid lines represent a linear fit to the data with coefficients given in Eq. (3.47).

It is clear that we must take more terms in the high-temperature expansion to obtain sensible results because Eq. (3.46) gives $m < 0$, which is impossible. However considering the uncertainties in the theory and experiment this discrepancy is not surprising.

When we attempt the same type of comparison with M_4, the situation is even worse, as one might expect, since M_4 is a more rapid function of the parameters than M_2. Experimentally one finds at $T = 6$ °K,

$$m_4 \equiv [M_4(T) - M_4(\infty)]/[x(1-x)] \approx 5 \times 10^3\ \mathrm{kHz},$$

essentially independent of x, whereas theory would give

$$m_4 = (2.4 + 9.4x - 0.7x^2) \times 10^3\ \mathrm{kHz}^4\,. \tag{3.48}$$

This result was obtained by numerically evaluating the various results in Appendix C. To show that the slow convergence of the high-temperature expansion is playing a crucial role, let us compare the experimental values of m_4 to their theoretical values using experimental values of M_2 in the semiempirical relation, Eq. (3.45d). Since this term is in fact the dominant contribution to m_4 in the temperature and concentration range being considered, we partially eliminate convergence difficulties by use of this relation. In this way we obtain the theoretical estimate

$$m_4 = [0.6 + 0.7\,x(1-x)] \times 10^3\ \text{kHz}^4 + \tfrac{16}{3} m(x) M_2(\infty)\ . \tag{3.49}$$

Better agreement between the theoretical and experimental values of m_4 are obtained using this formulation, as can be seen from Fig. 3 where the comparison is illustrated. It must be emphasized that experimental uncertainties are larger in M_4 than in M_2, and also the high-temperature expansion is less reliable for M_4 than for M_2 because M_4 is comparable to M_2^2. Hence, we cannot really expect much better agreement than is obtained in Fig. 3.

From these comparisons and discussions we conclude that the effects of partial orientational ordering in the orientationally disordered phase are reasonably well understood. It seems likely that a more quantitative agreement between theory and experiment would be obtained if (a) more terms in the high-temperature expansion of M_2 and M_4 were evaluated, and (b) a better theory of the zero-point phonon motion in solid H_2 were used to calculate K_{eff}.

IV. MOMENTS OF NMR SPECTRUM OF D_2

In this section we consider how the previous results for H_2 should be modified to treat the case of D_2. The reason for treating D_2 separately is that there are special complications caused by the fact that (a) I is not a good quantum number, and (b) more than one species contributes to the resonance.

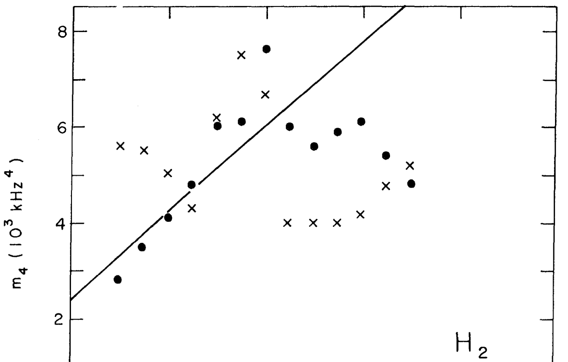

FIG. 3. Temperature dependence of M_4. We plot $m_4 \equiv [M_4(T) - M_4(\infty)]/[x(1-x)]$ versus x for $T = 6\,°\text{K}$. The crosses are the experimental points, the solid curve is Eq. (3.48), and the dots are obtained using experimental values of $M_2(T)$ in Eq. (3.49). For $x > 0.7$ the data are essentially meaningless because then $M_4(T) - M_4(\infty)$ is much smaller than $M_4(\infty)$.

A. Second Moment

Let us start by developing a general formula for M_2 analogous to Eq. (3.19). To do this it is convenient to write the truncated Hamiltonian for D_2 in the form

$$h^{-1}\mathcal{H}' = \sum_i \mathcal{H}_{Zi} + \mathcal{H}_{DD} + \sum_{\text{odd } J_i} h^{-1}\mathcal{H}'_{\text{odd},\,i} + \sum_{\text{even } J_i} h^{-1}\mathcal{H}'_{\text{even},\,i}\ , \tag{4.1}$$

where $\mathcal{H}_{Zi}$ and $\mathcal{H}_{DD}$ are the obvious analogs of the corresponding quantities defined in Eqs. (3.4a) and (3.4c) and

$$\mathcal{H}'_{\text{odd},\,i} = -\tfrac{1}{3}\, dA_i(3I_{zi}^2 - 2)\ , \tag{4.2a}$$

$$\mathcal{H}'_{\text{even},\,i} = -\tfrac{1}{3} d_M A_i (3 i_{zi}^{(1)} i_{zi}^{(2)} - \vec{\text{i}}_i^{\,(1)} \cdot \vec{\text{i}}_i^{\,(2)}) + \tfrac{1}{3} d_Q A_i [3(i_{zi}^{(1)})^2 + 3(i_{zi}^{(2)})^2 - 4]\ , \tag{4.2b}$$

where A_i was defined in Eq. (3.5b). In Eq. (4.1) the last two sums over i are restricted to odd- and even-J molecules, respectively. Note that $I = 1$ is a good quantum number for odd-J molecules, but $I = 2$ is not a good quantum number for even-J molecules because the Hamiltonian $\mathcal{H}'_{\text{even},\,i}$ of Eq. (4.2b) has matrix elements between states with $I = 2$ and $I = 0$.

Still, it is easy to show that for D_2 one can again write M_2 as

$$M_2 = M_2^{\text{inter}} + M_2^{\text{intra}} \tag{4.3}$$

in analogy to Eq. (3.18) and that there are no cross terms. It is also obvious that M_2^{inter} is obtained by a trivial extension of the previous results for H_2. In Eq. (3.19a) one simply replaces the value of $\langle\langle X \rangle\rangle$ for H_2, $2x$, by its value for D_2,

$$\langle\langle X \rangle\rangle = 5 - 3x\ , \tag{4.4}$$

so that now for D_2 we obtain

$$M_2^{\text{inter}} = \tfrac{3}{5}(5 - 3x)\,[(S_0 - 12)K_0^2 + 12K_{\text{eff}}^2]\ . \tag{4.5}$$

The calculation of M_2^{intra} is slightly more subtle. We have from the general formalism, cf. Eq. (3.9), that

$$I_0 M_2^{\text{intra}} = \sum_{\text{odd } J_i} \langle [I_i^+, \mathcal{H}'_{\text{odd},\,i}]\,[\mathcal{H}'_{\text{odd},\,i}, I_i^-] \rangle + \sum_{\text{even} J_i} \langle [I_i^+, \mathcal{H}'_{\text{even},\,i}] \langle [\mathcal{H}'_{\text{even},\,i}, I_i^-] \rangle\ , \tag{4.6}$$

which gives

$$\tfrac{2}{3}(5 - 3x) M_2^{\text{intra}} = x \langle\langle \{ \langle [I_i^+, \mathcal{H}'_{\text{odd},\,i}]\,[\mathcal{H}'_{\text{odd},\,i}, I_i^-] \rangle \} \rangle\rangle_{pa}$$

$$+(1-x)\langle\langle \{\langle [I_i^+, \mathcal{H}'_{\text{even},\,i}]\,[\mathcal{H}'_{\text{even},\,i}, I_i^-]\rangle\}\rangle\rangle_{pa}\ . \tag{4.7}$$

The first term is of the same form as for H_2, so that we have

$$\langle\langle \{\langle [I_i^+, \mathcal{H}'_{\text{odd},\,i}]\,[\mathcal{H}'_{\text{odd},\,i}, I_i^-]\rangle\}\rangle\rangle_{pa} = 2d^2\langle\langle A^2_{i,\,\text{odd}}\rangle\rangle_{pa}\ . \tag{4.8}$$

The second term can be evaluated directly by writing out matrix elements in the even-parity subspace. An easier alternative method is to calculate $I_0 M_2^{\text{intra}}$ for the special case $x=\frac{1}{3}$ when all the nuclear-spin states have the same weight. Then the calculation of $I_0 M_2^{\text{intra}}$ is identical to that for two spins coupled by the Hamiltonian of Eq. (4.2b). In this way we obtain for $x=\frac{1}{3}$,

$$I_0 M_2^{\text{intra}} = (\tfrac{8}{3} d_Q^2 + \tfrac{16}{9} d_M^2) A_i^2\ . \tag{4.9}$$

Combining this result with Eq. (4.7) and (4.8) we have that

$$\langle\langle \{\langle [I_i^+, \mathcal{H}'_{\text{even},\,i}]\,[\mathcal{H}'_{\text{even},\,i}, I_i^-]\rangle\}\rangle\rangle_{pa}$$
$$= \tfrac{1}{3}\langle\langle A^2_{i,\,\text{even}}\rangle\rangle_{pa}\ (10 d_Q^2 - 4 d_Q d_M + 6 d_M^2)\ , \tag{4.10}$$

so that the general result for M_2^{intra} becomes

$$M_2^{\text{intra}} = \frac{9\pi(1-x)}{5-3x}\ (5d_Q^2 - 2d_M d_Q + 3d_M^2)\sum_l |\langle Y_2^l(\omega_i)\rangle_{\text{even}}|^2 + \frac{18 d^2 \pi x}{5-3x}\sum_l |\langle Y_2^l(\omega_i)\rangle_{\text{odd}}|^2 \tag{4.11}$$

in agreement with our previously published result.[56]

The deformation of the $(J=0)$ state is very small, so that A_i^2 (J_i even) $\ll A_i^2$ (J_i odd). Hence, we can neglect the even-J term:

$$M_2^{\text{intra}} \approx \frac{18 d^2 \pi x}{5-3x}\sum_l |\langle Y_2^l(\omega_i)\rangle\rangle_{\text{odd}}|^2\ . \tag{4.12}$$

The required thermodynamic average is identical to that encountered in Sec. III, whence the result

$$M_2^{\text{intra}} = \tfrac{125}{3}\ [2x/(5-3x)]\, d^2 (\beta\Gamma)^4 x(1-x)$$
$$\times [1 - \beta\Gamma(2 + \tfrac{415}{64}\ x)]\ . \tag{4.13}$$

B. Discussion

Normally a discussion would belong at the end of the calculation. However, in this case we must pause to consider what calculations are worth pursuing at the present time. In this connection it is worth noting that these results for D_2 show a qualitative difference between H_2 and D_2. In H_2 we have at $x=0.5$

$$[M_2^H(5\ ^\circ\text{K}) - M_2^H(\infty)]/M_2^H(\infty) \approx 0.2 \ll 1,$$

where the superscript H indicates H_2, and below D indicates D_2. To obtain an empirical estimate for D_2 we proceed as follows.[57] From Eqs. (3.19a) and (4.5) we have

$$\frac{M_2^H(\infty)}{M_2^D(\infty)} = \frac{2x(K^H_{\text{eff}}/K^D_{\text{eff}})^2}{5-3x}\ . \tag{4.14}$$

From Eqs. (3.19b) and (4.11) we see that M_2^{intra} scales with d^2, providing we neglect the difference between the values of Γ for H_2 and D_2,[58] and if we set $\langle Y_2^l(\omega_i)\rangle\rangle_{\text{even}} = 0$. Then we write

$$\frac{M_2^H(T) - M_2^H(\infty)}{M_2^D(T) - M_2^D(\infty)} = \frac{5-3x}{2x}\left(\frac{d^H}{d^D}\right)^2, \tag{4.15}$$

so that

$$\left[\frac{M_2^D(T) - M_2^D(\infty)}{M_2^D(\infty)}\right] \Big/ \left[\frac{M_2^H(T) - M_2^H(\infty)}{M_2^H(\infty)}\right]$$
$$\equiv r = \left[\left(\frac{2x}{5-3x}\right)\left(\frac{d^D}{d^H}\right)\left(\frac{K^H_{\text{eff}}}{K^D_{\text{eff}}}\right)\right]^2, \tag{4.16}$$

and for $x=0.5$ and $T=5\ ^\circ$K we find $r\approx 20$. Thus, one expects an extremely rapid temperature dependence for M_2 in D_2. This is indeed found to be the case for high $(J=1)$ concentration.[7]

On the other hand, for lower concentrations it is found that the temperature dependence is nowhere near as large as predicted by Eq. (4.16). From this result we conclude that possibly the $(I=1)$ nuclei are effectively not contributing to the NMR signal. A tentative explanation for why this might occur at, say, $x=0.5$ is as follows: First, the intensity of the absorption from the $(I=1)$ nuclei is only $\frac{2}{5}$ as large as that from the $(I=2)$ nuclei. In addition, the latter have a much narrower line shape, as is shown schematically in Fig. 4. Thus it may be that the $(I=1)$ resonance is simply too broad to be observed. At very high concentrations it appears that the $(I=1)$ molecules have a narrower line shape (recall that M_2^{intra} vanishes for $x=1$) and are making noticeable contributions to the second moment. We may attempt an analysis of the

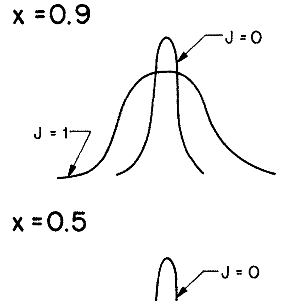

FIG. 4. Schematic diagram showing the contributions of $(I=1)$ and $(I=2)$ nuclei to the NMR line shape. For $x=0.9$ the relative intensity of the $(I=1)$ molecules is large, and their linewidth is not too large to prevent their observation. For $x=0.5$ the $(I=1)$ absorption has a small intensity, and its linewidth is extremely large and hence is quite possibly undetectable.

experimental data[7] within this interpretation. The temperature dependence of M_2 is then presumably due to the temperature dependence of the absorption of the $(J=0,\ I=2)$ molecules. In Appendix D we therefore evaluate the second moment assuming only even-J molecules take part in the resonance. In this model the temperature dependence in M_2 arises from the intramolecular interactions which depend in turn on the thermal alignment of the $(J=0)$ molecules. This alignment is, of course, very small, and so the temperature dependence of M_2 is very much smaller than that given in Eq. (4.16). To illustrate the results of Appendix D we quote the numerical evaluation $M_2^{\text{intra}} \approx 0.012$ kHz^2 for $x=0.5$ and for $T=6$ °K. Since this estimate is of the correct order of magnitude, we tentatively conclude that our proposed explanation has some merit.

Note added in proof. The explanation offered here for the small observed values of M_2 has recently been confirmed by NMR pulse measurements of Weinhaus, Maravigilia, and Meyer. They have observed the free induction decay (FID) over a wide range of concentrations and temperature. At intermediate values of concentration and temperature (i.e., $x \approx 0.5$ and $T \approx 4$ °K) they find that the FID can be resolved into two components, one attributed to $(J=0)$ molecules, the other to $(J=1)$ molecules. The continuous wave (cw) signal corresponding to the latter component is indeed very broad, and hence difficult to observe.

V. CORRELATION FUNCTIONS FOR PAIRS OF $(J=1)$ MOLECULES

Although the energy-level scheme for a pair of $(J=1)$ molecules interacting via EQQ interactions is well known, there has been no study of the corresponding dynamical properties. We shall study these properties since they will be useful in analysis of low-concentration phenomena.

We shall be interested in the following correlation (Green's) functions[59]:

$$\langle\langle A(t); B(t')\rangle\rangle \equiv \sum_{nm} p(n)\{\langle n|A|m\rangle\langle m|B|n\rangle \times \exp[i(E_n - E_m)(t-t')/\hbar] + \langle n|B|m\rangle\langle m|A|n\rangle \times \exp[i(E_m - E_n)(t-t')/\hbar]\}, \tag{5.1}$$

which are given in terms of the spectral weight function $\rho_{AB}(\omega)$:

$$\langle\langle A(t); B(t')\rangle\rangle = \int_{-\infty}^{+\infty} \rho_{AB}(\omega) e^{-i\omega(t-t')}\ \hbar dw \ . \tag{5.2}$$

Here

$$\rho_{AB}(\omega) = \sum_{nm} p(n)\langle n|A|m\rangle\langle m|B|n\rangle \times (1+e^{-\beta\hbar\omega})\,\delta(\hbar\omega + E_n - E_m), \tag{5.3}$$

where $p(n)$ is the Boltzmann factor for the state $|n\rangle$. In terms of this spectral function one can compute the usual correlation functions

$$\langle A(t)B(0)\rangle = \int_{-\infty}^{+\infty} \rho_{AB}(\omega)(1+e^{-\beta\hbar\omega})^{-1} e^{-i\omega t}\ \hbar dw. \tag{5.4}$$

Properties such as the cross section for the inelastic scattering of neutrons or the spin-lattice relaxation times are directly related to the spectral weight function for appropriate choices of the operators A and B.

It is most convenient to use for A and B the irreducible tensor operators of Table II. First let us take the quantization axis to lie along the separation vector between the two molecules. For later applications we will study the spectral functions $\rho_L^{MM'}(\omega)$ defined by Eq. (5.3) with the choice $A = \mathcal{T}_L^M(J_1)$ and $B = (-1)^{M'}\,\mathcal{T}_L^{-M'}(J_1)$. By symmetry $\rho_L^{MM'}(\omega)$ vanishes unless $M=M'$. From the definition of Eq. (5.3) we also note that

$$\rho_{AB}(\omega) = \rho_{B^\dagger A^\dagger}(\omega)^* \ . \tag{5.5}$$

Using the eigenvalues and eigenvectors of Table IV we determined the independent spectral functions as

$$\rho_1^{11}(\omega) = Q^{-1}\ (1+e^{-\beta\hbar\omega})\,(3/8\pi)\,[\tfrac{3}{2}p_{-4}\,\delta(\hbar\omega - 10\Gamma) + \tfrac{3}{2}p_6\,\delta(\hbar\omega + 10\Gamma) + \tfrac{1}{6}\delta(\hbar\omega - 6\Gamma) + \tfrac{1}{6}p_6\,\delta(\hbar\omega + 6\Gamma) + p_{-4}\,\delta(\hbar\omega - 5\Gamma) + p_1\,\delta(\hbar\omega + 5\Gamma) + \tfrac{1}{2}p_{-4}\,\delta(\hbar\omega - 4\Gamma) + \tfrac{1}{2}\delta(\hbar\omega + 4\Gamma) + \delta(\hbar\omega - \Gamma) + p_1\,\delta(\hbar\omega + \Gamma) + \tfrac{11}{3}\,\delta(\hbar\omega)], \tag{5.6a}$$

$$\rho_1^{00}(\omega) = Q^{-1}\ (1+e^{-\beta\hbar\omega})\ (3/4\pi)\,[\tfrac{1}{3}\,\delta(\hbar\omega - 6\Gamma) + \tfrac{1}{3}p_6\,\delta(\hbar\omega + 6\Gamma) + \tfrac{1}{2}p_{-4}\,\delta(\hbar\omega - 4\Gamma) + \tfrac{1}{2}\,\delta(\hbar\omega + 4\Gamma) + (\tfrac{1}{2}p_{-4} + 2p_1 + \tfrac{11}{6})\,\delta(\hbar\omega)]\ , \tag{5.6b}$$

$$\rho_2^{22}(\omega) = Q^{-1}(1+e^{-\beta\hbar\omega})\,(15/32\pi)\,[\tfrac{2}{3}p_1\,\delta(\hbar\omega - 5\Gamma) + \tfrac{2}{3}p_6\,\delta(\hbar\omega + 5\Gamma) + p_{-4}\,\delta(\hbar\omega - 4\Gamma) + \delta(\hbar\omega + 4\Gamma) + \tfrac{10}{3}\delta(\hbar\omega - \Gamma) + \tfrac{10}{3}p_1\,\delta(\hbar\omega + \Gamma) + (1+p_{-4})\,\delta(\hbar\omega)], \tag{5.6c}$$

$$\rho_2^{11}(\omega) = Q^{-1}(1+e^{-\beta\hbar\omega})\ (15/32\pi)\,[\tfrac{1}{6}p_{-4}\,\delta(\hbar\omega - 10\Gamma) + \tfrac{1}{6}\,p_6\,\delta(\hbar\omega + 10\Gamma) + \tfrac{3}{2}\,\delta(\hbar\omega - 6\Gamma) + \tfrac{3}{2}p_6\,\delta(\hbar\omega + 6\Gamma) + p_{-4}\,\delta(\hbar\omega - 5\Gamma) + p_1\,\delta(\hbar\omega + 5\Gamma) + \tfrac{11}{6}p_{-4}\delta(\hbar\omega - 4\Gamma) + \tfrac{11}{6}\delta(\hbar\omega + 4\Gamma) + \delta(\hbar\omega - \Gamma) + p_1\delta(\hbar\omega + \Gamma) + \delta(\hbar\omega)], \tag{5.6d}$$

$$\rho_2^{00}(\omega) = Q^{-1}(1+e^{-\beta\hbar\omega})\,(5/16\pi)\,[2\delta(\hbar\omega - 6\Gamma) + 2p_6\delta(\hbar\omega + 6\Gamma) + \tfrac{9}{2}p_{-4}\,\delta(\hbar\omega - 4\Gamma) + \tfrac{9}{2}\,\delta(\hbar\omega + 4\Gamma) + (\tfrac{1}{2}p_{-4} + \tfrac{3}{2} + 2p_1 + p_6)\,\delta(\hbar\omega)]\ . \tag{5.6e}$$

Here

$$p_n = \exp(-n\Gamma/kT)\ , \tag{5.7a}$$

$$Q = 2p_{-4} + 4 + 2p_1 + p_6\ . \tag{5.7b}$$

Obviously, we can calculate all the moments of these spectral functions:

$$M_{L;n}^{M;M'} \equiv \int_{-\infty}^{+\infty} \rho_L^{MM'}(\omega)\,(\hbar\omega)^n\ \hbar dw\qquad . \tag{5.8}$$

In fact, we checked our work by evaluating

$$M_{L;0}^{M;M'} = \Delta_{M,M'}\,\langle \{\mathcal{T}_L^M(J_1),\ \mathcal{T}_L^{-M}(J_1)\}_+\rangle\,(-1)^M, \tag{5.9a}$$

$$M_{L;2}^{M;M'} = \Delta_{M,M'}\langle \{[\mathcal{T}_L^M(J_1), \mathcal{H}],\ [\mathcal{H}, \mathcal{T}_L^{-M}(J_1)]\}_+\rangle\,(-1)^M. \tag{5.9b}$$

Here we mention that $\rho_L^{MM'}(\omega)$ is an even function of ω. This property is a consequence of the time-reversal invariance of the pair Hamiltonian. For later applications we use the form of the normalized spectral function at infinite temperature :

$$\rho_L^{MM}(\omega)/M_{L;0}^{M;M} = \sum_{E_n > 0} C_L^M(E_n)\,[\delta(\hbar\omega + E_n) + \delta(\hbar\omega - E_n)] + C_L^M(0)\,\delta(\hbar\omega)\ . \tag{5.10}$$

The coefficients $C_L^M(E_n)$ are given in Table V.

We can also compute the spectral function $\rho_{LL'}^{MM'}(\omega)_{\hat{n}}$ corresponding to the choice in Eq. (5.2) of $A = \mathcal{T}_L^M(J_1)$ and $B = (-1)^{M'}\,\mathcal{T}_{L'}^{M'}(J_1)$, where now the axis of quantization $\hat{n}$ is at an arbitrary orientation specified by the Euler angles $\chi = (\alpha', \beta', \gamma')$ with respect to the intermolecular pair axis $\vec{r}_{12}$ used above. Using the transformation properties of the irreducible tensor operators we have

$$\rho_{LL'}^{MM'}(\omega)_{\hat{n}} = \sum_\mu D_{M\mu}^{(L)}(\chi)\,D_{M'\mu}^{(L')}(\chi)^*\,\rho_{LL'}^{\mu\mu}(\omega)_{\hat{r}_{12}}, \tag{5.11}$$

where $D_{MM'}^{(L)}(\chi)$ is the rotation matrix. Finally, we can compute the powder average of the spectral functions using Eq. (5.11) as

$$\langle\langle \rho_{LL'}^{MM'}(\omega)_{\hat{n}}\rangle\rangle_p \equiv (1/4\pi)\int \rho_{LL'}^{MM'}(\omega)_{\hat{n}}\,d\Omega_{\hat{n}} \tag{5.12a}$$

$$= \Delta_{LL'}\,\Delta_{MM'}\sum_\mu \rho_L^{\mu\mu}(\omega)\,(2L+1)^{-1}\quad . \tag{5.12b}$$

Later we shall use the result for infinite temperature

$$\langle\langle \rho_{LL'}^{MM'}(\omega)_{\hat{n}}\rangle\rangle_p / M_{L;0}^{M;M} = \Big(\sum_{E_n>0} \{C_L(E_n)\,[\delta(\hbar\omega + E_n) + \delta(\hbar\omega - E_n)]\} + C_L(0)\,\delta(\hbar\omega)\Big)\,\Delta_{MM'}\,\Delta_{LL'}, \tag{5.13}$$

where the coefficients $C_L(E_n)$ can be related to the $C_L^M(E_n)$ of Eq. (5.10) as

$$C_L(E_n) \equiv (2L+1)^{-1}\sum_M C_L^M(E_n) \tag{5.14}$$

and are listed in Table V. These coefficients are the weight factors for the various frequencies in the correlation functions.

TABLE V. Spectral coefficients.

E_n/Γ =	10	6	5	4	1	0
$36C_2^2(E_n)$ =	0	0	2	3	10	6
$36C_2^1(E_n)$ =	$\frac{1}{2}$	$\frac{9}{2}$	3	$\frac{11}{2}$	3	3
$36C_2^0(E_n)$ =	0	4	0	9	0	10
$36C_1^1(E_n)$ =	$\frac{9}{2}$	$\frac{1}{2}$	3	$\frac{3}{2}$	3	11
$36C_1^0(E_n)$ =	0	2	0	3	0	26
$180C_2(E_n)$ =	1	13	10	26	26	28
$36C_1(E_n)$ =	3	1	2	2	2	16

VI. GAUSSIAN APPROXIMATION FOR T_1

A. Formulation

The relaxation of the nuclear spins of the $(J=1)$ molecules is due to the fluctuations in the local fields experienced by the nuclear spins. These fluctuations can be related to the fluctuations in the molecular coordinates. An expression for the spin-lattice relaxation time T_1 valid under rather broad conditions has been given by Wangsness and Bloch.[60] We write their result as

$$T_1^{-1} = \tfrac{16}{3}\pi^3\,[c^2\,\mathcal{J}_1^1(\omega_0) + \tfrac{9}{5}d^2\,\mathcal{J}_2^1(\omega_0) + \tfrac{36}{5}\,d^2\,\mathcal{J}_2^2(2\omega_0)]\ , \tag{6.1}$$

where $\mathcal{J}_L^M(\omega)$ is the "spectral function" in Abragam's terminology,[61]

$$\mathcal{J}_L^M(\omega) \equiv h\ (1 + e^{-\beta\hbar\omega})^{-1}\,\rho_{LL}^{MM}(\omega)_{\hat{n}} \tag{6.2}$$

and $\rho_{LL'}^{MM'}(\omega)_{\hat{n}}$ is the spectral weight function in Eq. (5.10) when $\hat{n}$ is taken along the direction of the magnetic field. Normally the observed relaxation rate T_1^{-1} is the average of the relaxation rate over different local configurations when the sample is an alloy.

In this section we study these spectral functions by calculating their moments. These calculations are extensions of those first performed by Moriya and Motizuki.[8] Even these calculations cannot be done exactly, so we shall have recourse to a high-temperature expansion of which we calculate only the leading terms. Such a calculation only has meaning if the shape (frequency dependence) of the spectral functions is approximately given. We shall assume a Gaussian shape. If a molecule interacted with many neighbors, we could invoke the central limit theorem[62] to support this assumption. Since there are 12 nearest neighbors, we can say that to the extent that six, say, is a large number, this reasoning justifies our method when the concentration x of $(J=1)$ molecules is 0.50. The Gaussian assumption is probably not as reasonable for EQQ interactions as for dipolar interactions because the former are essentially of short range, whereas the latter are of long range. Thus, the success of the Gaussian model for NMR line shapes[45] is not very relevant here. The fact that different configurations are averaged over may effectively increase the number of random variables, thus making plausible the use of the central limit theorem. In view of this uncertainty and in order to quantitatively assess the validity of the Gaussian assumption, we have calculated the second and fourth moments, σ_L^M and π_L^M, of the spectral functions $\rho_{LL}^{MM}(\omega)_{\hat{n}}$ for a powder at infinite temperatures. We find results consistent with a Gaussian line shape. We have also calculated the dependence of σ_L^M on the orientation of the magnetic field for a single crystal. From this calculation we conclude that the anisotropy of T_1 is too small to be observable. Finally, we have calculated the second term in the high-temperature expansion for $\langle\langle \sigma_L^M \rangle\rangle_p$ in order to discuss the temperature dependence of T_1. In conclusion, we compare our results with the experimental values of T_1.

From the definition of $\rho_{AB}(\omega)$, Eq. (5.3), we see that the second and fourth moments are given by

$$I_0\sigma_L^M = \langle\langle \{\langle \{[\mathcal{T}_L^M(J_0), \mathcal{H}], [\mathcal{H}, \mathcal{T}_L^{-M}(J_0)]\}_+\rangle_T\}\rangle\rangle_a(-1)^M, \tag{6.3a}$$

$$I_0\pi_L^M = \langle\langle \{\langle \{[[\mathcal{T}_L^M(J_0), \mathcal{H}], \mathcal{H}],\; [\mathcal{H}, [\mathcal{H}, \mathcal{T}_L^{-M}(J_0)]]\}_+\rangle_T\}\rangle\rangle_a(-1)^M, \tag{6.3b}$$

where

$$I_0 = \langle \{\mathcal{T}_L^M(J_0),\; \mathcal{T}_L^{-M}(J_0)\}_+\rangle_T(-1)^M. \tag{6.4}$$

For simplicity we shall take account only of nearest-neighbor interactions. For the program outlined above, we only need to calculate I_0 correct to order $1/T$:

$$I_0 = (L+3)/4\pi + O(1/T^2) . \tag{6.5}$$

For the average $\langle \mathcal{O} \rangle_T$, we have

$$\langle \mathcal{O} \rangle_T = \langle \mathcal{O}(1-\beta\mathcal{H})\rangle_\infty + \cdots , \tag{6.6}$$

because $\langle \mathcal{H}\rangle_\infty = 0$. Thus, $I_0\, \sigma_L^M$ can be written as

$$I_0\sigma_L^M = \langle\langle \{\langle \{[\mathcal{T}_L^M(J_0), \mathcal{H}],\; [\mathcal{H}, \mathcal{T}_L^{-M}(J_0)]\}_+ (1-\beta\mathcal{H})\rangle_\infty\}\rangle\rangle_a(-1)^M \tag{6.7a}$$

$$\equiv I_0[\sigma_L^{M\,(0)} + \beta\Gamma\sigma_L^{M\,(1)}] \tag{6.7b}$$

to first order in $1/T$.

B. Anisotropy of the Second Moments for a Single Crystal at $T = \infty$

First, we evaluate $\sigma_L^{M\,(0)}$ for a single crystal. We have

$$I_0\sigma_L^{M\,(0)} = \langle\langle \sum_{J_{\vec{\delta}}=1} \langle \{[\mathcal{T}_L^M(J_0), \mathcal{H}_{0\vec{\delta}}],\; [\mathcal{H}_{0\vec{\delta}}, \mathcal{T}_L^{-M}(J_0)]\}_+\rangle_\infty(-1)^M\rangle\rangle_a \tag{6.8a}$$

$$= \sum_{\vec{\delta},\mu} \left| D_{M\mu}^{(L)}(\Omega_{\vec{H}\vec{\delta}})\right|^2 m_{L2}^{\mu\mu} . \tag{6.8b}$$

Here $\Omega_{\vec{H}\vec{\delta}} = (\alpha'', \beta'', \gamma'')$, where β'' and α'' are the polar and azimuthal angles of $\vec{\delta}$ in a coordinate system where the z axis is along the direction of the magnetic field. Also we define $m_{Ln}^{MM'}$ as the moments of the normalized spectral weight functions, $\rho_L^{MM'}(\omega)/M_{L0}^{MM'}$, so that $m_{Ln}^{MM'} = M_{Ln}^{MM'}/I_0(L)$. In Eq. (6.8) we have omitted contributions involving three molecules because these terms vanish. Equation (6.8b) enables us to express the moments with quantization axis along the magnetic field in terms of those with quantization axis along $\vec{\delta}$. These can be found using Eq. (5.6) at infinite temperature or, alternatively, using Table V as

$$m_{22}^{22} = m_{22}^{-2,-2} = 6\Gamma^2 , \tag{6.9a}$$

$$m_{22}^{11} = m_{22}^{-1,-1} = 21\Gamma^2 , \tag{6.9b}$$

$$m_{22}^{00} = 16\Gamma^2 , \tag{6.9c}$$

$$m_{12}^{11} = m_{12}^{-1,-1} = \tfrac{95}{3}\Gamma^2 , \tag{6.9d}$$

$$m_{12}^{00} = \tfrac{20}{3}\Gamma^2 . \tag{6.9e}$$

Inserting these evaluations into Eq. (6.8b) we obtain

$$\sigma_2^{\pm 2\,(0)} = x\Gamma^2 \textstyle\sum_{\vec{\delta}} [-\tfrac{6}{7}P_4(y) - \tfrac{50}{7}P_2(y) + 14] , \tag{6.10a}$$

$$\sigma_2^{\pm 1\,(0)} = x\Gamma^2 \textstyle\sum_{\vec{\delta}} [\tfrac{24}{7}P_4(y) + \tfrac{25}{7}P_2(y) + 14], \tag{6.10b}$$

$$\sigma_2^{0\,(0)} = x\Gamma^2 \textstyle\sum_{\vec{\delta}} [-\tfrac{36}{7}P_4(y) + \tfrac{50}{7}P_2(y) + 14], \tag{6.10c}$$

$$\sigma_1^{\pm 1\,(0)} = x\Gamma^2 \textstyle\sum_{\vec{\delta}} [\tfrac{5}{4}P_2(y) + \tfrac{70}{3}] , \tag{6.10d}$$

$$\sigma_1^{0\,(0)} = x\Gamma^2 \textstyle\sum_{\vec{\delta}} [-\tfrac{5}{2}P_2(y) + \tfrac{70}{3}] , \tag{6.10e}$$

where $y = \cos\beta''$ and $P_n(y)$ is the Legendre polynomial. In deriving these formulas we have considered only nearest-neighbor interactions. This approximation introduces very little error into our results, because the nearest neighbors completely dominate the lattice sums. Note that for the axis of quantization along the crystal c axis one has

$$\textstyle\sum_{\vec{\delta}} Y_4^n(\hat{\delta}) = 0 , \quad n \neq 0 \tag{6.11a}$$

$$\textstyle\sum_{\vec{\delta}} Y_2^n(\hat{\delta}) = 0 . \tag{6.11b}$$

Thus, in evaluating the sum over $\vec{\delta}$ in Eq. (6.10) by using the addition theorem for spherical harmonics, we cannot omit terms involving $Y_L^M(\hat{\delta})$ with $M \neq 0$. Hence, we write

$$\textstyle\sum_{\vec{\delta}} P_2(y) = \sum_{\vec{\delta}} P_2(\cos\theta_{Hc})\, P_2(\cos\theta_{\delta c}) = 0, \tag{6.12a}$$

$$\textstyle\sum_{\vec{\delta}} P_4(y) = \sum_{\vec{\delta}} P_4(\cos\theta_{Hc}) P_4(\cos\theta_{\delta c}) = \tfrac{7}{6}\, P_4(\cos\theta_{Hc}), \tag{6.12b}$$

where $\theta_{\delta c}$ and θ_{Hc} are the angles between the crystal c axis and $\vec{\delta}$ and the magnetic field, respectively. Accordingly,

$$\sigma_2^{\pm 2\,(0)} = 168x\Gamma^2[1 - \tfrac{1}{168}\, P_4(\cos\theta_{Hc})], \tag{6.13a}$$

$$\sigma_2^{\pm 1\,(0)} = 168x\Gamma^2[1 + \tfrac{1}{42} P_4(\cos\theta_{Hc})], \tag{6.13b}$$

$$\sigma_2^{0\,(0)} = 168x\Gamma^2[1 - \tfrac{1}{28} P_4(\cos\theta_{Hc})], \tag{6.13c}$$

$$\sigma_1^{\pm 1\,(0)} = \sigma_1^{0\,(0)} = 280x\Gamma^2 . \tag{6.13d}$$

These results are consistent with the values quoted by Moriya and Motizuki,[8] whose Hamiltonian also included small interactions other than those of the EQQ type. From our results it is clear that the dependence on magnetic field orientation is completely negligible, so that all further calculations will be made for a powder. From Eq. (6.13) we have the results for a powder,

$$\langle\langle \sigma_L^{(0)} \rangle\rangle_{pa} \equiv \sigma_L = 840 x \Gamma^2/(2L+1) \ . \tag{6.14}$$

C. Fourth Moments for a Powder at $T=\infty$

Let us now calculate the fourth moment. The powder and alloy average of π_L^M denoted $\langle\langle \pi_L^M \rangle\rangle_{pa}$ is independent of M and can be found at infinite temperature as

$$\langle\langle \pi_L^M \rangle\rangle_{pa} = (2L+1)^{-1} \textstyle\sum_M \langle\langle \pi_L^{M(0)} \rangle\rangle_a \equiv \pi_L \tag{6.15}$$

in terms of an alloy average. To evaluate this expression we must construct

$$O_L^M \equiv [\mathcal{H}, [\mathcal{H}, \mathcal{T}_L^M(J_0)]] , \tag{6.16}$$

which consists of a sum of three types of terms:

$$O_L^M = \sum_{\vec{\delta}} O_L^M(\vec{\delta}, \vec{\delta}) + \sum_{\vec{\delta} \neq \vec{\delta}'} O_L^M(\vec{\delta}, \vec{\delta}') + \sum_{\vec{\delta} + \vec{\delta}' \neq 0} P_L^M(\vec{\delta}, \vec{\delta}'), \tag{6.17}$$

where

$$O_L^M(\vec{\delta}, \vec{\delta}') = [\mathcal{H}_{0\vec{\delta}'}, [\mathcal{H}_{0\vec{\delta}}, \mathcal{T}_L^M(J_0)]] , \tag{6.18a}$$

$$P_L^M(\vec{\delta}, \vec{\delta}') = [\mathcal{H}_{\vec{\delta}, \vec{\delta} + \vec{\delta}'}, [\mathcal{H}_{0\vec{\delta}}, \mathcal{T}_L^M(J_0)]] \ . \tag{6.18b}$$

From symmetry considerations it can be seen that contributions to π_L from cross terms between different types of terms in Eq. (6.17) vanish, so that

$$(2L+1)(L+3)(8\pi)^{-1} \pi_L = \sum_{i=1}^{5} T_i \ , \tag{6.19}$$

where

$$T_1 = x \sum_{M\vec{\delta}} \langle O_L^M(\vec{\delta}, \vec{\delta}) O_L^M(\vec{\delta}, \vec{\delta})^\dagger \rangle_\infty \ , \tag{6.20a}$$

$$T_2 = x^2 \sum_{M, \vec{\delta}, \vec{\delta}' ; \vec{\delta} \neq \vec{\delta}'} \langle O_L^M(\vec{\delta}, \vec{\delta}) O_L^M(\vec{\delta}', \vec{\delta}')^\dagger \rangle_\infty \ , \tag{6.20b}$$

$$T_3 = x^2 \sum_{M, \vec{\delta}, \vec{\delta}' ; \vec{\delta} \neq \vec{\delta}'} \langle O_L^M(\vec{\delta}, \vec{\delta}') O_L^M(\vec{\delta}, \vec{\delta}')^\dagger \rangle_\infty \ , \tag{6.20c}$$

$$T_4 = x^2 \sum \langle O_L^M(\vec{\delta}, \vec{\delta}') O_L^M(\vec{\delta}', \vec{\delta})^\dagger \rangle_\infty \ , \tag{6.20d}$$

$$T_5 = x^2 \sum \langle P_L^M(\vec{\delta}, \vec{\delta}') P_L^M(\vec{\delta}, \vec{\delta}')^\dagger \rangle_\infty \ . \tag{6.20e}$$

The first term in Eq. (6.20) would be the most tedious to evaluate, except that it related to the fourth moment of the spectral function for pairs. Using the results of Table V we find

$$T_1 = (2L+1)(L+3)(8\pi)^{-1} x 22\,040\, \Gamma^4, \quad L=1 \tag{6.21a}$$

$$= (2L+1)(L+3)(8\pi)^{-1} x 5304\, \Gamma^4, \quad L=2 . \tag{6.21b}$$

Also it is helpful to use

$$T_3 + T_4 = T_3' + T_4' \ , \tag{6.22}$$

where

$$T_3' = 2x^2 \sum_{\vec{\delta} \neq \vec{\delta}', M} \langle O_L^M(\vec{\delta}, \vec{\delta}') O_L^M(\vec{\delta}, \vec{\delta}')^\dagger \rangle_\infty , \tag{6.23a}$$

$$T_4' = -\tfrac{1}{2} x^2 \sum_{\vec{\delta} \neq \vec{\delta}', M} \langle [[\mathcal{H}_{0\vec{\delta}'}, \mathcal{H}_{0\vec{\delta}}], \mathcal{T}_L^M(J_0)] \, [\mathcal{T}_L^M(J_0)^\dagger, [\mathcal{H}_{0\vec{\delta}'}, \mathcal{H}_{0\vec{\delta}}]] \rangle \ . \tag{6.23b}$$

In Appendix B we have evaluated these terms and also T_2 and T_5 of Eq. (6.20). We find that

$$T_2 = \langle \mathcal{T}_L^M (\mathcal{T}_L^M)^\dagger \rangle \, 980 x^2 \Gamma^4 \times \{48(7-2L) - 100[(2L+1)/(7-2L)] S_L\}, \tag{6.24a}$$

$$T_3' = \langle \mathcal{T}_L^M (\mathcal{T}_L^M)^\dagger \rangle \, 1960 x^2 \Gamma^4 \times \left\{ 48(2L+1) - 100 \left[\frac{(7-2L)}{(2L+1)} \right] S_{3-L} \right\}, \tag{6.24b}$$

$$T_4' = -\langle \mathcal{T}_L^M (\mathcal{T}_L^M)^\dagger \rangle \, x^2 \Gamma^4 \, 7000(4L^2 - 1), \tag{6.24c}$$

$$T_5 = 12\,600 \langle \mathcal{T}_L^M (\mathcal{T}_L^M)^\dagger \rangle \, x^2 \Gamma^4 \ , \tag{6.24d}$$

where

$$S_1 = \tfrac{41}{98} \ , \tag{6.25a}$$

$$S_2 = \tfrac{1089}{12250} \ , \tag{6.25b}$$

so that

$$\pi_1 = \Gamma^4 (22\,040 x + 189\,600 x^2) \ , \tag{6.26a}$$

$$\pi_2 = \Gamma^4 (5304 x + 113\,760 x^2) \ , \tag{6.26b}$$

which gives

$$\pi_1 / 3\sigma_1^2 = 1.34 + 0.063 x^{-1}, \tag{6.27a}$$

$$\pi_2 / 3\sigma_2^2 = 0.81 + 0.094 x^{-1} \ . \tag{6.27b}$$

Since the ratio $\pi/3\sigma^2$ is unity for Gaussian shape, these results confirm that the Gaussian approximation is quite satisfactory for the calculation of T_1, at least at very high temperatures. From Eq. (6.27) we see that whereas $\rho_1^M(\omega)$ is more peaked than a Gaussian, $\rho_2^M(\omega)$ is flatter than a Gaussian. Since these two departures from Gaussian shape tend to cancel one another, we expect reasonable results until the terms in Eq. (6.27) proportional to x^{-1} become important, say at $x \leq 0.1$. However, these results do not include the effects of other than nearest-neighbor interactions. Indeed, these moments are quite insensitive to further-neighbor interactions. One can estimate that if a molecule has only one $(J=1)$ neighbor at a separation $(2)^{1/2} R_0$, it will relax approximately $(2)^{5/2} \sim 5$ times faster than if it had one nearest-neighboring $(J=1)$ molecule. Thus, the fact that the interaction falls off rapidly, $\sim R^{-5}$, weights isolated configurations very heavily in T_1^{-1}. The moment calculation averages the energy width. What we need to do is to average the reciprocal of the energy width. This explains why the statistical model used by Sung[10] and modified by us in Sec. VII is appropriate at low concentrations.

D. High-Temperature Expansion for Second Moments

Finally, let us calculate $\langle\langle \sigma_L^{(1)} \rangle\rangle_{pa}$, the powder and alloy average of $\sigma_L^{M(1)}$, which can be written as

$$\langle\langle \sigma_L^{(1)} \rangle\rangle_{pa} = (2L+1)^{-1} \textstyle\sum_M \langle\langle \sigma_L^{M(1)} \rangle\rangle_a , \tag{6.28}$$

which we write in the form

$$\langle\langle \sigma_L^{(1)} \rangle\rangle_{pa} = -\beta \langle\langle \sigma_L^{(0)} \rangle\rangle_{pa} [A + Bx] , \tag{6.29}$$

where

$$A = \Gamma_0^{-2} [4\pi/35(L+3)] \textstyle\sum_\mu (-1)^\mu \langle [\mathcal{T}_L^\mu(J_0), \mathcal{H}_{0\vec{\delta}}] \times [\mathcal{H}_{0\vec{\delta}}, \mathcal{T}_L^{-\mu}(J_0)] \mathcal{H}_{0\vec{\delta}} \rangle_\infty , \tag{6.30a}$$

$$B = \Gamma_0^{-2} [16\pi/35(L+3)] \textstyle\sum_\mu (-1)^\mu \langle [\mathcal{T}_L^\mu(J_0), \mathcal{H}_{0\vec{\delta}}] \times [\mathcal{H}_{0\vec{\delta}'}, \mathcal{T}_L^{-\mu}(J_0)] \mathcal{H}_{\vec{\delta}\vec{\delta}'} \rangle_\infty . \tag{6.30b}$$

We have taken advantage of the invariance of $\langle\langle \sigma_L^{(1)} \rangle\rangle_p$ with respect to the choice of quantization axis to sum these expressions over $\vec{\delta}$ and $\vec{\delta}'$. Thus in Eq. (6.30b) both $\vec{\delta}$ and $\vec{\delta}'$ are nearest neighbors and in both Eq. (6.30a) and (6.30b) one should count only one configuration. Again, A can be obtained by calculating the second moment of the spectral function for pairs correct to order $1/T$, so that

$$A = \tfrac{9}{14} \Gamma . \tag{6.31}$$

The coefficient B is evaluated in Appendix B. Our results for $\langle\langle \sigma_L^{(1)} \rangle\rangle_p$ correct to order $1/T$ then give

$$\langle\langle \sigma_L^{(0)} + \sigma_L^{(1)} \rangle\rangle_{pa} = \langle\langle \sigma_L^{(0)} \rangle\rangle_{pa} (1 - \tfrac{9}{14}\beta\Gamma - \tfrac{1857}{1792} x\beta\Gamma), \tag{6.32}$$

with $\langle\langle \sigma_L^{(0)} \rangle\rangle_{pa}$ given in Eq. (6.14).

E. Numerical Evaluation of T_1 and Discussion

We now calculate the relaxation time T_1. Neglecting the small anisotropy of the moments and assuming a Gaussian shape, our calculations yield the spectral weight functions as

$$\rho_L^M(\omega) = (L+3)(4\pi)^{-1} (2\pi \langle\langle \sigma_L^{(0)} + \sigma_L^{(1)} \rangle\rangle_{pa})^{-1/2} \times \exp[-\tfrac{1}{2}(\hbar\omega)^2 / \langle\langle \sigma_L^{(0)} + \sigma_L^{(1)} \rangle\rangle_{pa}]. \tag{6.33}$$

Since $\hbar\omega_0 \ll \sigma_L^{(0)}$, we set $\omega = 0$. Then, collecting the results of the previous subsections we can evaluate Eq. (6.1) as

$$T_1 = (\Gamma/hc_0) x^{1/2} 12 c_0 (210/8\pi^3)^{1/2} \times (1 - \tfrac{9}{14}\beta\Gamma - \tfrac{1857}{1792} x\beta\Gamma)^{1/2} (4c^2\sqrt{3} + 45d^2\sqrt{5})^{-1}, \tag{6.34}$$

where c_0 denotes the speed of light. Numerically we obtain

$$T_1 = 0.780 (\Gamma/hc_0) x^{1/2} (1 - \tfrac{9}{14}\Gamma\beta - \tfrac{1857}{1792} x\Gamma\beta)^{1/2} \quad \text{for } H_2 \tag{6.35a}$$

$$T_{1,\text{odd}} = 5.12 (\Gamma/hc_0) x^{1/2} (1 - \tfrac{9}{14}\Gamma\beta - \tfrac{1857}{1792} x\Gamma\beta)^{1/2} \quad \text{for } \mathrm{D}_2. \tag{6.35b}$$

Here $T_{1,\text{odd}}$ is the relaxation time of the odd-J molecules. As Moriya and Motizuki point out,[8] one must relate $T_{1,\text{odd}}$ in D_2 to the observed spin-lattice relaxation time T_1 of the total nuclear-spin system. In the high-temperature regime we assume that the nuclei of the even-J molecules relax rapidly towards those of the odd-J molecules. In that case Moriya and Motizuki show that

$$T_1 = T_{1,\text{odd}} (5 - 3x/2x) . \tag{6.36}$$

For H_2 our calculations can be compared them to extensive experimental data of Amstutz *et al.*[63] They have analyzed their data and compared it to our formula, so we will not repeat their analysis here. Two comments about their results may be made. First of all, their experimental results agree quite closely with the temperature and concentration dependence predicted in Eq. (6.35a). For a quantitative agreement for the absolute magnitude of T_1 they need to use the value $\Gamma_{\text{eff}} \approx 0.46$ cm^{-1} which corresponds to $\Gamma_{\text{eff}}/\Gamma_0 = 0.66$. This value of Γ_{eff} agrees fairly well with those obtained[64] from other methods.[6, 21, 51, 65–69] In fact, it is possible that here the effects on Γ_{eff} of thermal phonons might be important.[70] In any event, small departures from the Gaussian model would not be surprising. In particular, from our results in Eq. (6.27) it can be shown that our analysis will lead to underestimating slightly (i.e., by ~10%) the value of Γ_{eff}.

Note added in proof. Hama and Nakamura have analyzed this point in detail in a preprint we have received.

In D_2 there have also been measurements of T_1 in the high-temperature regime,[71, 7] and the two measurements are quite consistent with one another. For $(J=1)$ concentrations above $x = 0.30$ the experimental results for T_1 at infinite temperature can be represented by

$$T_{1,\text{odd}}(T \to \infty) = 2.7 x^{1/2} \text{ sec}. \tag{6.37}$$

This result again leads to a determination of Γ. Comparison with Eq. (6.35b) yields $\Gamma_{\text{eff}} = 0.53$ cm^{-1} $= 0.63\Gamma_0$. In this case the value of Γ_{eff} is somewhat lower than that found by other methods; however, the discrepancy is not so large that any firm conclusions can be reached. It is also possible to make qualitative statements about the experimentally determined temperature dependence of T_1. An analysis is difficult because above 10 °K,[71] where the theory might be expected to apply, the temperature dependence of T_1 is too small to be very significant. Below 10 °K[7] it is not certain that the two-term high-temperature expansion in Eq. (6.35) is reliable.[6] Thus we cannot expect quantitative agreement with experiment, at present. In fact, the theoretical values of $T_1(\infty) - T_1(T)$ are within a factor of 2 of the corresponding experimental values, which is a reasonable result considering the difficulties involved in such a comparison.

Finally, we make some pedagogical comments about the method of calculation. We have chosen to perform our calculations using the moments of the spectral weight function corresponding to the anticommutator in Eq. (5.1). We have done this because this function, and not the spectral function $\mathcal{G}_L^M(\omega)$, is expected to be an even function of ω. In fact, for the pair system we see from Eq. (5.6) that the spectral weight function is an even function of ω. More generally, for the full many-body system, the "diagonal" spectral weight functions, i.e., those of the type $\rho_{LL}^{MM}(\omega)$, will be even functions of ω assuming, as is quite reasonable, that the magnetic energies ha and hb can be neglected. The evenness in ω is then a consequence of time-reversal symmetry. Thus, it seemed more natural to invoke a Gaussian assumption for these patently even functions of ω than for the spectral functions, which we know are even functions of ω only at infinite temperatures. As far as the nuclear-spin system is concerned, we are working in the infinite-temperature limit. Thus, in our calculations of Secs. IV and V it did not matter which spectral function we used to compute moments.

There is still another way in which our calculations differ in method from those of Moriya and Motizuki.[8] They compute moments of spectral weight functions corresponding to the choice of operators in Eq. (6.3), $A=J_+J_z$, $B=A^\dagger$. This brings up the question of determining, if possible, the optimum way to approximate $\rho_{AB}(\omega)$ by one or more Gaussian functions. Our approximations correspond to writing

$$\rho_{J_+J_z;J_zJ_+}(\omega)=\tfrac{1}{4}\rho_{(J_+J_z+J_zJ_+;J_zJ_-+J_-J_z)}(\omega)+\tfrac{1}{4}\rho_{J_+;J_-}(\omega)\,, \qquad (6.38)$$

and then approximating each of the spectral weight functions on the right-hand side of this equation by a Gaussian, whereas Moriya and Motizuki approximate the spectral weight function on the left-hand side by a single Gaussian. Our scheme seems more reasonable, since operators of different symmetry are independent in some sense.[60] Furthermore, we believe it is likely that applying the criterion developed by Roth[72] would lead to results similar to those we have obtained. Fortunately, the numerical difference between the two approximation schemes is completely negligible, so the point is an academic one in the present context.

VII. NMR RELAXATION TIMES AT LOW $(J=1)$ CONCENTRATION

We have seen in Sec. VI that the Gaussian approximation for $\rho_{LL}^{MM}(\omega)$ becomes poor in the limit of low $(J=1)$ concentration. The reason for this is that the Gaussian approximation gives roughly the average over configurations of the energy width, whereas the observed relaxation rate is expected to be the average over configurations of the relaxation rate, which is inversely proportional to the energy width. Furthermore, since $(J=1)$ molecules with no nearest-neighboring $(J=1)$ molecules relax much faster than those with even one nearest neighbor, it is essential to treat such configurations correctly. Thus one should take the average over configurations of the inverse of the energy width. As Sung[10] has shown, this can be accomplished by the use of the statistical model.[11] Accordingly, in Sec. VII A we give a treatment of this model which becomes exact in the limit when only pairwise interactions are important, i.e., at low concentration. However, in contrast to Sung's later work,[73] we would not attach much significance to an ultralow $(x<10^{-3})$ concentration calculation, because then the smaller and more uncertain terms in the Hamiltonian become important. In Sec. VII B we analyze Sung's treatment of the statistical model. From our analysis we conclude that the apparent agreement between Sung's theory and the experimental data is the fortuitous result of several computational errors. When these errors are corrected, we find that his theory predicts relaxation times which are about twice as long as those actually observed.

A. Statistical Model at Low $(J=1)$ Concentration

As we have mentioned, we abandon the Gaussian approximation for $\rho_{LL}^{MM}(\omega)$. Here we shall determine $\rho_{LL}^{MM}(\omega)$ by calculating its Fourier transform $f_L^M(t)$, defined as

$$f_L^M(t)=\int_{-\infty}^{+\infty}\rho_L^M(\omega)\,e^{-i\omega t}\,\hbar\,d\omega \qquad (7.1a)$$

$$=\langle\{\mathcal{T}_L^M(0,t),\ \mathcal{T}_L^{-M}(0,0)\}_+\rangle\,(-1)^M, \qquad (7.1b)$$

where

$$\mathcal{T}_L^M(\vec{\mathrm{R}},t)=e^{i\mathcal{H}t}\,\mathcal{T}_L^M(J_{\vec{\mathrm{R}}})\,e^{-i\mathcal{H}t}. \qquad (7.2)$$

Now the Hamiltonian is the sum of two-body terms,

$$\mathcal{H}=\sum_{i<j}\mathcal{H}_{ij}\,, \qquad (7.3)$$

where the sum is carried only over $(J=1)$ molecules. As Sung points out, it is reasonable to assume that the molecule at $\vec{r}$ interacts only with a small number of other molecules and that as a first approximation the oscillatory contributions from each term are completely independent. Also we shall evaluate all thermodynamic averages at infinite temperature. As will be clear later, the dominant contributions to $f_L^M(t)$ come from $(J=1)$ molecules which are at a separation $\sim R_0x^{-1/3}$. Thus the high-temperature regime is essentially $\Gamma(R_0/R_0x^{-1/3})^5\ll kT$, i.e., for $kT\gg\Gamma x^{5/3}$, a condition which is well satisfied in the data we will analyze.

Within these approximations we can write

$$f_L^M(t)=f_L^M(0)\langle\langle \prod_{\vec{R}} F_L^M(\vec{R},t)/F_L^M(\vec{R},0)\rangle\rangle_{pa}\,, \qquad (7.4)$$

where $F_L^M(\vec{R},t)$ is the exact $f_L^M(t)$ for an isolated pair of $(J=1)$ molecules at a separation $\vec{R}$. We shall take the average over random configurations of $(J=1)$ molecules, completely neglecting possible correlations in the probability distribution function for clusters of $(J=1)$ molecules. This approximation is probably reasonable except for H_2 for $x<0.1$ and $T<3$ °K when the $(J=1)$ molecules have a tendency to cluster.[50,51] For a random alloy Eq. (7.4) becomes

$$f_L^M(t)=f_L^M(0)\prod_{\vec{R}}\,[1-x+xF_L^M(\vec{R},t)/F_L^M(\vec{R},0)] \qquad (7.5)$$

or

$$f_L^M(t)=f_L^M(0)\prod_{\vec{R}}\,[1-x\varphi_L^M(\vec{R},t)]\,, \qquad (7.6)$$

where

$$\varphi_L^M(\vec{R},t)=1-F_L^M(\vec{R},t)/F_L^M(\vec{R},0), \qquad (7.7)$$

$$f_L^M(0)=(L+3)/4\pi\,. \qquad (7.8)$$

The powder average will be taken later. We write Eq. (7.6) as

$$f_L^M(t)=f_L^M(0)\exp\{\textstyle\sum_{\vec{R}}\ln[1-x\varphi_L^M(\vec{R},t)]\} \qquad (7.9a)$$

$$\approx f_L^M(0)\exp[-xQ_L^M(t)]\,, \qquad (7.9b)$$

where

$$Q_L^M(t)=\textstyle\sum_{\vec{R}}\varphi_L^M(\vec{R},t). \qquad (7.10)$$

In going from Eq. (7.9a) to Eq. (7.9b) we have dropped terms in the exponent of order x^2 or higher. In this way we do not describe properly correlations or interference effects, but such effects are at least of order x^2. Hence our treatment seems to be rigorous in the low-concentration limit.

Since the relaxation rate T_1^{-1} is dominated by $(J=1)$ molecules for which $R\gg R_0$, we convert the sum to an integral using

$$\textstyle\sum_{\vec{R}}\to\int\rho\,d\vec{R}=\sqrt{2}\,R_0^{-3}\int d\vec{R}\,, \qquad (7.11)$$

where the density of molecules ρ is $\sqrt{2}R_0^{-3}$ for an hcp lattice. Thus, we have

$$Q_L^M(t)=\sqrt{2}R_0^{-3}\int d\vec{R}\,\varphi_L^M(\vec{R},t)\,. \qquad (7.12)$$

Recall that the quantization axis in Eq. (6.1) is along the magnetic field, so that we shall make this choice of coordinates for the present discussion. But according to Eq. (5.11) we can express $F_L^M(\vec{R},t)$ in terms of functions defined with respect to the pair axis which we indicate by a tilde. Thus

$$\varphi_L^M(\vec{R},t)=\textstyle\sum_\mu |D_{M\mu}^{(L)}(\Omega_{\vec{R}\vec{H}})|^2\,\tilde{\varphi}_L^\mu(\vec{R},t), \qquad (7.13)$$

where $\Omega_{\vec{R}\vec{H}}$ is the orientation of $\vec{R}$ with respect to the magnetic field. Using the definition Eq. (5.1) together with Eq. (5.10) at infinite temperature we obtain

$$\tilde{\varphi}_L^\mu(\vec{R},t)=1-\int_{-\infty}^{+\infty}\rho_L^{\mu\mu}\left[\omega\left(\frac{R}{R_0}\right)^5\right]\left(\frac{R}{R_0}\right)^5 e^{-i\omega t}\,\hbar d\omega \qquad (7.14a)$$

$$=1-\textstyle\sum_n C_L^\mu(E_n)\cos[(R_0/R)^5(E_nt/\hbar)]. \qquad (7.14b)$$

In writing these equations we have used the fact that the energy levels of a pair of $(J=1)$ molecules scale with R^{-5}. Substituting Eq. (7.13) and (7.14) into (7.12) we find that

$$Q_L^M(t)=\sqrt{2}\,R_0^{-3}\int R^2dR\int d\Omega_{\vec{R}\vec{H}}\sum_{\mu n}|\,D_{M\mu}^{(L)}(\Omega_{\vec{R}\vec{H}})|^2 \times C_L^\mu(E_n)\left\{1-\cos\left[\left(\frac{R_0}{R}\right)^5(E_nt/\hbar)\right]\right\} \qquad (7.15a)$$

$$=(4\pi\sqrt{2}\,R_0^{-3})\int R^2dR\textstyle\sum_n C_L(E_n) \times\{1-\cos[(R_0/R)^5(E_nt/\hbar)]\}\,. \qquad (7.15b)$$

This result can be written as

$$Q_L^M(t)=\tfrac{4}{5}\pi\sqrt{2}\,|t|^{3/5}\langle E_n^{3/5}\rangle_L\,\hbar^{-3/5} \times\int_0^\infty u^{-8/5}(1-\cos u)\,du\,, \qquad (7.16)$$

where $\langle E_n^s\rangle_L$ is the average of $(E_n)^s$:

$$\langle E_n^s\rangle_L\equiv\textstyle\sum_n C_L(E_n)\,|E_n|^s. \qquad (7.17)$$

Numerically we find

$$\tfrac{4}{5}\pi\sqrt{2}\int_0^\infty u^{-8/5}(1-\cos u)\,du$$

$$=\tfrac{4}{3}\pi\sqrt{2}\,\mathrm{Im}\int_0^\infty e^{iu}u^{-3/5}\,du \qquad (7.18a)$$

$$=\tfrac{4}{3}\pi\sqrt{2}\;\Gamma(\tfrac{2}{5})\sin\tfrac{1}{5}\pi\,, \qquad (7.18b)$$

where $\Gamma(z)$ is the gamma function. Taking account of Eq. (7.1) and (7.9b) we find the spectral functions,

$$h\rho_{LL}^{MM}(\omega)=f_L^M(0)\int_{-\infty}^{+\infty}dt \times\exp(i\omega t-7.75x|t|^{3/5}\langle E_n^{3/5}\rangle_L\,\hbar^{-3/5}). \qquad (7.19)$$

In the low-frequency regime, $\hbar\omega\ll x^{5/3}\langle E_n^{3/5}\rangle_L^{5/3}$, we find

$$\rho_{LL}^{MM}(\omega)=\tfrac{10}{3}f_L^M(0)\,(7.75x)^{-5/3}\,\Gamma(\tfrac{5}{3})\,\langle E_n^{3/5}\rangle_L^{-5/3} \qquad (7.20a)$$

$$=0.0992\,[(L+3)/4\pi]\,\langle E_n^{3/5}\rangle_L^{-5/3}\,x^{-5/3}; \qquad (7.20b)$$

whereas in the high-frequency regime, $\hbar\omega\gg x^{5/3}\times\langle E_n^{3/5}\rangle_L^{5/3}$, we have

$$h\rho_{LL}^{MM}(\omega)=2f_L^M(0)\,\mathrm{Re}\int_0^\infty dt\,e^{i\omega t}\,e^{-\gamma_L x|t|^{3/5}} \qquad (7.21a)$$

$$=2f_L^M(0)\,\mathrm{Re}\,i\int_0^\infty du\,e^{-\omega u}\,e^{-\gamma_L u^{3/5}xe^{3\pi i/10}} \qquad (7.21b)$$

$$=2f_L^M(0)\,\gamma_L x\,\omega^{-8/5}\,\Gamma(\tfrac{8}{5})\sin\tfrac{3}{10}\pi\,, \qquad (7.21c)$$

where $\gamma_L=7.75\langle E_n^{3/5}\rangle_L\,\hbar^{-3/5}$.

Experimentally one is usually in the low-frequency regime, in which case one finds T_1, using Eq. (7.20) in (6.1), to be

$$T_1^{-1}=0.198\pi h\left(\frac{2c^2}{3\langle E_n^{3/5}\rangle_1^{5/3}}+\frac{15\,d^2}{2\langle E_n^{3/5}\rangle_2^{5/3}}\right)x^{-5/3}. \tag{7.22}$$

From Table V we evaluate $\langle E_n^{3/5}\rangle_L$ as

$$\langle E_n^{3/5}\rangle_1=1.48\Gamma, \tag{7.23a}$$

$$\langle E_n^{3/5}\rangle_2=1.71\Gamma, \tag{7.23b}$$

which gives

$$T_1=3.29\Gamma\,x^{5/3}\quad\text{for H}_2, \tag{7.24a}$$

$$T_1=24.3\Gamma\,x^{5/3}\quad\text{for D}_2, \tag{7.24b}$$

when Γ is expressed in cm^{-1} and T_1 is in sec. Note that since the important interactions are those between distant neighbors the phonon renormalizations are completely negligible. However, as pointed out by Hardy and Gaines[33] one must take account of dielectric screening. To do this we simply scale the interactions by the dielectric constant,

$$T_1=3.29\Gamma\,x^{5/3}/\epsilon_0=2.53\,\Gamma\,x^{5/3}\quad\text{for H}_2, \tag{7.25a}$$

$$T_1=24.3\,\Gamma\,x^{5/3}/\epsilon_0=18.7\,\Gamma\,x^{5/3}\;\text{for D}_2, \tag{7.25b}$$

where we have taken the dielectric constant to be $\epsilon_0=1.3$.[74]

We can compare the above predictions with the experimental data of Hardy and Gaines[9] for H_2 and of Wang and White[71] and Weinhaus *et al.*[7] for D_2. In both cases the data are fit reasonably well by the $x^{5/3}$ law first found by Sung.[10] For D_2 the temperature dependence of T_1 at low concentration causes some uncertainty in the interpretation. While it is expected that T_1 should vary rapidly in the diffusion-dominated regime ($T>10$ °K), it is not easy to understand a temperature dependence[7] below that regime. On account of this unexplained dependence it is not easy to perform the extrapolation of the T_1 data to "infinite" temperature as is desired for comparison with theory. Therefore, our analysis for D_2 must be regarded with caution. By fitting the data to an $x^{5/3}$ law we find the results

$$T_1\,x^{-5/3}=1\text{ sec}\quad\text{for H}_2; \tag{7.26a}$$

$$T_1\,x^{-5/3}=9\text{ sec}\quad\text{for D}_2. \tag{7.26b}$$

Comparing these results with Eq. (7.25) leads to a determination of Γ_{eff}:

$$\Gamma_{\text{eff}}=0.40\text{ cm}^{-1}=0.57\Gamma_0\quad\text{for H}_2, \tag{7.27a}$$

$$\Gamma_{\text{eff}}=0.47\text{ cm}^{-1}=0.57\Gamma_0\quad\text{for D}_2. \tag{7.27b}$$

It is interesting that these values of Γ_{eff} are comparable with those determined by fitting the experimental data at higher concentration to the Gaussian model, although they are somewhat smaller than the values obtained by other methods.

B. Critique of Sung's Theory

In view of the fact that our version of the statistical theory does not give the magnitude of T_1 correctly, we are led to reexamine Sung's theory[10] to see why he obtains such good agreement with experiment. His success is surprising because it would seem that our approximations ought to be more reliable than his. In fact, we find this to be the case. We find that there are some numerical and algebraic errors in his work. When these are corrected, his theoretical results are in worse agreement with the data than those found above.

Although Sung's approximations are quite similar to ours, there are some physical differences which should be noted. He uses Eq. (7.4), but instead of the exact $f_L^M(\vec{R},t)$ for pairs he uses an approximate function with a single frequency. This characteristic frequency is determined by the condition that

$$\omega_0^2=\frac{d^2F_L^M(\vec{R},t)}{dt^2}\Big/F_L^M(\vec{R},t)\bigg|_{t=0}, \tag{7.28}$$

so that the second frequency moment is correctly given by the approximate function. The difference between using this approximate function with a single frequency and the exact pair function with several (see Table V) frequencies can be deduced by considering the fourth frequency moment of the two distributions. Clearly the fourth moment of the exact function is significantly larger than that of the approximate function, since the latter involves a single frequency. As a result, in analogy with the phenomenon of exchange narrowing of NMR line shapes,[75] one expects a larger spectral density and hence a faster relaxation rate, from the exact function. In fact, the result of Sung's theory can be put in the form of Eq. (7.22):

$$T_1^{-1}=0.198\pi h\left(\frac{2c^2}{3\langle E_n^2\rangle_1^{1/2}}+\frac{15d^2}{2\langle E_n^2\rangle_2^{1/2}}\right)x^{-5/3}, \tag{7.29}$$

which gives for H_2

$$T_1x^{-5/3}=5.54\Gamma/\epsilon_0\,, \tag{7.30}$$

which is to be compared to Eq. (7.25a). Thus, we see that using Sung's theory to fit the experimental data leads to even smaller values of Γ_{eff} than does the theory presented above.

The reasons for the discrepancy between the result Eq. (7.29) and that cited in Ref. 10 are the following. First, the Hamiltonian for EQQ interactions, Eq. (4) of Ref. 6, is incorrect because this form implies the use of Rose's phase[31] convention for spherical harmonics, whereas the Condon and Shortly phase convention[76] is actually employed. Also, the factor of $\sqrt{2}$ in Eq. (7.12) has not been included in Ref. 10. There appears to be some difference also in the evaluation of integrals, e.g., see our Eqs. (7.18) and (7.21). In particular, the last result has some physics connected with it. At ultralow concentration, i.e., in the high-frequency regime, $\hbar\omega \gg x^{5/3}\langle E_n^{3/5}\rangle_L^{5/3}$, the spectral density must be proportional to the probability of finding another $(J=1)$ molecule within some finite separation determined by ω. Clearly this probability is proportional to x as we find and not $x^{5/4}$ as given by Sung. This evaluation will also affect the results of Ref. 73, but since the numerical constants were not given, no estimates of these effects can be given.

VIII. NUCLEAR SPIN-LATTICE RELAXATION IN THE ORDERED STATE

In this section we shall calculate the nuclear spin-lattice relaxation time T_1 for $(J=1)$ molecules in the orientationally ordered phase of solid hydrogen. A preliminary report of this work was presented earlier.[77] Meanwhile, a more detailed calculation leading to essentially the same result has been given by Homma.[78] However, the results we obtain here may be useful owing to their simple and explicit form.

First, we remark that Eq. (6.1) can be modified for the case of a powder.[79] Using the transformation properties of the irreducible tensor operators, one sees that the powder average of $\mathcal{J}_L^M(\omega)$ is

$$(2L+1)^{-1}\sum_{M'} \mathcal{J}_L^{M'}(\omega) \ .$$

Thus, for a powder we have

$$T_1^{-1} = \tfrac{16}{3}\pi^3 \left(\frac{c^2}{3} \sum_{\mu=-1}^{1} \mathcal{J}_1^{\mu}(0) + \frac{9d^2}{5} \sum_{\mu=-2}^{2} \mathcal{J}_2^{\mu}(0) \right) . \qquad (8.1)$$

In writing Eq. (8.1) we assume that the NMR resonance frequency ω_0 is much less than the frequencies of the rotational system, so that effectively $\omega_0 = 0$, and initially we shall consider the case of a homogeneous solid of $(J=1)$ molecules. In evaluating these spectral densities one must take account of the nature of the elementary excitations. As Homma *et al.*[41] and others[42,22,12] have shown, these excitations are quite similar to those in a magnetic insulator with a large anisotropy gap. The elementary excitations consist of removing molecules from the $J_z = 0$ state into the $J_z = \pm 1$ states, where the axis of quantization is along the local symmetry axis which coincides with one of the [111] directions. Since Eq. (8.1) is invariant with respect to the choice of quantization axis, we naturally take it to coincide with the local symmetry axis. Then it is clear that the spectral densities $\mathcal{J}_1^{\pm1}(\omega)$ and $\mathcal{J}_2^{\pm1}(\omega)$, which describe primarily the creation or destruction of a single excitation, cannot contribute to the relaxation process. The analogous situation obtains for magnetic insulators,[80–82] since in both cases the energy gap in the excitation spectrum is much larger than the nuclear Zeeman energy. Accordingly, the only processes which we need to consider are those in which the elementary excitations scatter off one another. These processes are primarily included in the spectral densities $\mathcal{J}_1^0(\omega)$, $\mathcal{J}_2^0(\omega)$, and $\mathcal{J}_2^{\pm2}(\omega)$.

In analogy with the case of magnetic insulators,[80–82] and as shown by Homma's more detailed calculations,[78] we know that these spectral densities must be of the form

$$\mathcal{J}_L^M(\omega) \approx C_L^M N^{-2} \sum_{\vec{k}\vec{k}'} \delta(\hbar\omega + E_{\vec{k}} - E_{\vec{k}'})\, n_{\vec{k}'} (1 + n_{\vec{k}}) \ , \qquad (8.2)$$

where N is the total number of molecules and C_L^M is a normalization constant to be determined. Since kT is much less than the quadrupole wave-energy gap, we may write

$$\mathcal{J}_L^M(\omega) \approx C_L^M N^{-2} \sum_{\vec{k}\vec{k}'} \delta(\hbar\omega + E_{\vec{k}} - E_{\vec{k}'})\, n_{\vec{k}'} \ . \qquad (8.3)$$

Here we ignore the fact that the quadrupole wave spectrum consists of several branches. This approximation is essential for a simple theory and probably does not affect the result noticeably. To determine the constants C_L^M we evaluate $\int_{-\infty}^{+\infty} d\omega \mathcal{J}_L^M(\omega)$. On the one hand, from Eq. (8.3) we have

$$\int_{-\infty}^{+\infty} d\omega\, \mathcal{J}_L^M(\omega) = 2C_L^M (\hbar N)^{-1} \textstyle\sum_{\vec{k}} n_{\vec{k}} \qquad (8.4a)$$

$$= 2\hbar^{-1} C_L^M \langle J_z^2 \rangle_T \ , \qquad (8.4b)$$

since there are two libron modes per molecule, whereas from the definition of the spectral function we obtain[83]

$$\int_{-\infty}^{+\infty} \mathcal{J}_L^M(\omega)\, (1/2\pi)\, d\omega = \langle \mathcal{T}_L^M(J_{\vec{R}}) \mathcal{T}_L^{-M}(J_{\vec{R}}) \rangle_T (-1)^M - \langle \mathcal{T}_L^M(J_{\vec{R}}) \rangle^2 \ . \qquad (8.5)$$

Evaluating the right-hand side of Eq. (8.5) to lowest order in the number of excitations and comparing the result to Eq. (8.4b) leads to a determination of C_L^M. In this way we find

$$C_1^0 = \tfrac{3}{4}\hbar \ , \qquad (8.6a)$$

$$C_2^0 = \tfrac{45}{16}\hbar \ , \qquad (8.6b)$$

$$C_2^{\pm2} = \tfrac{15}{16}\hbar \ , \qquad (8.6c)$$

To obtain explicit numerical results we rewrite Eq. (8.3) in terms of the density of states, defined by

$$\rho(E) \equiv \tfrac{1}{2} N^{-1} \textstyle\sum_{\vec{k}} \delta(E - E_{\vec{k}}) \ . \qquad (8.7)$$

Thus we have

$$\mathcal{J}_L^M(0) = C_L^M \int \delta(E - E')\, \rho(E)\, \rho(E')\, n(E)\, dE\, dE' \qquad (8.8a)$$

$$= C_L^M \int \rho^2(E)\, n(E)\, dE \ , \qquad (8.8b)$$

where

$$n(E) = [\exp(\beta E) - 1]^{-1} \ . \qquad (8.9)$$

We use the density of states as determined by Ueyama and Matsubara[42] or by Mertens *et al.*[12]

From the graph in Ref. 12 we estimate that[84]

$$\rho(E)=0, \qquad E<12\Gamma \qquad (8.10a)$$

$$\rho(E)=0.03(E-12\Gamma)/\Gamma^2, \qquad 12\Gamma<E<18\Gamma \qquad (8.10b)$$

$$\rho(E)=0.01(28\Gamma-E)/\Gamma^2, \qquad 18\Gamma<E<28\Gamma \qquad (8.10c)$$

$$\rho(E)=0, \qquad E>28\Gamma. \qquad (8.10d)$$

One can take account of the renormalization of the excitation spectrum[42,22,85] as a function of temperature by using a temperature-dependent EQQ coupling constant Γ in our results. Using this density of states we have evaluated the right-hand side of Eq. (8.8b) in the limit $(12\Gamma/kT)\gg 1$ as

$$\mathcal{J}_L^M(0)\approx(kT)^{-1}C_L^M(10y)^{-4}[18\exp(-12y) -(224y^2+128y+16)\exp(-18y) -2\exp(-28y)], \qquad (8.11)$$

where $y=(\Gamma/kT)$. For an alloy of $(J=0)$ and $(J=1)$ molecules the simplest approximation is to assume that all fields scale with the concentration x of $(J=1)$ molecules. Then Eq. (8.11) is still valid providing we take $y=x\Gamma/kT$, which gives a law of corresponding states. Substitution of Eq. (8.11) into Eq. (8.1) yields the following numerical results:

$$T_1/T=5.5\times10^4\ \mathrm{sec\,K^{-1}}, \quad y=1.00 \qquad (8.12a)$$

$$T_1/T=1.0\times10^3\ \mathrm{sec\,K^{-1}}, \quad y=0.75 \qquad (8.12b)$$

$$T_1/T=14\ \mathrm{sec\,K^{-1}}, \quad y=0.50 \qquad (8.12c)$$

$$T_1/T=2.2\ \mathrm{sec\,K^{-1}}, \quad y=0.40 \qquad (8.12d)$$

for H_2, and

$$T_1/T=3.2\times10^5\ \mathrm{sec\,K^{-1}}, \quad y=1.00 \qquad (8.13a)$$

$$T_1/T=0.6\times10^4\ \mathrm{sec\,K^{-1}}, \quad y=0.75 \qquad (8.13b)$$

$$T_1/T=80\ \mathrm{sec\,K^{-1}}, \quad y=0.50 \qquad (8.13c)$$

$$T_1/T=13\ \mathrm{sec\,K^{-1}}, \quad y=0.40 \qquad (8.13d)$$

for D_2. However, for D_2 this relaxation time is that of the $(J=1)$ molecules towards the lattice. A systematic comparison of these calculations with experimental data is not yet possible, owing to the scarcity of data, but we can check the order of magnitude against the measurements of Smith *et al.*[13,14] They find $T_1(0.93, 2)=195$ sec and $T_1(0.87, 1.5)=130$ sec, where the arguments of T_1 are the concentration x and temperature T. From Eq. (8.11) taking $\Gamma_{\mathrm{eff}}=0.67\ \mathrm{cm}^{-1}=0.80\Gamma_0$, we obtain the theoretical values $T_1(0.93, 2)=28$ sec and $T_1(0.87, 1.5)=230$ sec. It is clear that more data are needed to make a meaningful comparison, because the theoretical value of T_1 depends critically on the parameters. Taken at face value the comparison above would suggest that perhaps the libron spectrum does not scale linearly with concentration, and it is obvious that one cannot reproduce the concentration dependence of the order-disorder transition temperature T_λ with this approximation.

Clearer evidence on this point may be obtained from the measurements by Ramm *et al.*[66] of $(\partial p/\partial T)_V$ in ordered D_2. They find that for $x>0.8$ the gap scales as

$$\Delta/k=(38.9x-19.0)\ {}^\circ\mathrm{K}\ . \qquad (8.14)$$

Accordingly, for given values of x and T we replace y in Eq. (8.13) by $y_{\mathrm{eff}}=\Delta/19kT$, where Δ is the empirically determined libron energy gap of Eq. (8.14). Using these values of y_{eff} we find from Eq. (8.14) the theoretical values $T_1(0.93, 2)=90$ sec and $T_1(0.87, 1.5)=600$ sec. Thus, even use of Eq. (8.14) does not reproduce the very sharp concentration dependence implied by the experimental values of T_1.

In fact, one can derive a direct relationship between T_1 and the specific heat C_V which is proportional to $(\partial p/\partial T)_V$. For this purpose consider Eq. (8.2) when $\omega=\omega_0\approx 0$. Note that the factor $n_{\vec{k}}^{\pm}(1+n_{\vec{k}}^{\pm})$ is just the specific heat of an oscillator of energy $E_{\vec{k}}^{\pm}$, apart from the missing factor $(E_{\vec{k}}^{\pm}/kT)^2$. Since this factor varies much more slowly with energy than the exponentials in the occupation numbers, we consider it equal to $(\Delta/kT)^2$, where Δ is the average libron energy gap. This argument thus leads to the relation

$$T_1^{-1}\propto\left(\frac{kT}{\Delta}\right)^2 C\propto\left(\frac{kT}{\Delta}\right)^2\left(\frac{\partial p}{\partial T}\right)_V \quad . \qquad (8.15)$$

Using Eq. (8.14) for the scaling factor of the libron energy gap we obtain

$$T_1^{-1}\propto\left(\frac{T}{38.9x-19.0}\right)^2\left(\frac{\partial p}{\partial T}\right)_V . \qquad (8.16)$$

From the work of Ref. 65, it is clear that the energy gap Δ is not temperature independent at concentrations low enough that $\Delta(x)$ is much less than its value for $x=1$. Then Δ will vary weakly with temperature, so the ratio $T_1^{-1}/[T^2(\partial p/\partial T)_V]$ will vary much less with temperature than either T_1^{-1} or $T^2(\partial p/\partial T)_V$.

IX. PAKE SPLITTING OF $(J=0)$ MOLECULES IN D_2

In I we discussed the Pake splitting for $(J=1)$ molecules in both H_2 and D_2. A slight refinement of these calculations is presented in Appendix E. Here we consider the influence of $(J=0)$ molecules on the nuclear-magnetic-resonance behavior of solid D_2 in its orientationally ordered phase. We shall show that the NMR spectrum of the $(J=0)$ molecules is similar to, but less pronounced than, the $(J=1)$ molecules. To see this we consider the interactions which align the molecules. According to the effective field picture,[85,86] each molecule sees a potential due to the other ordered molecules,

$$V_{\text{eff}} = -\tfrac{95}{6} x\Gamma\,(3\cos^2\theta_s - 1)\,, \tag{9.1}$$

where θ_s is the angle between the molecular axis and the local symmetry axis. In writing Eq. (9.1) we have noted that V_{eff} scales in proportion to the concentration x of $(J=1)$ molecules.[87] We can calculate the orientational ordering of even-J molecules ($J=0$ is no longer a perfect quantum number) by

$$C_{\text{even}} \equiv \langle\, 3\cos^2\theta_s - 1\,\rangle_{\text{even}} = -\frac{6}{95x}\,\frac{\partial E_0}{\partial \Gamma}\,. \tag{9.2}$$

Using second-order perturbation theory we find

$$E_0 = -\,(2/15B)\,(\tfrac{95}{6} x\Gamma)^2\,, \tag{9.3}$$

so that[88]

$$C_{\text{even}} = 38x\Gamma/9B \equiv C \tag{9.4}$$

to lowest order in Γ/B. To find the nuclear-spin states of the $(J=0)$ molecules we use $\mathcal{H}_{\text{even},\,i}$ of Eq. (4.2b), because for the value of C_{even} given in Eq. (9.4) the *inter*molecular dipolar interactions are much smaller than the *intra*molecular interactions of $\mathcal{H}'_{\text{even},\,i}$. In fact, since $d_Q \gg d_M$, we shall treat d_M perturbatively. Then the $(J=0)$ nuclear-spin states are those given in Table VI. Thus, the NMR spectrum will consist of absorptions at the frequencies $a \pm \nu'$ and $a \pm \nu''$, where

$$\nu' = \tfrac{1}{8}C(3\cos^2\theta_{Hs} - 1)\,(15d_Q + 5d_M)\,, \qquad I' = \tfrac{2}{5} \tag{9.5a}$$

$$\nu'' = \tfrac{1}{8}C(3\cos^2\theta_{Hs} - 1)\,(15d_Q - 15d_M), \quad I'' = \tfrac{3}{5} \tag{9.5b}$$

with the corresponding relative intensities I' and I'' as indicated. When averaged over a powder each of these components gives rise to a Reif-Purcell[16] line shape with peaks at

$$a \pm \tfrac{1}{8}C(15d_Q + 5d_M)\,, \tag{9.6a}$$

$$a \pm \tfrac{1}{8}C(15d_Q - 15d_M)\,. \tag{9.6b}$$

Thus, the $(J=0)$ molecules have an average Pake splitting of

$$\Delta\nu \approx \tfrac{15}{4} C d_Q \tag{9.7a}$$

$$\approx (95x\Gamma d_Q/6B) \approx 8.8x \text{ kHz}, \tag{9.7b}$$

which is about one-tenth as large as that for the $(J=1)$ molecules. For this estimate of $\Delta\nu$ we used the renormalized value[63] of $\Gamma_{\text{eff}} \approx 0.67\ \text{cm}^{-1}$ and also took account of the interactions of distant molecules[89, 90] by replacing Γ_{eff} by $1.1\Gamma_{\text{eff}}$. A Pake splitting has recently been observed via NMR[91] with very nearly the frequency we predict with an intensity and concentration dependence in agreement with our calculation. As mentioned, the anomalous width in the NMR line shape of the $(J=0)$ resonance observed by Gaines *et al.*[17] is probably also due to the Pake splitting discussed here. Hence, we feel that our prediction has been substantiated.

X. CONCLUSION

In this paper we have analyzed several phenomena associated with the NMR properties of solid hydrogen. Generally, our calculations are in reasonable agreement with the experimental data considering the difficulties involved in such a comparison, viz., high-temperature expansions are only valid at temperatures, say, above 10 °K, whereas the data are meaningful only at lower temperatures.

More specifically, we summarize the results of our calculations and the comparison with experiment as follows:

(a) The contribution to the moments of the NMR spectrum of H_2 from intermolecular dipolar interactions is well understood. In particular, the concentration dependence of the phonon renormalization of the dipolar interactions agrees with our predictions.

(b) The temperature dependence of the second and fourth moments in H_2 agrees qualitatively with theory, especially in its concentration dependence.

(c) From the dependence of the second moment in D_2 on temperature we conclude that the $(I=1)$ nuclear spins do not always contribute to the NMR. The weak temperature dependence is of the right order of magnitude to be due to deformation of the $(J=0)$ state.

(d) The temperature and concentration dependence of T_1 in both H_2 and D_2 agree quite well with theory over a wide range of concentrations and temperatures above 4 °K. The values of Γ_{eff} needed to fit the data at large x where the Gaussian approximation is useful agree with those obtained from the

TABLE VI. Nuclear-spin states of $(J=0)$ D_2 molecules.

State[a]	Energy[b]
$\lvert \pm 2) \equiv \lvert \pm 1, \pm 1)$	$\mp 2a + \frac{1}{4}C(3\cos^2\theta_{HS} - 1)(5d_Q - 5d_M)$
$\lvert \pm 1) \equiv 2^{-1/2}\{\lvert \pm 1, 0) + \lvert 0, \pm 1)\}$	$\mp a + \frac{1}{8}C(3\cos^2\theta_{HS} - 1)(-5d_Q + 5d_M)$
$\lvert 0, 0) \equiv \lvert 0, 0)$	$-\frac{5}{2}C(3\cos^2\theta_{HS} - 1)d_Q$
$\lvert 0, 1) \equiv 2^{-1/2}\{\lvert 1, -1) + \lvert -1, 1)\}$	$\frac{1}{4}C(3\cos^2{}_{HS} - 1)(5d_Q + 5d_M)$

[a] States on the right are given in terms of the m_I values of the two nuclear spins.

[b] Parameters a, d_Q, and d_M are given in Table I, C is given by Eq. (9.4), and θ_{HS} is the angle between the magnetic field and the local symmetry axis.

low-concentration regime where our modification of Sung's theory is valid. These values of Γ_{eff} are slightly smaller, however, than those derived from other experimental determinations[63] of Γ_{eff}.

(e) We have supporting evidence for the validity of the Gaussian approximation at infinite temperature in that the fourth frequency moment of the spectral function is about three times the square of the second moment. We also found that the dependence of T_1 on magnetic field orientation is negligibly small.

(f) We presented explicit analytical formulas for T_1 in the orientationally ordered phase based on the model of libron scattering and using the density of states calculated by Mertens *et al.* Only crude comparisons could be made with experimental data at the present time.

(g) We calculated, for ordered D_2 – and NMR measurements have since detected – a Pake splitting of about 9 kHz for the $(J=0)$ molecules. This splitting is due to intramolecular interactions which are not completely washed out when the perturbative alignment of $(J=0)$ molecules in the effective field due to EQQ interactions is taken into account.

We seem to have a reasonable understanding of the topics treated here. Other topics which are less well understood and which are under investigation at present are (a) cross relaxation in D_2 in (i) the diffusion-dominated regime and (ii) in the ordered phase, and (b) the NMR spectrum at low concentration in the millidegree temperature range. Both these phenomena depend more sensitively on the details of the processes involved and are less susceptible to moment methods which we have used so extensively in this paper.

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APPENDIX A: HIGH-TEMPERATURE EXPANSION FOR M_2

In this Appendix we evaluate the second term in the high-temperature expansion of the second moment of the NMR spectrum M_2^{intra} and thereby verify Eq. (3.39). Substituting Eq. (3.30c) into Eq. (3.19b) we obtain, correct to order β^5,

$$M_2^{\text{intra}}=9d^2\pi(\tfrac{1}{2}\beta^2)^2\langle\langle \textstyle\sum_l(-1)^l\langle Y_2^{-l}(\omega_0)\times(\mathcal{H}^2-\tfrac{1}{3}\beta\mathcal{H}^3)\rangle_\infty\langle Y_2^l(\omega_0)\,(\mathcal{H}^2-\tfrac{1}{3}\beta\mathcal{H}^3)\rangle_\infty\rangle\rangle_a. \tag{A1}$$

We have already evaluated this expression to order β^4 in Eq. (3.37). Let us therefore consider only those terms in M_2^{intra} proportional to β^5, which we denote by $M_2^{(5)}$. From Eq. (A1) we have

$$M_2^{(5)}=-\tfrac{3}{2}d^2\pi\beta^5\langle\langle\textstyle\sum_l(-1)^l\langle Y_2^{-l}(\omega_0)\mathcal{H}^3\rangle_\infty\times\langle Y_2^l(\omega_0)\mathcal{H}^2\rangle_\infty\rangle\rangle_a \tag{A2a}$$

$$=-\tfrac{5}{3}d^2\pi\beta^5\Gamma^2\langle\langle\sum_{l,\vec{\delta}}\langle Y_2^{-l}(\omega_0)\mathcal{H}^3\rangle_\infty Y_2^l(\hat{\delta})\rangle\rangle_a\,, \tag{A2b}$$

where $\vec{\delta}$ is a nearest-neighbor vector, and we have used Eq. (3.33). In Eq. (A2b) the quantization axis is arbitrary. Expressing $\mathcal{H}$ in terms of the individual pairwise interactions and using the operator equivalents, we may write

$$M_2^{(5)}=\tfrac{2}{3}d^2\pi(\beta\Gamma)^5\langle\langle A+B+C\rangle\rangle_a\,, \tag{A3}$$

where

$$A\Gamma^3=\sum_{l,\vec{\delta},\vec{\delta}'}(-1)^l\,Y_2^l(\hat{\delta})\langle\mathcal{T}_2^{-l}(J_0)\mathcal{H}^3_{0\vec{\delta}'}\rangle_\infty, \tag{A4a}$$

$$B\Gamma^3=3\sum_{l,\vec{\delta},\vec{\delta}',\vec{r}}(-1)^l\,Y_2^l(\hat{\delta})\times\langle\mathcal{T}_2^{-l}(J_0)\mathcal{H}_{0\vec{\delta}'}\,\mathcal{H}^2_{\vec{\delta}',\vec{r}}\rangle_\infty(1-\Delta_{\vec{r},0}), \tag{A4b}$$

$$C\Gamma^3=3\sum_{l,\vec{\delta},\vec{\delta}',\vec{\delta}''}(-1)^l\,Y_2^l(\hat{\delta})\times\langle\mathcal{T}_2^{-l}(J_0)\mathcal{H}_{0\vec{\delta}'}\mathcal{H}_{\vec{\delta}',\vec{\delta}''}\mathcal{H}_{0\vec{\delta}''}\rangle_\infty\,. \tag{A4c}$$

Since the average of three spherical harmonics is independent of how they are ordered [see Eq. (A11b) below], it is unnecessary to symmetrize the products of operators appearing in these equations. Here $\vec{\delta}$, $\vec{\delta}'$, and $\vec{\delta}''$ are nearest-neighbors vectors.

First let us evaluate A. Here it is obviously convenient to choose the quantization axis to lie along $\hat{\delta}'$. From Table IV we find

$$\text{Tr}(3J_z^2-2)\mathcal{H}^3_{0\vec{\delta}}=-150\Gamma^3\,, \tag{A5a}$$

which yields

$$\langle\mathcal{T}_2^{-l}(J_0)\mathcal{H}^3_{0\vec{\delta}'}\rangle_\infty=-\Delta_{l,0}\,\tfrac{50}{3}\Gamma^3(5/16\pi)^{1/2}, \tag{A5b}$$

so that

$$A=-\tfrac{50}{3}(5/16\pi)^{1/2}\sum_{\vec{\delta},\vec{\delta}'}Y_2^0(\hat{\delta})_{\hat{\delta}'}\ . \tag{A6}$$

Thus, using Eqs. (3.36) and (3.38) we find

$$\langle\langle A\rangle\rangle_a=-125x(1-x)/\pi\ . \tag{A7}$$

Substitution of this evaluation into Eq. (A3) yields the term proportional to $\beta\Gamma$ in the square bracket of Eq. (3.39).

We now complete the verification of Eq. (3.39) by showing that the evaluation of B and C in Eq. (A3) gives the other term in the square bracket of Eq. (3.39). It is easy to see that the alloy average of B may be written as

$$\langle\langle B\rangle\rangle_a=b_1+b_2\,, \tag{A8}$$

where

$$b_1\Gamma^3 = 3x^2(1-x)\sum_{l,\vec\delta,\vec\delta'}(-1)^l Y_2^l(\hat\delta)(1-\Delta_{\vec\delta,\vec\delta'})$$
$$\times\langle \mathcal{T}_2^{-l}(J_0)\mathcal{H}_{0\vec\delta}\mathcal{H}^2_{\vec\delta,\vec\delta-\vec\delta'}\rangle_\infty\,, \tag{A9a}$$
$$b_2\Gamma^3 = 3x^2(1-x)\sum_{l,\vec\delta,\vec\delta'}(-1)^l Y_2^l(\hat\delta)$$
$$\times\langle \mathcal{T}_2^{-l}(J_0)\mathcal{H}_{0\vec\delta'}\mathcal{H}^2_{\vec\delta',\vec\delta}\rangle_\infty\,. \tag{A9b}$$

In b_1 we take the quantization axis along $\hat\delta'$ to simplify $\mathcal{H}^2_{\vec\delta,\vec\delta-\vec\delta'}$. Then using Eq. (2.9) we have

$$b_1 = 3x^2(1-x)\left(\tfrac{8}{15}\pi\right)^3(70)^{3/2}\left(\tfrac{4}{9}\pi\right)^{1/2}$$
$$\times\sum_{s,l,\vec\delta,\vec\delta'}(-1)^l Y_2^l(\hat\delta)\langle\mathcal{T}_2^{-l}(J_0)\mathcal{T}_2^m(J_0)\mathcal{T}_2^n(J_{\vec\delta})\mathcal{T}_2^s(J_{\vec\delta})$$
$$\times\mathcal{T}_2^{-s}(J_{\vec\delta-\vec\delta'})\mathcal{T}_2^{-t}(J_{\vec\delta})\mathcal{T}_2^t(J_{\vec\delta-\vec\delta'})\rangle_\infty C(2,2,4;m,n)$$
$$\times C(2,2,4;s,-s)\,C(2,2,4;t,-t)$$
$$\times(1-\Delta_{\vec\delta,\vec\delta'})\,Y_4^{m+n}(\hat\delta)^*. \tag{A10}$$

Since operators on different sites are independent, we can evaluate the average in Eq. (A10) using the averages for a single site,

$$\langle\mathcal{T}_2^m\mathcal{T}_2^{-n}\rangle_\infty = (-1)^m\Delta_{m,n}(5/8\pi), \tag{A11a}$$
$$\langle\mathcal{T}_2^m\mathcal{T}_2^n\mathcal{T}_2^r\rangle_\infty = (-1)^r\Delta_{m+n+r,0}(5/64\pi)(70/\pi)^{1/2}$$
$$\times C(2,2,2;m,n), \tag{A11b}$$

which can be obtained using Eq. (2.6). Thus, we have

$$b_1 = \tfrac{1225}{27}x^2(1-x)\sum_{l,s,\vec\delta,\vec\delta'}(1-\Delta_{\vec\delta,\vec\delta'})$$
$$\times C(2,2,2;0,s)\,C(2,2,4;l,0)$$
$$\times C(2,2,4;s,-s)^2\,Y_2^l(\hat\delta)\,Y_4^l(\hat\delta)^*\,. \tag{A12}$$

To evaluate this expression we use the relations

$$\textstyle\sum_m C(2,2,2;0,m)\,C(2,2,4;m,-m) = -\tfrac{5}{49}\sqrt{14} \tag{A13}$$

and[32]

$$\textstyle\sum_m C(L,L',J;m,M-m)\,Y_L^m(\Omega)\,Y_{L'}^{M-m}(\Omega)$$
$$=[(2L+1)\,(2L'+1)/(4\pi)\,(2J+1)]^{1/2}$$
$$\times\,C(L,L',J;0,0)\,Y_J^M(\Omega)\,, \tag{A14}$$

and also Eq. (3.38), whence

$$b_1 = 250x^2(1-x)/\pi\,. \tag{A15}$$

The evaluation of b_2 is similar. The quantization axis is taken to lie along $\vec\delta-\vec\delta'$. We again use Eq. (A13), but not (A14) because the arguments of the spherical harmonics are different in the present case. Thus, we find

$$b_2 = -\tfrac{125}{27}\sqrt{14}\,x^2(1-x)\sum_{l,\vec\delta,\vec\delta'}{}' C(2,2,4;l,0)Y_2^l(\hat\delta)Y_4^l(\hat\delta')^*, \tag{A16}$$

where here and below the prime indicates that the sum is taken over values such that $\vec\delta-\vec\delta'$ is a nearest-neighbor vector. Numerically we obtain

$$b_2 = -(7375/16\pi)\,x^2(1-x)\,. \tag{A17}$$

Finally, we evaluate the powder average of C as defined in Eq. (A4c). We take the powder average by inclusion in the lattice sum of the factor

$$x^3+\Delta_{\vec\delta\vec\delta'}\,x^2(1-x)+\Delta_{\vec\delta,\vec\delta''}\,x^2(1-x)\,. \tag{A18}$$

Note that by Eq. (3.38) the term proportional to x^3 vanishes. Keeping only those terms whose average is nonvanishing we have

$$\langle\langle C\rangle\rangle_a = 6x^2(1-x)\,(5/4\pi)^{1/2}\left(\tfrac{8}{15}\pi\right)^3(70)^{3/2}\left(\tfrac{4}{9}\pi\right)^{1/2}$$
$$\times\sum_{\vec\delta,\vec\delta',m,n}{}'\langle\mathcal{T}_2^0(J_0)\,\mathcal{T}_2^m(J_0)\mathcal{T}_2^{-m}(J_{\vec\delta})\mathcal{T}_2^{-m}(J_0)\,\mathcal{T}_2^n(J_{\vec\delta'})$$
$$\times\mathcal{T}_2^m(J_{\vec\delta})\,\mathcal{T}_2^{-n}(J_{\vec\delta'})\rangle_\infty\,C(2,2,4;m,-m)$$
$$\times C(2,2,4;m,-n)^2\,Y_4^{n-m}(\hat\delta')^*\,Y_4^{m-n}(\Omega_{\vec\delta\vec\delta'})^*, \tag{A19}$$

where $\Omega_{\vec\delta\vec\delta'}$ specifies the orientation of $\vec\delta-\vec\delta'$ with respect to $\hat\delta$. Since we have taken the quantization axis to lie along $\hat\delta$, only the $(l=0)$ term in Eq. (A4c) is nonzero. Again we may evaluate the average using Eq. (A11). Also we note that all the 24 equilateral triangles $(0,\vec\delta,\vec\delta')$ give the same contribution to Eq. (A19) so that

$$\langle\langle C\rangle\rangle_a = (39\,200\sqrt5/27)\,x^2(1-x)$$
$$\times\sum_{mr}C(2,2,2;m,-m)\,C(2,2,4;m,-m)\,(-1)^r$$
$$\times C(2,2,4;\,m,r-m)^2\left|Y_4^r(\hat\delta')\right|^2 \tag{A20a}$$
$$\equiv(35\sqrt5/192\pi)\textstyle\sum_m S_m\,C(2,2,2;m,-m)$$
$$\times\,C(2,2,4;m,-m), \tag{A20b}$$

where we have set

$$Y_4^{-r}(\Omega_{\vec\delta\vec\delta'})^* = Y_4^r(\hat\delta')$$

and

$$S_m = 70\tfrac{1024}{9}\pi\textstyle\sum_r\left|Y_4^r(\hat\delta')\right|^2(-1)^r\,C(2,2,4;m,r-m)^2. \tag{A21}$$

Numerically we find

$$S_2=-\tfrac{1691}{4}\,,\quad S_1=-2039,\quad S_0=-\tfrac{513}{2}\,, \tag{A22}$$

which gives

$$\langle\langle C\rangle\rangle_a = -125(199/128\pi)\,x^2(1-x)\,. \tag{A23}$$

Combining the results of Eqs. (A15), (A17), and (A23), we reproduce Eq. (3.39) of the text.

APPENDIX B: MOMENTS OF SPECTRAL WEIGHT FUNCTION

1. Moments of Spectral Weight Function at High Temperature

In this section we evaluate the constant B defined in Eq. (6.30b). As we shall see, this constant is related to one of the terms appearing in the high-temperature expansion of the specific heat.

Inserting the explicit expression for the Hamiltonian into Eq. (6.30b), and taking the quantization axis along $\hat{\delta}$, we may write B as

$$B=[\tfrac{16}{35}\pi\,(L+3)]\,(\tfrac{8}{15}\pi)^2\,(70)(\tfrac{4}{9}\pi)^{1/2}$$

$$\times\sum_{\mu mn} C(2,2,4;m,-m)\,C(2,2,4;m,-n)\,Y_4^{n-m}$$

$$\times(\Omega_{\vec{\delta},\vec{\delta}'})^*\,\langle\mathcal{T}_2^{-m}(J_{\vec{\delta}})\mathcal{H}_{\vec{\delta},\vec{\delta}'}\,\mathcal{T}_2^{n}(\vec{\delta}')\rangle_\infty$$

$$\times\langle[\mathcal{T}_L^{\mu}(J_0),\,\mathcal{T}_2^{m}(J_0)]\,[\mathcal{T}_2^{-m}(J_0),\,\mathcal{T}_L^{-\mu}(J_0)]\rangle_\infty(-1)^{\mu},\tag{B1}$$

where $\Omega_{\vec{\delta}\vec{\delta}'}$ specifies the orientation of $\vec{\delta}-\vec{\delta}'$ with respect to $\hat{\delta}$. Here and below we need consider only the special values $L=1$ and $L=2$. Then, according to Eqs. (2.6a) and (2.8) we have

$$\langle[\mathcal{T}_2^{\mu}(J_0),\,\mathcal{T}_2^{m}(J_0)]\,[\mathcal{T}_2^{-m}(J_0),\,\mathcal{T}_L^{-\mu}(J_0)]\rangle_\infty$$

$$=[\alpha(L,2,3-L)\;C(L,2,3-L;\mu,m)]^2$$

$$\times(-1)^{\mu+m}(6-L)/8\pi,\tag{B2}$$

so that

$$B=[(6-L)/(L+3)]\tfrac{2}{35}\,(\tfrac{8}{15}\pi)^2\,(70)\,(\tfrac{4}{9}\pi)^{1/2}$$

$$\times\sum_{mn}(-1)^m C(2,2,4;m,-m)\;C(2,2,4;m,-n)$$

$$\times\langle\mathcal{T}_2^{-m}(J_{\vec{\delta}})\mathcal{H}_{\vec{\delta}\vec{\delta}'}\,\mathcal{T}_2^{n}(J_{\vec{\delta}'})\rangle_\infty\sum_{\mu}[C(L,2,3-L;\mu,m)$$

$$\times\alpha(L,2,3-L)]^2\,Y_4^{n-m}(\Omega_{\vec{\delta}\vec{\delta}'})^*.\tag{B3}$$

Noting that

$$\textstyle\sum_\mu C^2(L,2,3-L;\mu,m)=\tfrac{1}{5}(7-2L),\tag{B4}$$

and also using the values from Table III, $[\alpha(2,2,1)]^2=(750/64\pi)$ and $[\alpha(1,1,2)]^2=(9/2\pi)$, we write

$$B=(9/28\pi)\,(\tfrac{8}{15}\pi)^2\,(70)\,(\tfrac{4}{9}\pi)^{1/2}$$

$$\times\sum_{mn}(-1)^m C(2,2,4;m,-m)\;C(2,2,4;m,-n)$$

$$\times Y_4^{n-m}(\Omega_{\vec{\delta}\vec{\delta}'})^*\langle\mathcal{T}_2^{-m}(J_{\vec{\delta}})\mathcal{H}_{\vec{\delta}\vec{\delta}'}\,\mathcal{T}_2^{n}(J_{\vec{\delta}'})\rangle_\infty\,.\tag{B5}$$

As mentioned above, this expression is quite similar to the average

$$\langle\mathcal{H}_{0\vec{\delta}}\mathcal{H}_{\vec{\delta}\vec{\delta}'}\mathcal{H}_{0\vec{\delta}'}\rangle\equiv\hat{B}\Gamma^3\,,$$

which Nakamura[23] evaluated as that part of the specific heat at high temperature which is proportional to $(\beta\Gamma x)^3$. We have

$$\hat{B}\Gamma=(5/8\pi)\,(\tfrac{8}{15}\pi)^2(70)\,(\tfrac{4}{9}\pi)^{1/2}$$

$$\times\sum_{mn}(-1)^m\;C(2,2,4;m,-m)\;C(2,2,4;m,-n)$$

$$\times\,Y_4^{n-m}(\Omega_{\vec{\delta}\vec{\delta}'})^*\langle\mathcal{T}_2^{-m}(J_{\vec{\delta}})\mathcal{H}_{\vec{\delta}\vec{\delta}'}\,\mathcal{T}_2^{n}(J_{\vec{\delta}'})\rangle_\infty\tag{B6a}$$

$$=\tfrac{3095}{1536}\,.\tag{B6b}$$

By comparing Eqs. (B5) and (B6), we see that

$$B=\tfrac{18}{35}\hat{B}\Gamma\,,\tag{B7}$$

which gives

$$B=\tfrac{1857}{1792}\Gamma\,,\tag{B8}$$

in agreement with Eq. (6.32).

2. Fourth Moment of Spectral Weight Function

In this section we sketch the evaluation of the contributions to the fourth moment of the spectral weight function at infinite temperature. Since the calculations are rather long and nearly repetitive, this exposition will be illustrative rather than comprehensive. For these calculations of the constants T_2, T_3', T_4', and T_5 introduced in Sec. VI we need the following expressions for $O_L^M(\vec{\delta},\vec{\delta}')$ and $P_L^M(\vec{\delta},\vec{\delta}+\vec{\delta}')$, which may be obtained using Eqs. (2.6) and (2.9):

$$O_L^M(\vec{\delta},\vec{\delta}')=(\tfrac{16}{45}\pi\Gamma)^2\,(70\pi)\sum_{m,n,\mu,\nu}C(2,2,4;m,n)$$

$$\times C(2,2,4;\mu,\nu)\,Y_4^{m+n}(\hat{\delta})^*\,Y_4^{\mu+\nu}(\hat{\delta}')^*$$

$$\times\;\alpha(2,L,3-L)\;C(2,L,3-L;m,M)$$

$$\times\{\alpha(2,3-L,L)\;C(2,3-L,L;\mu,m+M)$$

$$\times\;\mathcal{T}_L^{M+m+\mu}(J_0)\,\mathcal{T}_2^{\nu}(J_{\vec{\delta}'})\,\mathcal{T}_2^{n}(J_{\vec{\delta}})$$

$$+\Delta_{\vec{\delta},\vec{\delta}'}[\alpha(2,2,1)\;C(2,2,1;\nu,n)$$

$$\times\mathcal{T}_{3-L}^{M+m}(J_0)\,\mathcal{T}_2^{\mu}(J_0)\,\mathcal{T}_1^{n+\nu}(J_{\vec{\delta}})]\},\tag{B9}$$

$$P_L^M(\vec{\delta},\vec{\delta}+\vec{\delta}')=(\tfrac{16}{45}\pi\Gamma)^2\,(70\pi)\sum_{m,n,\mu,\nu}C(2,2,4;m,n)$$

$$\times\;C(2,2,4;\mu,\nu)\,\alpha(2,2,1)$$

$$\times\;\alpha(2,L,3-L)\;C(2,2,1;\nu,n)$$

$$\times\;C(2,L,3-L;m,M)\,Y_4^{m+n}(\hat{\delta})^*$$

$$\times Y_4^{m+\nu}(\hat{\delta}')^*\,\mathcal{T}_{3-L}^{M+m}(J_0)\,\mathcal{T}_2^{\mu}(J_{\vec{\delta}+\vec{\delta}'})\,\mathcal{T}_1^{n+\nu}(J_{\vec{\delta}}).\tag{B10}$$

We first consider T_2 and note that the operators of site $\vec{\delta}$ do not appear in $O_L^M(\vec{\delta}',\vec{\delta}')$ and that those of site $\vec{\delta}'$ do not appear in $O_L^M(\vec{\delta},\vec{\delta})$. Hence, the terms in $\mathrm{T}_1^{M+\nu}$ will vanish when the average at infinite temperature is taken. Thus, we have

$$T_1=(\tfrac{16}{45}\pi\Gamma)^4\,(70\pi)^2x^2\sum_{M,m,n,\mu,\nu}\;\sum_{m',n',\mu',\nu'}\;\sum_{\vec{\delta}\neq\vec{\delta}'}C(2,2,4;m,n)\;C(2,2,4;\mu,\nu)\;C(2,2,4;m',n')\;C(2,2,4;\mu',\nu')$$

$$\times Y_4^{m+n}(\hat{\delta})^*\,Y_4^{m'+n'}(\hat{\delta}')\,Y_4^{\mu+\nu}(\hat{\delta})^*\,Y_4^{\mu'+\nu'}(\hat{\delta}')\;C(2,L,3-L;m,M)\,C(2,L,3-L;m',M)\,[\alpha(2,3-L,L)]^2$$

$$\times C(2,3-L,L;\mu,M+m)\;C(2,3-L,L;\mu',M+m')$$

$$\times\langle\mathcal{T}_L^{M+m+\mu}(J_0)\,\mathcal{T}_2^{\nu}(J_{\vec{\delta}})\,\mathcal{T}_2^{n}(J_{\vec{\delta}})\,[\mathcal{T}_L^{M+m'+\mu}(J_0)\,\mathcal{T}_2^{\nu'}(J_{\vec{\delta}'})\,\mathcal{T}_2^{n'}(J_{\vec{\delta}'})]^\dagger\rangle_\infty\,.\tag{B11}$$

We take the quantization axis along $\hat{\delta}$, so that $\mu+\nu=m+n=0$ and $m+\mu=m'+\mu'$. Thus, we obtain

$$T_2=(\tfrac{16}{45}\pi\Gamma)^4\,(70\pi)^2\,(9/4\pi)\,[\alpha(2,L,3-L)\,\alpha(2,3-L,L)]^2\,x^2\sum_{M,m,n',\sigma}\;\sum_{\vec{\delta}\neq\vec{\delta}'}C(2,2,4;m,-m)^2\,C(2,2,4;m+\sigma,n')^2$$
$$\times Y_4^{m+\sigma+n'}(\hat{\delta}')\,Y_4^{-m-\sigma-n'}(\hat{\delta}')\,C(2,L,3-L;m,M)\,C(2,L,3-L;m+\sigma,M)\,C(2,3-L,L;-m,m+M)$$
$$\times C(2,3-L,L;-m-\sigma,M+m+\sigma)\langle\mathcal{T}_L^M(J_0)\mathcal{T}_L^M(J_0)^\dagger\rangle_\infty(-1)^{m+n'}(5/8\pi)^2\,, \qquad \text{(B12)}$$

where we have set $m'=m+\sigma$.

Throughout this section we shall find it convenient to use the approximation

$$\sum_{\vec{\delta}'}(1-\Delta_{\vec{\delta}\vec{\delta}'})\,|Y_4^\rho(\hat{\delta}')|^2$$
$$\approx z/4\pi-|Y_4^\rho(0)|^2=(12-9\Delta_{\rho0})/4\pi, \qquad \text{(B13)}$$

where $z=12$ is the number of nearest neighbors. After some manipulations we find

$$T_2=\langle\mathcal{T}_L\mathcal{T}_L^\dagger\rangle_\infty x^2\Gamma^4(98\,000)\,\{\tfrac{12}{375}(2L+1)\,(7-2L)^2$$
$$-[3(2L+1)S_L/(7-2L)]\}\,, \qquad \text{(B14)}$$

where

$$S_L=\sum_{n,m,M}C(2,2,4;m,-m)^2\,C(2,2,4;n,-n)^2\,C(2,L,3-L;-n,M)^2\,C(2,L,3-L;m,M)^2 \qquad \text{(B15)}$$

and S_L assumes the values given in Eq. (6.25).

Next we construct T_3' using Eq. (B9) for $O_L^M(\vec{\delta},\vec{\delta}')$:

$$T_3'=2x^2(\tfrac{16}{45}\pi\Gamma)^2\,(70\pi)^2\,[\alpha(2,L,3-L)\,\alpha(2,3-L,L)]^2\sum_{m,n,\mu,\nu,M}\;\sum_{m',n',\mu',\nu'}\;\sum_{\vec{\delta}\neq\vec{\delta}'}C(2,2,4;m,n)\,C(2,2,4;\mu,\nu)$$
$$\times C(2,2,4;m',n')\,C(2,2,4;\mu',\nu')\,C(2,L,3-L;m,M)\,C(2,L,3-L;m',M)\,C(2,3-L;\mu,M+m)$$
$$\times C(2,3-L,L;\mu',M+m')\,Y_4^{m+n}(\hat{\delta})^*\,Y_4^{\mu+\nu}(\hat{\delta}')^*\,Y_4^{m'+n'}(\hat{\delta})$$
$$\times Y_4^{\mu'+\nu'}(\hat{\delta}')\langle\mathcal{T}_L\mathcal{T}_L^\dagger\rangle_\infty\langle\mathcal{T}_2^n(\mathcal{T}_2^{n'})^\dagger\rangle_\infty\langle\mathcal{T}_2^\nu(\mathcal{T}_2^{\nu'})^\dagger\rangle_\infty\,\Delta_{m+\mu,m'+\mu'}\,. \qquad \text{(B16)}$$

After a calculation similar to that for T_2 we find that

$$T_3'=\langle\mathcal{T}_L\mathcal{T}_L^\dagger\rangle_\infty x^2\Gamma^4(19\,600)\,\{\tfrac{12}{375}(2L+1)^2\,(7-2L)-[(7-2L)S_{3-L}/(2L+1)]\}\,. \qquad \text{(B17)}$$

To evaluate T_4' we start from the expression

$$[[\mathcal{H}_{0\vec{\delta}'},\mathcal{H}_{0\vec{\delta}}],\mathcal{T}_L^M(J_0)]=-(\tfrac{16}{45}\pi\Gamma)^2\,(70\pi)\sum_{m,n,\mu,\nu}C(2,2,4;m,n)\,C(2,2,4;\mu,\nu)\,Y_4^{m+n}(\hat{\delta}')^*\,Y_4^{\mu+\nu}(\hat{\delta})^*\alpha(2,2,1)\,\alpha(L,1,L)$$
$$\times C(2,2,1;m,\mu)\,C(L,1,L;M,m+\mu)\,\mathcal{T}_2^n(J_{\vec{\delta}'})\,\mathcal{T}_2^\nu(J_{\vec{\delta}})\,\mathcal{T}_L^{M+m+\mu}(J_0)\,, \qquad \text{(B18)}$$

which can be obtained from Eqs. (2.6) and (2.9). Inserting this expression into Eq. (6.23b) we find that

$$T_4'=-\tfrac{1}{2}x^2\,(\tfrac{16}{45}\pi\Gamma)^4\,(70\pi)^2\,(5/8\pi)^2\langle\mathcal{T}_L\mathcal{T}_L^\dagger\rangle_\infty\sum_{M,m,n,\mu,\nu,\sigma}\;\sum_{\vec{\delta}\neq\vec{\delta}'}C(2,2,4;m,n)\,C(2,2,4;\mu,\nu)\,C(2,2,4;m+\sigma,n)$$
$$\times C(2,2,4;\mu-\sigma,\nu)\,Y_4^{m+n}(\hat{\delta}')^*\,Y_4^{m+n+\sigma}(\hat{\delta}')\,Y_4^{\mu+\nu}(\hat{\delta})^*\,Y_4^{\mu+\nu-\sigma}(\hat{\delta})\,[\alpha(2,2,1)\,\alpha(L,1,L)]^2\,C(2,2,1;m,\mu)$$
$$\times C(2,2,1;m+\sigma,\mu-\sigma)\,C(L,1,L;M,m+\mu)^2. \qquad \text{(B19)}$$

After simplification this may be written as

$$T_4'=-\langle\mathcal{T}_L\mathcal{T}_L^\dagger\rangle_\infty x^2\Gamma^4(2L+1)\,(2L-1)\,\tfrac{280}{9}(36-25T), \qquad \text{(B20)}$$

where

$$T=\sum_{m,\mu}C(2,2,4;m,-m)^2\,C(2,2,4;\mu,-\mu)^2$$
$$\times C(2,2,4;m,\mu)^2. \qquad \text{(B21)}$$

Numerical evaluation yields $T=\frac{27}{175}$, so that

$$T_4'=-7000\langle\mathcal{T}_L\mathcal{T}_L^\dagger\rangle_\infty x^2\Gamma^4(2L+1)\,(2L-1). \qquad \text{(B22)}$$

Finally, using the expression for $P_L^M(\vec{\delta},\vec{\delta}+\vec{\delta}')$ given in Eq. (B10) we write T_5 in the form

$$T_5=(\tfrac{16}{45}\pi\Gamma)^4\,(70\pi)^2\sum_{M,m,n,\mu,\nu}\;\sum_{m',n',\mu',\nu'}\;\sum_{\vec{\delta}\neq\vec{\delta}'}C(2,2,4;m',n')\,C(2,2,4;\mu,\nu)\,C(2,2,4;m,n)\,C(2,2,4;\mu',\nu')$$
$$\times C(2,2,1;\nu,n)\,C(2,2,1;\nu',n')\,C(2,L,3-L;m,M)\,C(2,L,3-L;m',M)\,[\alpha(2,2,1)\,\alpha(2,L,3-L)]^2$$
$$\times Y_4^{m+n}(\hat{\delta})^*\,Y_4^{m'+n'}(\hat{\delta})\,Y_4^{\mu+\nu}(\hat{\delta}')^*\,Y_4^{\mu'+\nu'}(\hat{\delta}')\langle\mathcal{T}_{3-L}\mathcal{T}_{3-L}^\dagger\rangle_\infty\Delta_{m,m'}\,(1/2\pi)\,\Delta_{\nu+n,\nu'+n'}\,\Delta_{\mu\mu'}\,(5/8\pi)\,. \qquad \text{(B23)}$$

When simplified, this expression becomes

$$T_5 = 3920\,x^2\Gamma^4\langle \mathcal{T}_L\mathcal{T}_L^\dagger\rangle_\infty\,(36-25T)\ , \tag{B24}$$

so that

$$T_5 = 12\,600\,x^2\Gamma^4\langle \mathcal{T}_L\mathcal{T}_L^\dagger\rangle_\infty\ . \tag{B25}$$

The results of this section are summarized in Eq. (6.24).

APPENDIX C: EVALUATION OF $M_4(T)$

In this appendix we evaluate the leading terms in the high-temperature expansion for M_4. We have already calculated the temperature-independent terms in Eq. (3.22) due to intermolecular interactions. Let us now evaluate those terms which involve A_i and which are thus temperature dependent.

First we consider the term linear in A_i and denote its contribution to M_4 as $M_4^{(1)}$. We have[92]

$$M_4^{(1)} = (\tfrac{2}{3}\langle\langle X\rangle\rangle)^{-1}\tfrac{48}{15}d\langle\langle \textstyle\sum_{\vec r} A_0 B_{0\vec r}^3\,(X_0^2-\tfrac{3}{4}X_0)\,X_{\vec r}\rangle\rangle_{pa}\ . \tag{C1}$$

From Eqs. (3.5) and (3.34) we see that to lowest order in $\beta\Gamma$

$$A_0 = \tfrac{25}{12}\beta^2\Gamma^2\sum_{\vec\delta,\,J_{\vec\delta}=1}(3\cos^2\theta_{\vec\delta}-1)\ . \tag{C2}$$

Thus, Eq. (C1) becomes

$$M_4^{(1)} = \tfrac{25}{2}d\beta^2\Gamma^2\langle\langle \sum_{\vec\delta,\vec r,J=1}(3\cos^2\theta_\delta-1)\,B_{0\vec r}^3 X_{\vec r}\rangle\rangle_{pa}\ . \tag{C3}$$

Again the alloy average is taken by including the factor $f_2(\vec\delta,\vec r)$. Using Eq. (3.38) and also Eq. (3.5a) for B_0, we find

$$M_4^{(1)} = \tfrac{25}{8}K_{\text{eff}}^3\,d(\beta\Gamma)^2x(1-x)\langle\langle \textstyle\sum_{\vec\delta}(3\cos^2\theta_{\vec\delta}-1)^4\rangle\rangle_p . \tag{C4}$$

Here and throughout this section we shall for convenience renormalize all interactions identically by replacing K_0 by K_{eff}. Since the effect of nearest neighbors is dominant, this approximation is a good one. It is readily verified that

$$\langle\langle(3\cos^2\theta_{\vec\delta}-1)^4\rangle\rangle_p = \tfrac{48}{35}\ , \tag{C5}$$

so that in all,

$$M_4^{(1)} = \tfrac{360}{7}K_{\text{eff}}^3\,d(\beta\Gamma)^2x(1-x)\ . \tag{C6}$$

The term in Eq. (3.21) in A_i^2 is denoted by $M_4^{(2)}$. We have from Eq. (3.21) the analog of Eq. (C3):

$$M_4^{(2)} = 32(\tfrac{25}{12}d\beta^2\Gamma^2)^2\langle\langle \sum_{\vec\delta,\vec\delta,\vec r;\,J=1}(3\cos^2\theta_{\vec\delta}-1)\times(3\cos^2\theta_{\vec\delta'}-1)\,(3\cos^2\theta_{\vec r}-1)^2K_{\text{eff}}^2(R_0/r)^6\rangle\rangle_{pa} . \tag{C7}$$

To take the alloy average we now include the probability factor

$$f_3(\vec\delta,\vec\delta',\vec r) = x^3 + x^2(1-x)\,(\Delta_{\vec\delta,\vec\delta'}+\Delta_{\vec\delta,\vec r}+\Delta_{\vec\delta',\vec r}) + x(1-x)\,(1-2x)\,\Delta_{\vec\delta,\vec\delta'}\,\Delta_{\vec\delta,\vec r} . \tag{C8}$$

Using Eq. (3.38) we can eliminate most of the terms:

$$M_4^{(2)} = 32x(1-x)\,(\tfrac{25}{24}K_{\text{eff}}\,d\beta^2\Gamma^2)^2\times\langle\langle x\sum_{\vec\delta\vec r}(3\cos^2\theta_{\vec\delta}-1)^2(3\cos^2\theta_{\vec r}-1)^2\,(R_0/r)^6 + (1-2x)\sum_{\vec\delta}(3\cos^2\theta_{\vec\delta}-1)^4\rangle\rangle_p . \tag{C9}$$

The second term inside the powder average is simple, cf. Eq. (C5). The first term is rather complicated. When the sum over $\vec r$ is restricted to nearest neighbors, the exact result is obtained after some manipulations as

$$\langle\langle[\textstyle\sum_{\vec\delta}(3\cos^2\theta_\delta-1)^2]^2\rangle\rangle_p = 92.8. \tag{C10}$$

However, a sufficient approximation for our purposes is to replace each term by its average:

$$\langle\langle(3\cos^2\theta_{\vec\delta}-1)^2\ (3\cos^2\theta_{\vec\delta'}-1)^2\rangle\rangle_p \approx\langle\langle(3\cos^2\theta_{\vec\delta}-1)^2\rangle\rangle_p\,\langle\langle(3\cos^2\theta_{\vec\delta'}-1)^2\rangle\rangle_p = (\tfrac{4}{5})^2\ , \tag{C11}$$

which then gives 92.16 instead of 92.8 in Eq. (C10). We shall make use of these types of approximations without comment wherever it is convenient. Thus, Eq. (C9) is

$$M_4^{(2)} = 384x(1-x)\,(\tfrac{25}{24}d\,K_{\text{eff}}\,\beta^2\Gamma^2)^2\times[\tfrac{16}{25}xS_0+\tfrac{48}{35}(1-2x)]. \tag{C12}$$

This term can be written in another form within the approximation of Eq. (C11):

$$M_4^{(2)} \approx 32d^2\langle\langle\tfrac{1}{2}A_0X_0\rangle\rangle_{pa}\,\langle\langle\sum_{\vec r,\,J_{\vec r}=1}B_{0\vec r}^2\rangle\rangle_{pa}\ . \tag{C13}$$

But these quantities are exactly expressible in terms of $M_2(T)$ and $M_2(\infty)$:

$$M_4^{(2)} \approx \tfrac{16}{3}\,[M_2(T)-M_2(\infty)]\,M_2(\infty)\ . \tag{C14}$$

We shall find this formula very useful, because it will enable us to avoid some of the uncertainties as associated with truncating the high-temperature expansion.

Finally, we consider the term in A_i^4 in Eq. (3.22) which we denote $M_4^{(4)}$. Using Eq. (C2) we write this term as

$$M_4^{(4)} \approx \tfrac{4}{7}(\tfrac{25}{12}d\beta^2\Gamma^2)^4\langle\langle\sum_{ijkl;\,J=1}(3\cos^2\theta_i-1)\,(3\cos^2\theta_j-1)\times(3\cos^2\theta_k-1)\,(3\cos^2\theta_l-1)\rangle\rangle_{pa}\ , \tag{C15}$$

the sums being restricted to $(J=1)$ molecules. The powder average is taken by including the probability factor

$$\begin{aligned}f_4(i,j,k,l) = {}& x^4 + x^3(1-x)\,(\Delta_{ij}+\Delta_{ik}+\Delta_{il}+\Delta_{jk}+\Delta_{jl}+\Delta_{kl})\\ &+ x^2(1-x)\,(1-2x)\\ &\times(\Delta_{ij}\Delta_{jk}+\Delta_{ij}\Delta_{jl}+\Delta_{ik}\Delta_{kl}+\Delta_{jk}\Delta_{kl})\\ &+ x^2(1-x)^2\,(\Delta_{ij}\Delta_{kl}+\Delta_{ik}\Delta_{jl}+\Delta_{il}\Delta_{jk})\\ &+ x(1-x)\,[1-6x(1-x)]\,\Delta_{ij}\Delta_{jk}\Delta_{kl}\ .\end{aligned} \tag{C16}$$

Again owing to Eq. (3.38) only a few terms survive:

$$M_4^{(4)} \approx \tfrac{4}{7}(\tfrac{25}{12} d\beta^2\Gamma^2)^4 x(1-x) \langle\langle 3x(1-x) \times [\textstyle\sum_{\vec\delta} (3\cos^2\theta_{\vec\delta} - 1)^2]^2 + [1 - 6x(1-x)] \times \textstyle\sum_{\vec\delta} (3\cos^2\theta_{\vec\delta} - 1)^4 \rangle\rangle_p . \qquad \text{(C17)}$$

We obtain a numerical evaluation of this result using Eq. (C5) and (C10):

$$M_4^{(4)} = (d\beta^2\Gamma^2)^4 x(1-x) [177 + 1913x(1-x)]. \quad \text{(C18)}$$

This completes our analysis of M_4 at high temperatures.

APPENDIX D: CALCULATION OF M_2 IN D_2 ASSUMING ONLY EVEN-J MOLECULES RESONATE

In this Appendix we evaluate the second moment assuming that only the nuclear spins of the even-J molecules take part in the resonance. To implement this assumption we revise the definition of D_i^+:

$$\sum_i D_i^+ = \sum_{\text{even } J_i} I_i^+ , \qquad \text{(D1)}$$

which gives, for instance,

$$I_0 = \tfrac{10}{3}(1-x) . \qquad \text{(D2)}$$

To calculate M_2^{inter} we consider the $(I=1)$ nuclear spins as being of a different species because their Pake splittings are large compared to the dipolar widths, at least at temperatures below 15 °K, say. We can thus use the formula for "unlike" spins given by Abragam.[93] Here the unlike spins have the same gyromagnetic ratios so we obtain

$$M_2^{\text{inter}} = [3(1-x) + \tfrac{8}{15}x][12K_{\text{eff}}^2 + (S_0 - 12)K_0^2] \qquad \text{(D3a)}$$

$$= \tfrac{1}{15}(45 - 37x)[12K_{\text{eff}}^2 + (S_0 - 12)K_0^2]. \qquad \text{(D3b)}$$

This result is actually not so very different from that obtained when all nuclear spins resonate, Eq. (4.5).

A more significant difference with the previous case will occur for M_2^{intra}. Here we wish to evaluate

$$M_2^{\text{intra}} = \tfrac{9}{5}\pi(5d_Q^2 - 2d_Q d_M + 3d_M^2) \textstyle\sum_l |\langle Y_2^l(\omega_i)\rangle_{\text{even}}|^2 . \qquad \text{(D4)}$$

This result can be obtained from Eq. (4.11) by noting that the odd-J term is deleted, and one must replace $5-3x$ by $5-5x$ to take account of the difference in I_0. To evaluate this expression it is necessary to calculate the deformation of the $(J=0)$ ground state in order to get a nonzero result for the summation.

We shall perform this calculation assuming that such a deformation is simply due to the off-diagonal (in J) terms in the EQQ interaction, which, for such work, must clearly be taken in the form given in Eq. (2.1) or (2.3). Using second-order perturbation theory, we find

$$\langle Y_2^{l''}(\omega_0)_{\hat n}\rangle = -\frac{1}{6B} \sum_{\vec\delta, m} \langle [\langle 00 | Y_2^{l''}(\omega_0)_{\hat n} | 2m\rangle \langle 2m | \mathcal{H}_{0\vec\delta} | 00\rangle + \langle 00 | \mathcal{H}_{0\vec\delta} | 2m\rangle \langle 2m | Y_2^{l''}(\omega_0)_{\hat n} | 00\rangle]\rangle_T , \qquad \text{(D5)}$$

where the quantum numbers are J and m_J for the even-J molecule at the origin, and the thermodynamic average is over the orientations of all other molecules. The sum over $\vec\delta$ is restricted to $(J=1)$ molecules for reasons which will become clear in a moment. Hence,

$$\langle Y_2^{l''}(\omega_0)_{\hat n}\rangle = -(1/3B) \sum_{\vec\delta m l} D_{l'' l}^{(2)}(\chi_{\hat n\hat\delta})^* \times \langle \{\langle 00 | Y_2^l(\omega_0)_{\vec\delta} | 2m\rangle \langle 2m | \mathcal{H}_{0\vec\delta} | 00\rangle \}\rangle_T , \qquad \text{(D6)}$$

or, using Eq. (2.3), we write

$$\langle Y_2^{l''}(\omega_0)_{\hat n}\rangle = -(1/3B) \sum_{\vec\delta, l} D_{l'' l}^{(2)}(\chi_{\hat n\hat\delta})^* \tfrac{5}{6}\sqrt{70}\,\Gamma_0 \times C(2,2,4; l, -l)(-1)^l \langle Y_2^l(\omega_{\vec\delta})_{\hat\delta}\rangle_T . \qquad \text{(D7)}$$

Because they are less oriented, even-J molecules make less of a contribution to the summation, and hence are omitted. Use of this result in Eq. (D4) yields

$$M_2^{\text{intra}} = \pi(\tilde d/B)^2 \sum_{\vec\delta, \vec\delta', l, l', l''} 70(\tfrac{5}{6}\Gamma_0)^2 D_{l'' l}^{(2)}(\chi_{\hat n\hat\delta})^* \times D_{l'' l'}^{(2)}(\chi_{\hat n\hat\delta'}) C(2,2,4; l, -l) C(2,2,4; l', -l') \times (-1)^{l+l'} \langle Y_2^l(\omega_{\vec\delta})_{\hat\delta}\rangle_T \langle Y_2^{l'}(\omega_{\vec\delta'})_{\hat\delta'}\rangle_T^* , \qquad \text{(D8)}$$

where

$$5\tilde d^2 = 5d_Q^2 - 2d_M d_A + 3d_M^2 .$$

We now substitute Eq. (3.34) and use the unitarity of the **D** matrices to write

$$M_2^{\text{intra}} = 70\pi\left(\frac{25\tilde d\beta^2\Gamma^3}{54B}\right)^2 \langle\langle \sum_{\vec\delta, \vec\delta', \vec\delta_1, \vec\delta_1', l, l'; J=1} D_{l' l}^{(2)}(\chi_{\hat\delta'\hat\delta})^* \times C(2,2,4; l, -l) C(2,2,4; l', -l')(-1)^{l+l'} \times Y_2^l(\hat\delta_1)_{\hat\delta} Y_2^{l'}(\hat\delta_1')_{\hat\delta'}^* \rangle\rangle_a . \qquad \text{(D9)}$$

We now must include the probability factor

$$\hat f_4(\vec\delta, \vec\delta + \vec\delta_1, \vec\delta', \vec\delta' + \vec\delta_1')$$

that the molecules at $\vec\delta$, $\vec\delta'$, $\vec\delta + \vec\delta_1$, and $\vec\delta + \vec\delta_1'$ have $J=1$ when the origin is occupied by an even-J molecule. For a random alloy

$$\begin{aligned} \hat f_4(a, b, c, d) &= x^4 + x^3(1-x)(\Delta_{ad} + \Delta_{bd} + \Delta_{ac} + \Delta_{bc}) \\ &\quad - x^4(\Delta_{b0} + \Delta_{d0}) - x^3(1-2x)\Delta_{b0}\Delta_{d0} \\ &\quad + x^2(1-x)^2(\Delta_{ac}\Delta_{bd} + \Delta_{ad}\Delta_{bc}) \\ &\quad - x^3(1-x)(\Delta_{ac}\Delta_{b0} + \Delta_{ad}\Delta_{b0} + \Delta_{bc}\Delta_{d0} + \Delta_{ac}\Delta_{d0}) \\ &\quad - x^2(1-x)(1-2x)\Delta_{ac}\Delta_{b0}\Delta_{d0} , \end{aligned} \qquad \text{(D10)}$$

when a, c, $b-a$, and $d-c$ are nearest-neighbor vectors. According to Eq. (3.38) free sums over $\vec{\delta}_1$ and $\vec{\delta}_1'$ vanish, so that the only nonzero terms are those arising from the following terms in $\hat{f}_4$:

$$\begin{aligned}\hat{f}_4 \sim\ & x^3(1-x)\,\Delta_{\vec{\delta}+\vec{\delta}_1,\vec{\delta}'+\vec{\delta}_1'} - x^3(1-2x)\,\Delta_{\vec{\delta},-\vec{\delta}_1}\Delta_{\vec{\delta}',-\vec{\delta}_1'}\\ & + x^2(1-x)^2\,\Delta_{\vec{\delta},\vec{\delta}'}\Delta_{\vec{\delta}_1,\vec{\delta}_1'} + x^2(1-x)^2\,\Delta_{\vec{\delta},\vec{\delta}'+\vec{\delta}_1'}\Delta_{\vec{\delta}+\vec{\delta}_1,\vec{\delta}'}\\ & - x^3(1-x)\,\Delta_{\vec{\delta},\vec{\delta}'+\vec{\delta}_1'}\Delta_{\vec{\delta},-\vec{\delta}_1'} - x^3(1-x)\Delta_{\vec{\delta}',\vec{\delta}+\vec{\delta}_1}\Delta_{\vec{\delta}',-\vec{\delta}_1'}\\ & - x^2(1-x)(1-2x)\,\Delta_{\vec{\delta},\vec{\delta}'}\Delta_{\vec{\delta}_1,\vec{\delta}_1'}\Delta_{\vec{\delta},-\vec{\delta}_1}\ . \end{aligned} \tag{D11}$$

We write M_2^{intra} as a sum of terms each one corresponding in order to each of the terms in Eq. (D11):

$$\begin{aligned} M_2^{\text{intra}} = 70\left(\frac{25\tilde{d}\beta^2\Gamma^3 x}{108B}\right)^2 & [C_1x(1-x) - C_2x(1-2x)\\ & + (C_3+C_4)(1-x)^2 - (C_5+C_6)\,x(1-x)\\ & - C_7(1-x)(1-2x)]\ . \end{aligned} \tag{D12}$$

We evaluated the constants C_i numerically and found the following results:

$$C_1 \approx 32\ , \tag{D13a}$$

$$C_2 = 0\ , \tag{D13b}$$

$$C_3 = 144, \tag{D13c}$$

$$C_4 \approx 32, \tag{D13d}$$

$$C_5 = C_6 \approx -16, \tag{D13e}$$

$$C_7 = 32\ . \tag{D13f}$$

To see the meaning of our results we give a numerical value of M_2^{intra} for $T = 6\ ^\circ\text{K}$ with

$$\begin{aligned} &\Gamma_{\text{eff}} = 0.70\ \text{cm}^{-1} = 0.83\Gamma_0\ ,\\ &M_2^{\text{intra}} \approx 0.012\,(\text{kHz})^2 \quad \text{for } x = 0.5\ . \end{aligned} \tag{D14}$$

At least this result is of the correct order of magnitude, as contrasted to the very much larger values obtained when the $(I=1)$ molecules are not excluded from the resonance. Hence, our explanation does seem to give a reasonable account of the experimental data.

APPENDIX E: CONTRIBUTION OF NEIGHBORING MOLECULES TO THE ELECTRIC FIELD GRADIENT

In this appendix we evaluate the shift in the Pake splitting of $(J=1)$ D_2 molecules due to the electric field gradient (EFG) present in the ordered cubic structure. In place of Eq. (2.15) we now write the nuclear-spin Hamiltonian for a molecule as

$$\begin{aligned} h^{-1}\mathcal{H}_{\text{S R}} &\\ = & -aI_z - bJ_z - c\vec{\text{I}}\cdot\vec{\text{J}}\\ & + (\mu/i)^2\langle r^{-3}\rangle[(\vec{\text{i}}^{(1)}\cdot\vec{\text{i}}^{(2)} - 3(\vec{\text{i}}^{(1)}\cdot\hat{n})(\vec{\text{i}}^{(2)}\cdot\hat{n})]\\ & + eQ_N\frac{\partial^2 V_e}{\partial z_0^2}[3(\vec{\text{i}}^{(1)}\cdot\hat{n})^2 + 3(\vec{\text{i}}^{(2)}\cdot\hat{n})^2 - 2i(i+1)]\\ & + eQ_N\frac{\partial^2 V_c}{\partial z^2}\ [3(\vec{\text{i}}^{(1)}\cdot\hat{n}_0)^2 + 3(\vec{\text{i}}^{(2)}\cdot\hat{n}_0)^2 - 2i(i+1)]. \end{aligned} \tag{E1}$$

Here $V_c(\vec{\text{r}})$ is the electrostatic potential due to the quadrupole moments of *other* molecules, $\hat{n}_0$ denotes the equilibrium orientation (along one of the [111] directions) of the molecule in question, and the z axis coincides with $\hat{n}_0$. It may be shown[16] that in the quantum-mechanical ground state we have approximately

$$3(\vec{\text{i}}^{(1)}\cdot\hat{n})^2 - 2 \approx \tfrac{2}{5}[3(\vec{\text{i}}^{(1)}\cdot\hat{n}_0)^2 - 2]\ . \tag{E2}$$

In that case we may write the last two terms in Eq. (E1) as

$$\begin{aligned} eQ_N&\left[\frac{2}{5}\left(\frac{\partial^2 V_e}{\partial z_0^2}\right) + \left(\frac{\partial^2 V_c}{\partial z^2}\right)\right]\\ &\times[3(\vec{\text{i}}^{(1)}\cdot\hat{n}_0)^2 + 3(\vec{\text{i}}^{(2)}\cdot\hat{n}_0)^2 - 4]\ . \end{aligned} \tag{E3}$$

Together with Eq. (2.16d) this result shows that we may include the effect of the EFG of other molecules by using an effective value of d,[94]

$$d_{\text{eff}} = eQ_N\left(\frac{2}{5}\ \frac{\partial^2 V_e}{\partial z_0^2} + \frac{\partial^2 V_c}{\partial z^2}\right)\ . \tag{E4}$$

Let us now evaluate the EFG, $\partial^2 V_c/\partial z^2$, for the ordered phase. We do this by calculating the libron energy via a semiclassical method whereby the result is expressed in terms of the EFG. By equating the libron energy to its known[12,22,41,42] value, we evaluate the EFG in terms of Γ. We start by writing the electrostic energy V as

$$V = \int V_c(\vec{\text{r}})\,\rho(\vec{\text{r}})\,d\vec{\text{r}}\ , \tag{E5}$$

where the integration is over the charge distribution $\rho(\vec{\text{r}})$ of the molecule. Expanding $V_c(r)$ about the center of gravity of the molecule, we obtain

$$V = \tfrac{1}{2}\int\rho(\vec{\text{r}})\frac{\partial^2 V_c}{\partial z^2}\ (\tfrac{3}{2}z^2 - \tfrac{1}{2}r^2)\,d\vec{\text{r}}\ . \tag{E6}$$

Here we have used the fact that $\nabla^2 V_c(\vec{\text{r}}) = 0$, and also that the EFG has symmetry about the equilibrium axis. We write Eq. (E6) as

$$V = \frac{1}{2}\frac{\partial^2 V_c}{\partial z^2}\left(\frac{4\pi}{5}\right)^{1/2}\int\rho(\vec{\text{r}})\,Y_2^0(\vec{\text{r}})_{\hat{n}_0}r^2\,d\vec{\text{r}}\ , \tag{E7}$$

where the outer subscript indicates the quantization axis. Using the transformation properties of spherical harmonics, we may write

$$V = \frac{2\pi}{5}\ \frac{\partial^2 V_c}{\partial z^2}\ Y_2^0(\hat{n})_{\hat{n}_0}\int\rho(\vec{\text{r}})\,Y_2^0(\vec{\text{r}})_{\hat{n}}r^2\,d\vec{\text{r}}, \tag{E8}$$

where $\hat{n}$ specifies the orientation of the molecule. We thus obtain the result

$$V = \frac{1}{4}\frac{\partial^2 V_c}{\partial z^2}\ Qe[3(\hat{n}\cdot\hat{n}_0)^2 - 1]\ . \tag{E9}$$

Using the operator equivalents, we write the quantum mechanical Hamiltonian $\mathcal{H}$ as

$$\mathcal{H} = -\frac{1}{10}\frac{\partial^2 V_c}{\partial z^2}\, Qe(3J_z^2-2)\ . \tag{E10}$$

Thus, from this calculation we obtain the libron energy 19Γ as

$$19\Gamma = \mathcal{H}(J_z=\pm 1) - \mathcal{H}(J_z=0) = -\tfrac{3}{10}\, Qe\, \frac{\partial^2 V_c}{\partial z^2}\ , \tag{E11}$$

so that

$$\frac{\partial^2 V_c}{\partial z^2} = -\frac{190}{3}\,\frac{\Gamma}{Qe}\ . \tag{E12}$$

Using Eq. (E3) we find $d_{\rm eff}$ to be

$$d_{\rm eff} = d\left(1 - \frac{190}{3}\,\frac{Q_N}{Q}\,\frac{\Gamma}{hd}\right)\ . \tag{E13}$$

Taking $Q_N = 2.74\times 10^{-27}$ cm^2 and $Q = 1.38\times 10^{-17}$ cm^2, we find[95]

$$d_{\rm eff} = 0.99d. \tag{E14}$$

It is easy to see that this 1% correction is in fact proportional to the concentration x of the $(J=1)$ molecules. Hence, we revise slightly Eq. (7.3b) of I to read

$$\Delta\nu = 75.72\,\xi(1+0.066x-0.02x^{-1}) \quad \text{for } D_2. \tag{E15}$$

We have also included in this result the factor ξ which incorporates the additional zero-point motion [$\xi \approx 0.98$, see Eq. (5.37) in I] due to libron-phonon interactions.

For H_2 there are obviously no EFG corrections, so that including the effect of ξ, we obtain from Eq. (7.3a) of I

$$\Delta\nu = 173.0\,\xi(1+0.032x-0.02x^{-1}) \quad \text{for } H_2. \tag{E16}$$

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[†] Alfred P. Sloan, postdoctoral fellow, 1967–1969.

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[95] We have carried out the calculation as if $d=d_Q$ with $d_M=0$. This is, in fact, a good approximation for D_2.