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Anomalous NMR Line Shapes in Solid Ordered Ortho-Hydrogen and Para-Deuterium*

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Some highly anomalous features have been observed in the low-temperature NMR spectrum of high-purity ($> 99\%$ $J = 1$), solid para-deuterium. The intensity of the low-frequency side of the Pake doublet is enhanced and that of the high-frequency side reduced, sometimes becoming negative, corresponding to an *emission* of power. The anomaly is particularly pronounced and of the opposite sign for the $I = 2$ resonance of the $J = 0$ impurity molecules which exhibit enhancements as large as 50. The effect, which has also been observed in high-purity ortho-hydrogen but with smaller enhancements, is ascribed to a pumping process resulting from ortho-para conversion. In the ordered phase, conversion takes place from only one of the $J = 1$ substates since the excited states, the librons, are not thermally populated. This results in a disturbance of the nuclear-spin populations away from thermal equilibrium, and the observed intensity depends on a balance between the ortho-para pumping mechanism and the normal spin-lattice relaxation processes. The results are compared to the theory of ortho-para conversion given in a companion paper. Measurements of the temperature dependence of the spin-lattice relaxation time T_1 in ordered para-D_2 are also presented. At high temperatures there is a fair agreement with theory based on the inelastic scattering of librons, but at lower temperatures T_1 is much shorter than predicted and depends strongly on the $J = 0$ impurity concentration. The two Pake doublets predicted by Harris for the $J = 0$ D_2 molecules have been resolved and an accurate determination made of the widths. Finally, some measurements of the order parameter via the width of the $J = 1$ Pake doublet are presented and compared to current theories and previous experiments.

I. INTRODUCTION

The main purpose of this paper is to present experimental results on the nuclear-magnetic-resonance (NMR) line shape in the ordered state of high-purity $J=1$ samples of H_2 and D_2, and to interpret the very striking anomalies observed in terms of a pumping process occasioned by ortho-para conversion in the ordered state. In addition, measurements of T_1 and of the Pake-doublet splitting in high-purity samples of ordered para-deuterium are presented and compared to current theories.

If one cools a polycrystalline sample of hydrogen below the molecular ordering temperature, the NMR line suddenly becomes very broad and assumes the peculiar shape of a Pake doublet[1] averaged over crystallite orientations. This phenomenon was first analyzed quantitatively by Reif and Purcell.[2] From very general considerations they demonstrated that the splitting arose from the magnetic dipole interaction of the two protons in H_2 molecule when the rotational degeneracy of the molecule was lifted by the crystalline potential of its neighbors. Since to a very good approximation the ortho-H_2 molecules are in the rotational state $J=1$, the problem reduces to one of knowing what happens to the three $J=1$ sublevels. Although the exact nature of the ordered state was unknown at the time, by the use of a simple molecular-field model in which transitions between the three $J=1$ substates were fast compared to the dipolar splitting, Reif and Purcell[2] were able to show that the ground molecular state was nondegenerate and separated from the nearest excited state by more than 4 K.

The ordered state of both ortho-H_2 and para-D_2 has been studied extensively over the past few years and is now known to be a cooperative ordering of the molecules, closely analogous to the ordering of spins in an antiferromagnet,[3] in this case driven almost entirely by the electrostatic quadrupole-quadrupole (EQQ) interactions between molecules. The excitations analogous to magnons are called librons and have been studied by Raman scattering[4] and far-infrared absorption.[5] The transition temperatures are strongly dependent on the concentration x of $J=1$ species, dropping precipitously for concentrations less than ~55%. In addition, the transition shows considerable hysteresis, presumably due to the fact that the hcp → fcc crystal-structure change accompanying the transition occurs at a temperature where normal translational diffusion is too slow to be effective.

Theoretical calculations based on a rigid lattice, and pure EQQ interactions, predict the ground-state configuration in the fcc phase to belong to the $Pa3$ space group.[6] Here the centers of the molecules sit on an fcc lattice, and the molecular ordering can be described in terms of the four simple-cubic sublattices making up the fcc structure, the symmetry axes of the molecular wave functions being the same on a given sublattice and along one of the four cubic diagonals; in the molecular-field approximation these wave functions correspond to $J=1$, $m_J=0$ substates with the z axis along the local symmetry direction. This structure has now been confirmed experimentally, by a fit of the theoretical $\vec{k}=0$ one-[7] and two-libron[8] frequencies to the observed Raman spectrum,[4] and independently by the polarization properties of the Raman spectrum in single crystals of both H_2 and D_2 ($x \gtrsim 96\%$).[4] Most recently, Mills, Yarnell, and Schuch[9] have found good agreement between the Pa 3 structure and their neutron-diffraction data on a powder of para-D_2 with $x = 96\%$. Thus the space group of the low-temperature phase is now well established.

Not so well established are the details of the order-disorder transition itself, which is complicated, as already noted, by considerable hysteresis. A quantity of particular interest is the order parameter $\sigma = \langle 3\cos^2\theta - 1\rangle$, where θ is the angle between the internuclear axis of a molecule and the local symmetry direction, and $\langle\,\rangle$ denotes an ensemble average. NMR is therefore a very powerful tool in the study of the ordered phase, since the width of the Pake doublet is directly proportional to σ. This has been exploited by Amstutz *et al.*,[10] who studied the Pake doublet in solid hydrogen for ortho-H_2 concentrations up to 95% and for temperatures from 0.5 K up to the transition temperature. The accuracy to which σ could be determined was limited by the intermolecular dipolar broadening of the Pake splitting, and the relatively high ortho-para conversion rate (~1.75%/h), in addition to putting a practical upper limit on the purities that could be studied, greatly complicated measurements close to T_c. Although the first observation of the Pake doublet in para-D_2 by Gaines *et al.*[11] showed that the resonance saturated at rather low rf levels, it was clear that the lower conversion rate (~0.1%/h) and intermolecular dipole broadening made para-D_2 a much better candidate for the detailed study of the ordered state. Preliminary measurements (unpublished) by one of the present authors (W.N.H.) in 96% para-D_2 revealed, in addition to the expected Pake doublet for the $I=1$ species, a rather complicated structure for the $I=2$ species which appeared to include a region of negative absorption. At about the same time, Maraviglia *et al.*[12] reported on extensive measurements of the concentration and temperature dependence of the order parameter in para-D_2. They observed a splitting of the central resonance from the $J=0$ molecules and explained it using results of Harris[13] as due to an admixture of the $J=2$ state produced by the electric field gradients of the ordered $J=1$ molecules. The absorption lines were otherwise well behaved, however, and the negative absorption observed by us remained unexplained. In order to rule out any instrumental problems as the source of the anomalies, the earlier measurements were repeated, but with purer samples ($x = 99\%$). The anomalous negative absorption was now very pronounced and it became clear that the nuclear-spin populations were being driven far from their thermal equilibrium values. Ortho-para conversion was immediately suspected, and from an examination of the theory of Motizuki and Nagamiya,[14] it was concluded that when conversion takes place from a single m_J state, as it must in the low-temperature ordered solid, then the conversion rate is not necessarily the same from the various initial nuclear-spin states. If one assumes, for example, that $J=1$ molecules having $m_I = 0$ convert faster than those with $m_I = \pm 1$, then one would be left with an excess of molecules having $m_I \pm 1$, and the $m_I = -1 \to 0$ transition would be enhanced positively and the $m_I = 0 \to 1$ enhanced negatively.

Anomalies were also observed in ordered ortho-H_2 ($x \geq 96\%$), although the effect was much weaker and appeared only as an asymmetry in the absorption line shape. It appears that the reason these effects were not seen or reported previously[15] is that at low temperatures, nuclear-spin relaxation, which short-circuits the pumping mechanism, is sensitive to the concentration of $J=0$ molecules. The samples used in the present investigation were purer than those used in the past, and consequently the nuclear spin-lattice times T_1 were considerably longer. For the resonance of the ortho-D_2 molecules there is the additional effect that the less there is of the impurity the greater the disturbance per conversion.

In both ortho-H_2 and para-D_2, there were significant differences between the experimental line shape and what would be predicted from the above simple model. These have now been largely resolved by a theory of ortho-para conversion in ordered ortho-H_2 described in the following paper. Reasonably good quantitative agreement is obtained for H_2 and the results in para-D_2 seem to be in good qualitative agreement with theory, which at the moment is only strictly valid for H_2.

II. THEORETICAL BACKGROUND

A. H_2

Following Reif and Purcell,[2] the Hamiltonian of an isolated hydrogen molecule in a magnetic field $\vec{H} = H_0\hat{k}$ can be expressed as

$$h^{-1}\mathcal{H} = -aI_z - bJ_z - c\vec{I}\cdot\vec{J} + 5d[\vec{i}^{(1)}\cdot\vec{i}^{(2)} - 3(\vec{i}^{(1)}\cdot\hat{n})(\vec{i}^{(2)}\cdot\hat{n})], \quad (2.1)$$

where $\vec{I} = \vec{i}^{(1)} + \vec{i}^{(2)}$ is the total nuclear spin and $\hat{n}$ is a unit vector along the internuclear axis. For the free molecule,

$$a = (2\mu_i/h)H_0 = 4.258H_0 \text{ kHz}, \quad (2.2a)$$

$$b = (\mu_J/hJ)H_0 = 0.6717H_0 \text{ kHz}, \quad (2.2b)$$

$$c = (2\mu_i/h)H' = 113.8 \text{ kHz}, \quad (2.2c)$$

$$d=\tfrac{4}{5}(\mu_i^2/h)\langle r^{-3}\rangle = 57.68\ \text{kHz}\quad \text{for } J=1\ . \qquad (2.2\text{d})$$

Here the terms a and b are the Zeeman interactions for the nuclear and rotational magnetic moments, respectively, and the c and d terms are the spin-rotation and dipolar intramolecular interactions. As explained by Reif and Purcell,[2] if the $J=1$ substates in the solid are nondegenerate and separated by amounts large compared to b, then the expectation value of $\vec{J}$ is zero in each of the states and the spin-rotation interaction is ineffective in splitting the $I=1$ NMR line. However, for the pure $J=1$ solid with space group $Pa3$ and molecular site symmetry C_{3i} there are degenerate excited states: in the molecular-field model the substates $m_J=\pm 1$ are degenerate in the absence of a magnetic field. In this case $\vec{J}$ is not necessarily quenched and one has to investigate the *dynamics* of the rotational system in order to see whether the spin-rotation interaction contributes to the splitting of the line or not.

Consider first the molecular-field picture at a finite temperature. The molecule spends a fraction $n(T)=\langle J_z^2\rangle_T$ of its time in one or other of the substates $m_J=\pm 1$. For $T=1$ K and $H_0=10^4$ G, $hb/kT\simeq 3\times 10^{-4}$ and the populations of the two excited states are very nearly equal. Now, if transitions between the three $J=1$ substates are slow compared to c and d, then in high fields ($a\gg c, d$) the nuclear-spin energy levels are given by[2]

$$h^{-1}E_{\overline{m}_J}=-am_I-c\gamma\overline{m}_J m_I$$
$$+d(3\gamma^2-1)(1-\tfrac{3}{2}\overline{m}_J^2)(1-\tfrac{3}{2}m_I^2)\ , \qquad (2.3)$$

where $\overline{m}_J$ denotes the projection of $\vec{J}$ along the symmetry axis, and γ is the cosine of the angle between H_0 and the symmetry axis. One should therefore observe a superposition of two line shapes: one for the state $\overline{m}_J=0$ with weighting factor $1-n(T)$ and one for the $m_J=\pm 1$ state with weighting factor $n(T)$. On the other hand, if transitions between the J states are fast compared to c and d, then motional narrowing sets in and the spin-rotation term averages to zero (except for the slight difference in the populations of the $m_J=\pm 1$ levels). The average energy levels become

$$h^{-1}E=-am_I+d(3\gamma^2-1)[1-\tfrac{3}{2}n(T)](1-\tfrac{3}{2}m_I^2)\ , \qquad (2.4)$$

with a width determined by the usual equations for motional narrowing.[1]

It is easy to show that transitions are, in fact, very fast. One can see intuitively that a local excitation will move from site to site in a time of order h/Γ, where Γ is the quadrupole coupling constant. A treatment in terms of the proper normal modes of the system, the librons, shows that the width of the line due to the spin-rotation interaction is determined by the spectral density[13]

$$\mathcal{J}_1^0(\omega)=G_1^0\int\rho(E)\rho(E+h\omega)n(E)\,dE\ , \qquad (2.5)$$

evaluated at $\omega=0$, where $\rho(E)$ is the libron density of states, G_1^0 is a constant, and

$$n(E)=(e^{\beta E}-1)^{-1} \qquad (2.6)$$

is the Bose factor. $\mathcal{J}_1^0(\omega)$ has a maximum at $\omega=0$ but extends out to frequencies equal to the libron bandwidth. In other words, the time scale of the motion is of order the inverse of the libron bandwidth and we are clearly in the regime of motional narrowing with $T_2=T_1$. We will see later that T_1 is very long so that the spin-rotation interaction can be completely ignored with regard to splitting of the NMR line, and both intramolecular interactions can be ignored with regard to broadening of the line. The broadening will be determined entirely by the intermolecular dipolar interactions.

Equation (2.4) was derived for simple molecular-field wave functions. More generally, the high-field energy levels are given by

$$h^{-1}E_T=-am_I-\tfrac{5}{2}d(\tfrac{3}{2}m_I^2-1)\langle 3\cos^2\alpha-1\rangle_T, \qquad (2.7)$$

where α is the angle between the internuclear axis and the magnetic field. Here, fast transitions have been assumed and the spin-rotation term dropped at the outset. Using the spherical-harmonic addition theorem,[15] $\langle 3\cos^2\alpha-1\rangle_T$ can be written as

$$\langle 3\cos^2\alpha-1\rangle_T=\tfrac{8}{5}\pi\sum Y_2^{m*}(\Omega)\langle Y_2^m(\omega)\rangle_T\ , \qquad (2.8)$$

where $\Omega=(\beta,\delta)$ and $\omega=(\theta,\phi)$ are the spherical polar coordinates of $\vec{H}$ and of the internuclear axis with respect to the local symmetry axis, respectively. It is assumed that in the pure crystal, the space group remains $Pa3$ for all temperatures up to the transition. This requires that $\langle Y_2^m(\omega)\rangle_T=0$ for $m\neq 0$, since $\mathcal{H}$ and, hence, the density matrix $\rho=e^{-\beta\mathcal{H}}$ must be invariant with respect to threefold rotations about the local symmetry axis. Putting $\gamma=\cos\beta$, the result can then be written

$$h^{-1}E_T=-am_I+d'(3\gamma^2-1)(1-\tfrac{3}{2}m_I^2)\ , \qquad (2.9)$$

where $d'=\tfrac{5}{4}\sigma d$ and $\sigma=\langle 3\cos^2\theta-1\rangle_T$ is the same order parameter used by Meyer *et al.*[16] Within the $J=1$ manifold, σ can also be expressed as

$$\sigma\equiv\langle 3\cos^2\theta-1\rangle_T=\tfrac{4}{5}\langle 1-\tfrac{3}{2}J_z^2\rangle_T$$
$$=\tfrac{4}{5}[1-\tfrac{3}{2}n(T)-\tfrac{3}{2}\langle J_z^2\rangle_0]\ . \qquad (2.10)$$

The NMR transition frequencies resulting from Eq. (2.9) are given by (see Fig. 1)

$$\nu_{\pm 1}=a\pm\tfrac{3}{2}d'(3\gamma^2-1)\ . \qquad (2.11)$$

For a single crystal, there are, in general, four pairs of lines corresponding to the four sublattice directions. For a powder, each of the pairs gives rise to a Pake line shape determined by a uniform average over all solid angles:

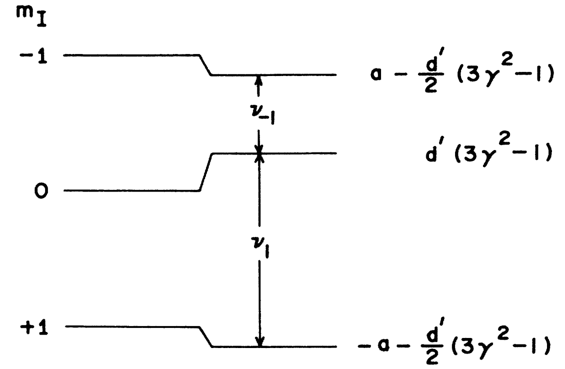

FIG. 1. High-field magnetic energy levels of $J=1$ ortho-hydrogen molecule.

$$P_{\pm1}(\nu)=\frac{1}{4\pi}\iint d\Omega\,\delta(\nu-\nu_{\pm1}(\gamma))$$
$$=\int_0^{\pi/2}d\beta\sin\beta\,\delta(\nu-\nu_{\pm1}(\gamma))\,, \qquad (2.12)$$

where δ is the Dirac δ function and $P_{\pm1}$ denotes the unbroadened line shapes for the two transitions, each normalized to unit area. Changing the variable of integration to $\nu_\pm(\gamma)$ one obtains (see also Reif and Purcell[2])

$$P_1(\bar{\nu})=\frac{d'}{9\sqrt{2}}\;\frac{1}{(\bar{\nu}+\frac{3}{2}d')^{1/2}}\,, \quad -\tfrac{3}{2}d'\leq\bar{\nu}\leq 3d' \qquad (2.13a)$$

$$P_{-1}(\bar{\nu})=P_1(-\bar{\nu})\,, \qquad (2.13b)$$

where $\bar{\nu}=\nu-a$. Equation (2.12) is a very convenient form for introducing the effect of intermolecular broadening. The δ function is simply replaced by the normalized dipolar line shape.

In Fig. 2 the line shapes for the ν_1 and ν_{-1} transitions are plotted separately in order to emphasize the origin of the features in the total powder pattern. For the simple model discussed in Sec. I, the effect of ortho-para conversion on the observed spectrum would be simply to multiply the ν_{+1} line shape by a constant greater than 1 and the ν_{-1} line shape by a constant correspondingly less than 1. On the other hand, the detailed theory developed in the following paper predicts a more complicated result. Evaluating Eq. (3.21) of the following paper for $t\gg T_1$, $1/3W_1$,

$$S^{\pm}(t)=s\,e^{-Rt}\left(\frac{2\mu_pH}{3kT}\pm\frac{R(r^0-r^1)}{9W_1}\right), \qquad (2.14)$$

where S^+ and S^- are the intensities of the ν^+ and ν^- transitions, respectively, R is the conversion rate averaged over all angles, and r^M, the normalized conversion rate from the nuclear-spin state M, is given by

$$r^0=1+\tfrac{1}{8}(3\gamma^2-1)\,, \qquad (2.15a)$$

$$r^{\pm1}=1-\tfrac{1}{16}(3\gamma^2-1)\,. \qquad (2.15b)$$

The rates r^M are plotted in Fig. 2 directly below the Pake line shape, there being a direct correspondence between the horizontal axes since the Pake splitting is also proportional to $(3\gamma^2-1)$. A little thought shows that in this case each part of the line is enhanced by an amount directly proportional to the distance from the center, the high-frequency side of the line having positive enhancements and the low-frequency side negative enhancements.

B. D_2

For D_2 the situation is complicated by the fact that an NMR signal is observed for both para ($I=1$, J odd) and ortho ($I=0, 2$; J even) species. Following Harris,[13] the Hamiltonian for a D_2 molecule can be written

$$h^{-1}\mathcal{H}=-aI_z-bJ_z-c\vec{\mathrm{I}}\cdot\vec{\mathrm{J}}$$
$$+\tfrac{5}{2}d_M[\vec{\mathrm{i}}^{(1)}\cdot\vec{\mathrm{i}}^{(2)}-3(\vec{\mathrm{i}}^{(1)}\cdot\hat{n})(\vec{\mathrm{i}}^{(2)}\cdot\hat{n})]$$
$$+\tfrac{5}{2}d_Q[3(\vec{\mathrm{i}}^{(1)}\cdot\hat{n})^2+3(\vec{\mathrm{i}}^{(2)}\cdot\hat{n})^2-2i(i+1)]\,, \qquad (2.16)$$

where the last term is the interaction of the nuclear quadrupole moment with the electric field gradient in the molecule.

For the free molecule,

$$a=0.6536H_0\ \mathrm{kHz}, \qquad (2.17a)$$

$$b=0.3368H_0\ \mathrm{kHz}, \qquad (2.17b)$$

$$c=8.773\ \mathrm{kHz}, \qquad (2.17c)$$

$$d_M=\tfrac{2}{5}\,\mu^2\langle r^{-3}\rangle=2.74\ \mathrm{kHz}, \qquad (2.17d)$$

$$d_Q=\tfrac{2}{5}\,eQ_N\frac{\partial^2V_e}{\partial Z_0^2}\ \mathrm{kHz}=2250\ \mathrm{kHz}. \qquad (2.17e)$$

The arguments presented in Sec. II A concerning the term $c\vec{\mathrm{I}}\cdot\vec{\mathrm{J}}$ apply equally well here and we will concern ourselves only with the last two terms, which are conveniently labeled $h^{-1}\mathcal{H}_M$ and $h^{-1}\mathcal{H}_Q$, respectively. These can be written in a spherical basis as

$$h^{-1}\mathcal{H}_M=\tfrac{5}{2}d_M\left(\frac{4\pi}{5}\right)^{1/2}\sum_{\mu\nu}C(112;\,\mu\nu)$$
$$\times i_\mu^{(1)}\,i_\nu^{(2)}\,Y_2^{\mu+\nu*}(\Omega)\,, \qquad (2.18a)$$

$$h^{-1}\mathcal{H}_Q=-\tfrac{5}{2}d_Q\left(\frac{4\pi}{5}\right)^{1/2}\sum_{\mu\nu}C(112;\,\mu\nu)$$
$$\times(i_\mu^{(1)}\,i_\nu^{(1)}+i_\mu^{(2)}\,i_\nu^{(2)})\,Y_2^{\mu+\nu*}(\Omega)\,, \qquad (2.18b)$$

where Ω denotes the direction of $\hat{n}$, and the conventions for the C's, Y_l^m, and spherical spin components i_μ are those of Rose.[16] If the z axis is chosen to be along H_0, then the secular terms (those that commute with I_z) are

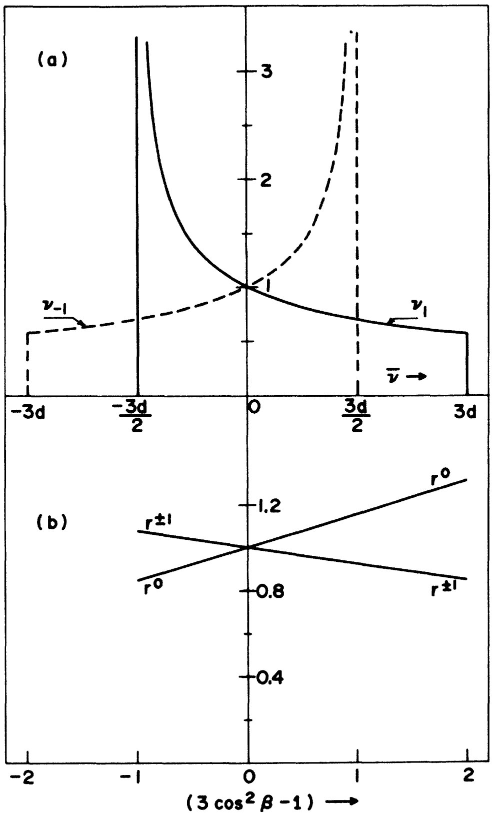

FIG. 2. (a) Unbroadened Pake line shape for a powder. The solid curve is for the transition $m_I = 1 \leftrightarrow 0$ and the dashed curve for $m_I = 0 \leftrightarrow -1$. The NMR absorption is given by the sum of the two. (b) Normalized conversion rate from the $m_I = 0$ and $m_I = \pm 1$ states as a function of $(3\cos^2\beta - 1)$. There is a direct correspondence of the horizontal axes in (a) and (b), since the splitting is also proportional to $(3\cos^2\beta - 1)$.

$$h^{-1}\mathcal{H}^S_M = \tfrac{5}{2} d_M \left(\frac{4\pi}{5}\right)^{1/2} Y^0_2(\Omega) \times \sum_\mu C(112;\mu, -\mu)\, i^{(1)}_\mu i^{(2)}_{-\mu}$$

$$= -\tfrac{5}{4} d_M (3\cos^2\alpha - 1) \times [3 i^{(1)}_z i^{(2)}_z - \vec{\mathrm{i}}^{(1)} \cdot \vec{\mathrm{i}}^{(2)}] \qquad (2.19a)$$

and

$$h^{-1}\mathcal{H}^S_Q = -\tfrac{5}{2} d_Q \left(\frac{4\pi}{5}\right)^{1/2} Y^0_2(\Omega) \times \sum_\mu C(112;\mu, -\mu)\, [i^{(1)}_\mu i^{(1)}_{-\mu} + i^{(2)}_\mu i^{(2)}_{-\mu}]$$

$$= \tfrac{5}{4} d_Q (3\cos^2\alpha - 1) \times [3(i^{(1)}_z)^2 + 3(i^{(2)}_z)^2 - 2i(i+1)] , \qquad (2.19b)$$

where $i = 1$ is the spin of the deuteron and α is as defined below Eq. (2.7). The quantities in the square brackets in Eqs. (2.19a) and (2.19b) are the 0th components of tensor operators of rank two in the space of the two spins. Therefore by the Wigner-Eckart theorem[16]

$$(3 i^{(1)}_z i^{(2)}_z - \vec{\mathrm{i}}^{(1)} \cdot \vec{\mathrm{i}}^{(2)}) = M_M(I)[3 I^2_z - I(I+1)] \qquad (2.20a)$$

and

$$[3(i^{(1)}_z)^2 + 3(i^{(2)}_z)^2 - 2i(i+1)] = M_Q(I)[3 I^2_z - I(I+1)] \qquad (2.20b)$$

where $I = i_1 + i_2$. By explicit evaluation of matrix elements one has, for $i = 1$,

$$M_M(I=1) = 1 \;, \qquad M_M(I=2) = \tfrac{1}{3} \;, \qquad (2.21a)$$

$$M_Q(I=1) = -1, \qquad M_Q(I=2) = \tfrac{1}{3} \;. \qquad (2.21b)$$

Thus for $I = 1$,

$$h^{-1}(\mathcal{H}^S_M + \mathcal{H}^S_Q) = -\tfrac{5}{4} d (3 I^2_z - 2)(3\cos^2\alpha - 1) , \qquad (2.22)$$

with $d = d_M + d_Q$. Hence Eqs. (2.7)–(2.13) are also valid for the $I = 1$ spin species of D_2 provided d is replaced by $d_M + d_Q$.

For the $I = 0, 2$ spin species one might, at first sight, expect the intramolecular interactions to vanish in the low-temperature ordered solid since $\langle 3\cos^2\beta - 1\rangle = 0$ for $J = 0$. However, Harris[13] has shown that the molecular field of the neighboring $J = 1$ molecules mixes in significant amounts of the $J = 2$ state ($J = 0$ is no longer a good quantum number) such that

$$C \equiv \langle 3\cos^2\theta - 1\rangle \qquad (2.23)$$

is no longer zero. (θ is measured with respect to the local symmetry direction.) In terms of C, the energy levels for $I = 2$, $m_I = \pm 2$, ± 1 can be obtained immediately using Eqs. (2.20) and (2.21). However, the otherwise degenerate states $I = 0$ and $I = 2$, $m_I = 0$ are mixed by $\mathcal{H}_M + \mathcal{H}_Q$, so that for these states total I is no longer a good quantum number and Eq. (2.19) must be used. Treating $\mathcal{H}_M$ perturbatively Harris[13] obtained the results shown in Fig. 3 for the nuclear-spin energies of an isolated ortho-D_2 molecule in ordered para-D_2. The corresponding NMR transition frequencies and intensities are given in Table I. The resulting spectrum consists of two Pake doublets at frequencies $a \pm \nu'$ and $a \pm \nu''$, with relative intensities I' and I'', where[17]

$$\nu' = \tfrac{15}{8} C(3\gamma^2 - 1)(d_Q + \tfrac{1}{3} d_M) , \quad I' = \tfrac{3}{5} \qquad (2.24a)$$

$$\nu'' = \tfrac{15}{8} C(3\gamma^2 - 1)(d_Q - d_M) , \quad I'' = \tfrac{2}{5} . \qquad (2.24b)$$

A splitting of the resonance from the $J = 0$ molecules has in fact been observed experimentally.[12,18] Although there was insufficient resolution to distinguish two Pake doublets, the observed width agrees well with the average splitting predicted by Eqs. (2.24) with C approximated by[13]

$$C = 38x\Gamma/9B , \qquad (2.25)$$

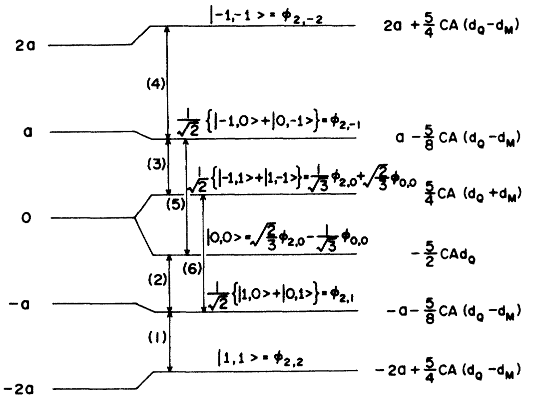

FIG. 3. Nuclear-spin states and energies for an isolated ortho-D_2 molecule in ordered para-D_2. In $|m_1, m_2\rangle$ the quantum numbers are the z components of the two nuclear spins. ϕ_{I,m_I} is labeled by the total nuclear spin I and the z component m_I of the nuclear spin of the molecule. The six vertical arrows represent transitions which may be observed by NMR ($\Delta m_I = \pm 1$). The energy differences and relative intensities for these transitions are given in Table I. The constants a, d_Q, and d_M are given in Eq. (2.17). C is defined in Eq. (2.23) and $A = (3\gamma^2 - 1)$.

where x is the para-D_2 concentration, Γ is the quadrupolar coupling constant, and B is the rotational constant.

Although a detailed theory for line-shape changes due to ortho-para conversion has not yet been worked out for ordered para-D_2, there are some general comments that can be made. First of all, the NMR spectrum of the impurity $J=0$ molecules will show enhancements that are approximately $x/(1-x)$ times as large as those observed for the $J=1$ molecules. For very pure samples this factor can become quite large. The exact constant of proportionality depends on, among other things, the relative value of T_1 for the two species. Although the $J=0$ molecules have a direct nuclear-spin relaxation path through the admixture of the $J=2$ state, the rate will be down by $\sim |C|^2$[19] from that of the $J=1$ molecules. However, the spectrum from the $J=0$ molecules falls within the $I=1$ spectrum and, hence, may relax indirectly via spin diffusion to $I=1$ molecules having the appropriate Larmor frequencies. A consideration of the four sublattice directions in the $Pa3$ structure shows that for a powder, only a fraction of the $J=0$ molecules can cross relax in this manner (assuming spin-diffusion distances to be smaller than the crystallite size). Consequently, the actual shape and magnitude of the enhancement for the impurity $J=0$ molecules is the result of a number of complicated competing processes, and hence will be very difficult to predict even when a theory for conversion in the ordered state is available.

To conclude this section, we note the various corrections to the quantity σd of Eq. (2.9) that are required in Sec. IV C. According to Harris[13]

$$\sigma(T=0)d = \tfrac{4}{5} d\, \xi (1 + 0.066x - 0.02x^{-1}) \text{ for } D_2 . \tag{2.26}$$

The term linear in x, the concentration of $J=1$ molecules, is a combination of an adjustment of the Pake splitting due to the electric field gradients of neighboring molecules, and a correction to the factor $\frac{4}{5}$ due to an admixture of the $J=3$ state. The term in $1/x$ gives the decrease in σ due to the zero-point motion of the librons, and $\xi \simeq 0.98$ accounts for the additional zero-point motion due to libron-phonon coupling. Finally, it has been estimated[20] that the value of d differs from its gas phase value by no more than a few tenths of a percent.

C. Nuclear Spin Relaxation in the Ordered State

Nuclear spin-lattice relaxation in the ordered state of H_2 and D_2 has been considered by Homma[21] and by Harris.[13] They concluded that because of the large gap separating the librons from the ground state, single-libron absorption processes did not occur and the dominant mechanism was the inelastic scattering of librons, the so-called Raman process. Both authors then calculated the powder average of T_1^{-1}, the spin-lattice relaxation rate, in terms of the libron density of states. However, in the ordered state the Pake splitting of the NMR absorption line largely separates the resonances corresponding to different crystallite orientations. Furthermore, since the resonance from a single molecule is a doublet, the recovery of the separate features involves not only T_1^{-1}, which is the recovery rate for the vector polarization, but also $3W_1$, which is the decay rate for the tensor polarization (see following paper). Accordingly we have

TABLE I. Energies and intensities of ($\Delta m_I = \pm 1$) nuclear spin transitions in ortho-D_2 molecules.

Transition[a]	$h^{-1}\Delta E - a$[b]	Intensity[c]
1	$-\frac{15}{8}\,CA(d_Q - d_M)$	1
2	$-\frac{15}{8}\,CA(d_Q + d_M/3)$	1
3	$-\frac{15}{8}\,CA(d_Q + d_M/3)$	$\frac{1}{2}$
4	$\frac{15}{8}\,CA(d_Q - d_M)$	1
5	$\frac{15}{8}\,CA(d_Q + d_M/3)$	1
6	$\frac{15}{8}\,CA(d_Q + d_M/3)$	$\frac{1}{2}$

[a] Transitions are numbered as in Fig. 3.

[b] The constants a, d_Q, and d_M are given in Eq. (2.17). C is defined in Eq. (2.23) and $A = (3\gamma^2 - 1)$.

[c] The over-all intensity of the spectrum from ($J=0$) molecules is $\frac{5}{2}(1-x)/x$ of that due to $J=1$ molecules.

generalized the previous results to obtain the angular dependence of both W_1 and $1/T_1$.

The usual equations for relaxation in H_2 and D_2 [see, for example, Harris,[13] Eq. (6.1)] can be rewritten in terms of the relaxation rates W_1 and W_2 associated with transitions $\Delta m_I = \pm 1$ and ± 2, respectively:

$$W_1 = \tfrac{16}{3}\pi^3 [c^2 \mathcal{J}_1^1(\omega_0) + \tfrac{9}{5} d^2 \mathcal{J}_2^1(\omega_0)] , \tag{2.27a}$$

$$W_2 = \tfrac{8}{3}\pi^3 [\tfrac{36}{5} d^2 \mathcal{J}_2^2(2\omega_0)] , \tag{2.27b}$$

with

$$1/T_1 = W_1 + 2W_2 . \tag{2.28}$$

$\mathcal{J}_1^m$ and $\mathcal{J}_2^m$ are spectral functions of first- and second-order irreducible tensors formed from $\vec{J}$, evaluated in the coordinate system with the z axis along $\vec{H}$. Transforming to the local symmetry axes in the crystals we have

$$\mathcal{J}_L^M(\omega) = \sum_\nu D_{M,\nu}^{(L)*}(\chi) D_{M,\nu}^{(L)}(\chi) j_L^\nu(\omega) , \tag{2.29}$$

where j_L^ν is the spectral function in the local coordinate system and the D's are rotation matrices. Using

$$D_{M,\nu}^{(L)*}(\chi) D_{M,\nu}^{(L)}(\chi) = \sum_\kappa (-1)^{M+\nu} C(LL\kappa;\, M, -M) \times C(LL\kappa; \nu, -\nu) D_{00}^{\kappa}(\chi) \tag{2.30a}$$

and

$$D_{00}^{(\kappa)}(\chi) = P_\kappa(\cos\beta) , \tag{2.30b}$$

it follows that

$$W_1 = \frac{16\pi^3}{3} \left(c^2 \sum_{\kappa,\nu} (-1)^{\nu+1} C(11\kappa; 1, -1) C(11\kappa; \nu, -\nu) j_1^\nu P_\kappa(\cos\beta) + \frac{9d^2}{5} \sum_{\kappa,\nu} (-1)^{\nu+1} C(22\kappa; 1, -1) C(22\kappa; \nu, -\nu) j_2^\nu P_\kappa(\cos\beta) \right) \tag{2.31a}$$

and

$$W_2 = \frac{8\pi^3}{3} \frac{36d^2}{5} \sum_{\kappa,\nu} (-1)^\nu C(22\kappa; 2, -2) C(22\kappa; \nu, -\nu) j_2^\nu P_\kappa(\cos\beta) . \tag{2.31b}$$

Harris[13] has evaluated the j_L^M for the case of thermally excited librons:

$$j_L^M(\omega_0) \simeq j_L^M(0) = 4C_L^M \int \rho^2(E) n(E)\, dE = 4C_L^M I , \tag{2.32}$$

where $\rho(E)$ is the single-libron density of states normalized to unit integral and $n(E) = (e^{\beta E} - 1)^{-1}$. The constants C_L^M have the values

$$C_1^0 = \tfrac{3}{4}\hbar , \tag{2.33a}$$

$$C_2^0 = \tfrac{45}{16}\hbar , \tag{2.33b}$$

$$C_2^{\pm 2} = \tfrac{15}{16}\hbar , \tag{2.33c}$$

from which

$$W_1 = \frac{16\pi^3}{3} \hbar I \left[\left(\frac{c^2}{4} + \frac{27d^2}{16} \right) - \left(\frac{c^2}{4} - \frac{27d^2}{112} \right) P_2(\cos\beta) - \frac{27}{14} d^2 P_4(\cos\beta) \right] \tag{2.34a}$$

and

$$\frac{1}{T_1} = \frac{16\pi^3}{3} \hbar I \left[\left(\frac{c^2}{4} + \frac{135d^2}{16} \right) - \left(\frac{c^2}{4} + \frac{27d^2}{16} \right) P_2(\cos\beta) \right] . \tag{2.34b}$$

The anisotropy in W_1 is substantial: $W_1 = 0$ for $\beta = 0$. For H_2, $1/T_1$ should vary by about 30%. We shall see later that in D_2 where the temperature dependence of T_1 has been measured, the isotropic part of T_1 agrees reasonably well with experiment down to about 2 K. Below this temperature the experimental values of T_1 fall increasingly below the theoretical curve and depend sharply on the amount of $J = 0$ impurity. In addition the expected anisotropy seems to be missing at low temperatures.

III. EXPERIMENTAL APPARATUS

Enriched samples of para-D_2 and ortho-H_2 were obtained by the method of Depatie and Mills[22] with certain precautions described elsewhere.[23] The initial purity of the para-D_2 was ~99.3%, as measured by the relative strengths of the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ Raman transitions[23]; the starting ortho-H_2 purity was of order 99%. Solid samples were produced by simply lowering the sample holder, which was a long glass tube with a 0.5 or 1 liter of glass bulb attached, into the liquid helium. The wand was then further lowered until the bottom 1 cm was inside the rf coil. Although some of the sample solidified directly from the gaseous state, this fraction was normally above the rf coil. Samples prepared in this way were often not good powders, as has been noted previously,[10] and in one experiment improvement was obtained by filling the bottom of the glass wand with high-purity NaCl grains. These are expected to have high thermal conductivity at ~ 15 K and should provide many nucleation centers.

The NMR spectrometer had the novel feature of a germanium field-effect-transistor preamplifier[24] immersed in the liquid helium adjacent to the rf coil. This allowed the tuned circuit to be completed at low temperatures, which resulted in a high-Q factor and lower thermal noise, and also made optimum use of the excellent low-noise properties of cooled field-effect transistors.[24] Originally, the configuration was that of a Robinson oscillating detector,[25] but for some of the strong features in the disordered phase there was a very substantial distortion due to frequency pulling of the oscillator by χ', the real part of the rf susceptibility. Instead, for some of the measurements Q-meter detection[1] was used; at the low-rf levels required because of long T_1's, microphonics were not a problem[25] and noise from the external generator (Hewlett-Packard model No. 608F) was found to be negligible. Undoubtedly this does not completely eliminate distortion when χ' is large, but a considerable improvement was observed. The absolute noise performance of the spectrometer was not measured, although it appeared to be quite good, as evidenced by the fact that the broad line in ordered para-D_2 could be easily observed without noticeable saturation when T_1 was as long as 27 000 sec.

Derivative signals were obtained using sinusoidal magnetic field modulation at ~ 200 Hz provided by coils mounted inside the helium Dewar, and subsequent synchronous demodulation of the detected rf. The spectrometer frequency was kept fixed at 11.27 MHz and the magnetic field swept linearly in time. For the precision measurements of the Pake splitting in para-D_2, a tracking NMR Gaussmeter was developed which gave a continuous indication of the field immediately adjacent to the tail of the cryostat. Corrections were then applied using a separately determined field profile.

IV. EXPERIMENTAL RESULTS

Although the effect of ortho-para conversion on the NMR line shape is much more spectacular in para-D_2 than in ortho-H_2, we choose to discuss the latter first, since it is simpler (only one observable spin species) and can be compared directly to theory.

A. Enhancement in Ortho-H_2

Figure 4(a) shows the derivative signal obtained at 1.1 K in ortho-H_2 with $c \gtrsim 96\%$. The asymmetry in the magnitude of the derivative peaks is evident and one should note that, for the main features at least, the enhancement is positive for the high-frequency side of the line and negative for the low-frequency side. (Although the field was swept in the actual experiment, it is convenient to transform this into an equivalent frequency sweep.) When the trace was integrated [Fig. 4(a)] in order to extract the detailed dependence of the enhancement, the curve did not return to a common value at the extremities of the spectrum, and it was suspected that there was considerable dispersion χ' mixed in with χ''. This was verified by computing the dispersion spectrum for an unenhanced Pake doublet convoluted with a Gaussian line shape (to account for intermolecular broadening). By adding it to the corresponding absorption spectrum, a reasonable representation of the data was obtained with a 30% admixture of χ' [see Figs. 4(c) and 4(d)]. The lack of detailed agreement, other than that due to the enhancement effect, was attributed to the fact that the sample was not a good powder. The mixture of χ' and χ'' seemed to preclude a determination of the enhancement factor throughout the powder spectrum, but it was noted that for the features occurring nominally at $a \pm \frac{3}{2}d$ and $a \pm 3d$, the *peaks* of the derivative spectrum were only weakly affected by the presence of χ'. Accordingly, the amplitude of the absorption signal at these positions was taken to be proportional to the peak of the derivative signal, with a small correction to be applied using the theoretical shape for a 30% admixture of χ' [Fig. 4(c)]. These results are tabulated in Table II.

If we denote by I^+ and I^- the intensity of the combined spectrum $(S^+ + S^-)$ at conjugate points above and below the center frequency, then from Eqs. (2.14) and (2.15)

$$\frac{I^+}{I^-} = \frac{1+\rho}{1-\rho} , \tag{4.1a}$$

where

$$\rho = \frac{R(r^0 - r^1)}{9W_1} \frac{3kT}{2\mu_p H_0} . \tag{4.1b}$$

The experimental values of $\rho = (I^+ - I^-)/(I^+ + I^-)$ are compared to the theoretical value, which is computed using an experimental value for R[14] (1.75%/h $= 4.86 \times 10^{-6}$ sec^{-1}) and a value of W_1 estimated from the recovery of the derivative peaks in the same sample. The procedure was to first saturate the whole line by sweeping through it at a high rf level, and then periodically sweeping through the line at a low rf level. To within experimental error the recovery of each feature was exponential with about the same time constant. The accuracy for the feature at $\nu = a - 3d$ was rather low, however, due to its weakness.

According to Eq. (3.21) of the following paper, the recovery of features $S^{\pm}$ after saturation are proportional to

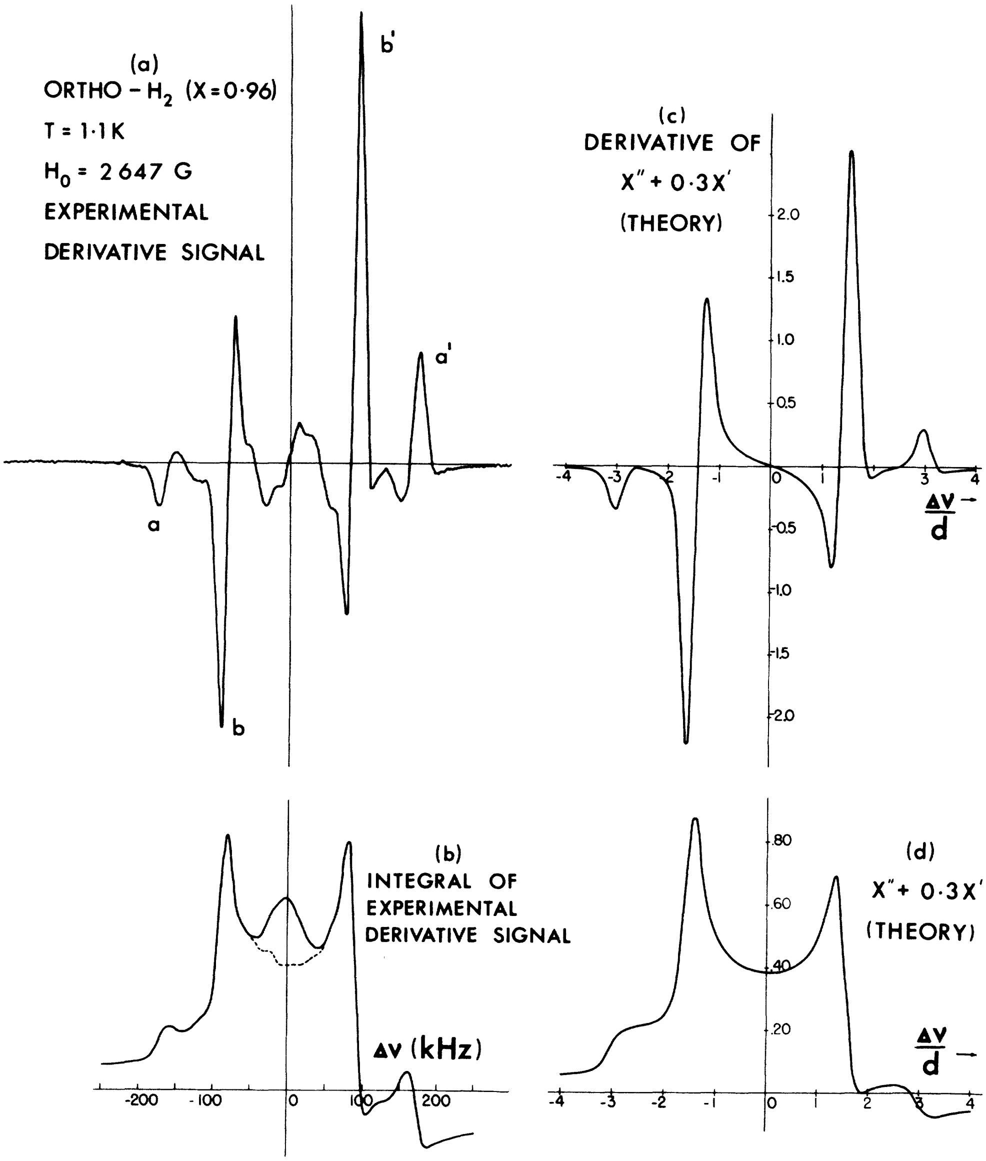

FIG. 4. Experimental and theoretical NMR spectra for ordered ortho-hydrogen. Trace (a) is the derivative spectrum observed in ortho-H_2 for $x = 0.96$, $T = 1.1$ K, and $H_0 = 2647$ G. Trace (b) is the integral of (a); the feature at the center of the spectrum is due to protons in the rf coil holder and the dashed line shows the spectrum due to ortho-H_2 only. Trace (c) is the derivative of a Gaussian-broadened Pake line shape for a 30% admixture of the dispersion signal. Trace (d) is the integral of (c).

$$\frac{2\mu_p H_0}{3kT}\,(1-e^{-t/T_1}) \pm \frac{R^0-R^1}{9W_1}\,(1-e^{-3W_1 t}) \;, \qquad (4.2)$$

and in the present case there should be a substantial admixture of both time constants. The fact that only one exponential is seen implies that $1/T \simeq 3W_1$ and this we adopt for evaluating Eq. (4.1). The resulting theoretical values of ρ, given in Table II, are seen to be in reasonable agreement with experiment in all respects: the sign, absolute magnitude, and dependence on γ. Since there are no adjustable parameters, such a comparison constitutes a stringent test of the theory, and there seems little doubt that in H_2 the theoretical model for the enhancement is basically correct.

In the above, the parameter $\alpha = 3W_1T_1$ was taken to be 1 on the basis that the experimental recoveries appeared to be exponential. Quantitative limits on α were obtained in the following way. By expanding the above expression at small t, the effective initial relaxation rates are easily shown to be

TABLE II. Enhancement factors in ortho-H_2 for $x \gtrsim 0.96$, $T = 1.1$ K, and $H_0 = 2657$ G.

Feature	Frequency ($\nu - a$)	T_1 (sec)	Peak of Derivative[a] uncorrected for χ'	corrected for χ'	$(I^+ - I^-)/(I^+ + I^-)$ Expt.	Theory[b]
b	$-3d/2$	78 ± 3	16.4	18.8	0.196	0.175
b'	$3d/2$	75 ± 5	27.9	27.9		
a	$-3d$	73 ± 10	2.50	2.20	0.518	0.350
a'	$3d$	76 ± 4	6.95	6.95		

[a] Arbitrary units, averaged over two traces.

[b] Using $R = 1.75\%$/h and a value W_1 derived from the average measured value of T_1: $W_1 = (3T_1)^{-1}$.

$$\left(\frac{1}{T_1}\right)_{\rm eff} = \left(\frac{1}{T_1}\right) \frac{1 \pm \rho\alpha}{1 \pm \rho} , \qquad (4.3)$$

where $\rho = (I^+ - I^-)/(I^+ + I^-)$ is the previously defined enhancement factor. Using the experimental values for ρ and taking $(1/T_1)_{\rm eff}$ to be the experimentally observed relaxation rate for the appropriate feature, it was found that for the inner doublet $(a \pm \frac{3}{2}d)$,

$$\alpha = 1.1(0.9 - 1.35) \qquad (4.4a)$$

and for the outer doublet $(a \pm 3d)$,

$$\alpha = 0.97(0.85 - 1.06) . \qquad (4.4b)$$

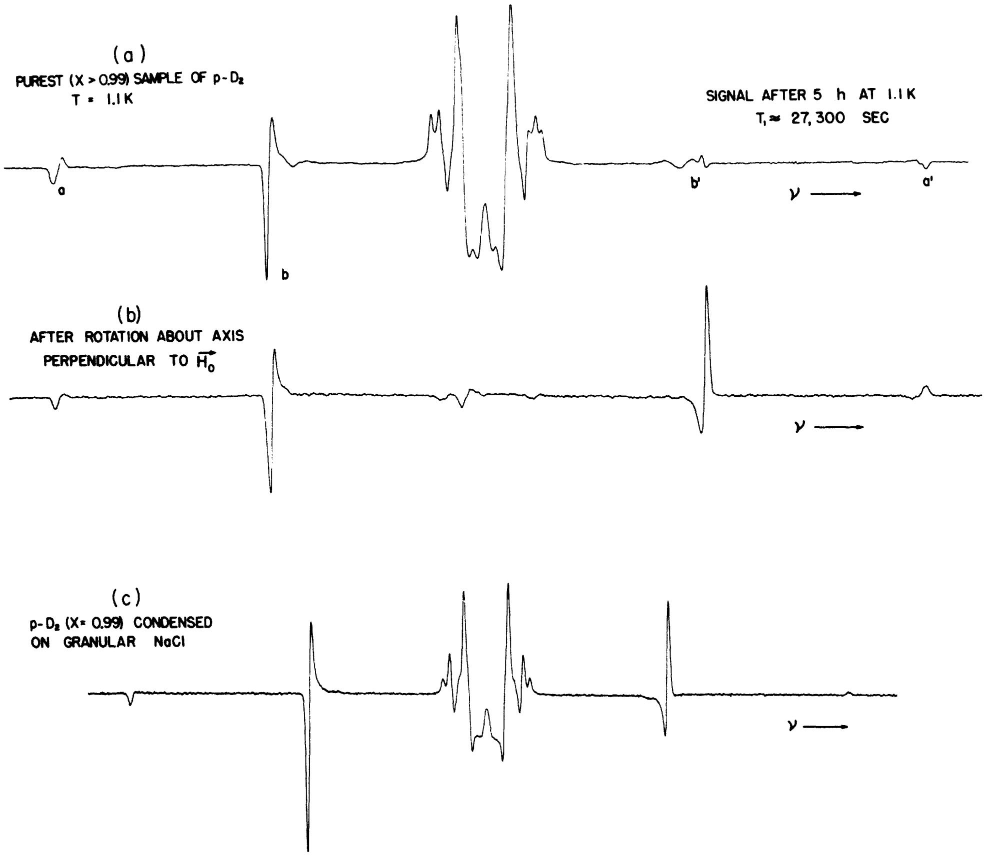

FIG. 5. Derivative NMR spectra observed in high-purity para-D_2 at $T = 1.1$ °K and $\vec{H}_0 = 17250$ G. Trace (a) is the signal observed after the sample had been kept at 1.1 K for 5 h. The sample was then rotated about an axis perpendicular to $\vec{H}_0$ and trace (b) obtained. The gain in trace (b) is a factor of 2 greater than that in (a). Trace (c) was obtained in a sample that had been condensed on fine NaCl grains in an attempt to obtain a uniform distribution of crystallite directions.

For simplicity it has been assumed that $\alpha = 1.0$ for all features.

The results obtained in Sec. II for relaxation due to the Raman process predict a large angular dependence of W_1 and T_1, in apparent disagreement with experiment. We have already noted, however, that the observed values of T_1 at low temperatures are considerably lower than theory. This extra relaxation mechanism, which is associated with the $J = 0$ impurities, may not be anisotropic.

B. Enhancement in D_2

Figure 5(a) shows the derivative spectrum observed in the purest of several para-D_2 samples studied. At the time the sample was taken through the hcp-fcc transition, the purity was ~99% (± 0.5%). The temperature was immediately lowered to 1.1 K, at which point the nuclear magnetization of the sample was reduced to zero by several sweeps through the line at a high rf level. The recovery of the absorption signal was then monitored periodically at a low rf level, the trace in Fig. 5(a) being the spectrum observed at the end of 6 h. Since the average relaxation time deduced from these measurements was of order 7.5 h the signal had still not reached its equilibrium value. Trace (b) in Fig. 5 was taken immediately after trace (a) [note that the gain has been increased by a factor 2 in trace (b)], but after the sample had been rotated several times about an axis perpendicular to the magnetic field (time for rotation ≃ 10 sec). This procedure was adopted in order to achieve a common spin temperature among the nuclear-spin levels by promoting spin exchange: when the sample is rotated, the $(3\gamma^2 - 1)$ angular dependence of the splittings causes the majority of the transition frequencies to cross or come close enough for rapid exchange of energy. If the spin system has reached a common temperature then the derivative of the absorption should have its usual antisymmetric shape. Figure 5(b) is, in fact, close to being antisymmetric and we believe that a common spin temperature has been reached; the apparent departure of the central structure from antisymmetry can be explained as a partial recovery to the shape of Fig. 5(a) during the time required to record the spectrum. Furthermore, the spectrum Fig. 5(b) is similar to that observed previously[12,18] in samples with higher concentration of $J = 0$ molecules. Therefore, taking the spectrum in Fig. 5(b) as being "normal". the enhancement factor for the $J = 0$ molecules seems to be very large—of order 50. Certain difficulties, to be discussed later, prevent a very accurate value being deduced from the present data.

The enhancement factor for the $I = 1$ spins, on the other hand, can be taken directly from Fig. 5(a) and used to derive a value for the difference in the conversion rates from the $M_I = 0$ and ± 1 states. (This is because the signal at b' is essentially zero and therefore independent of gain distortions.) Although the states to which the $I = 1$ states convert are more numerous in the case of D_2, the equations describing the time evolution of the $I = 1$ spin populations are formally identical to those for H_2. Proceeding just as in Sec. IV A, we use the fact that in D_2 the recovery of the features also appeared to be a single exponential and put

$$1/W_1 = 3R_1 \ . \tag{4.5}$$

Again taking the absorption signal to be proportional to the peak of the derivative (with appropriate sign changes), the quantities $(I^+ - I^-)/(I^+ + I^-)$ can be evaluated at positions $\nu = (a \pm \frac{3}{2}d)$ and $(a \pm 3d)$. Reliable values of T_1 were only obtained for the positively enhanced features at $(a - \frac{3}{2}d)$ and $(a - 3d)$; the corresponding negatively enhanced features remained small in all of the traces and, in addition, the feature at $(a - \frac{3}{2}d)$ had a very complicated shape. A further difficulty was that because of the long relaxation times the equilibrium values were not known, requiring a less accurate two-parameter fit to the recovery profile.

The values of T_1, $(I^+ - I^-)/(I^+ + I^-)$, and the values of the conversion anisotropy, $r^0 - r^1$, computed using Eq. (4.1b) (replacing $2\mu_p H$ by $\mu_D H$) are given in Table III. For comparison, the corresponding experimental values for H_2 are listed in parentheses. One should note that the anisotropy is much smaller in D_2, perhaps reflecting the fact that in D_2 there are two competing conversion mechanisms of comparable strength.[14]

It was suspected that the unusual shapes of some of the $J = 1$ features were due to the sample not being a good powder. The feature at $\nu = (a - 3d)$ could be due, for example, to a large crystallite with one of the sublattice directions along $\vec{H}_0$. In a subsequent experiment the para-D_2 was condensed on granular NaCl in the hopes of producing a large number of randomly oriented crystallites. The observed spectrum, shown in Fig. 5(c), is closer to the expected shape. Unfortunately the result is not definitive since now the purity is not quite as high, T_1 is shorter, and consequently the enhancement factors are smaller. Further experiments will be necessary to resolve this question completely.

Figures 6(a) and 6(c) are expanded traces of the central region of spectra 5(a) and 5(c). The amplitude of the magnetic field modulation has been reduced for these traces, revealing further fine structure that had been previously smeared out by overmodulation. The integrals of the spectra appear in Figs. 6(b) and 6(d). In gross, the line shape is antisymmetric at its extremities with a region of strong negative absorption (emission) at

TABLE III. Enhancement factors of $I=1$ spin species in para-D_2 for $x \simeq 0.984$, $T=1.1$ K, and $H_0 = 17\,250$ G ($f_0 = 11.270$ MHz).

Feature	Frequency ($\nu - a$)	T_1 (sec)	Peak of Derivative	$\frac{I^+ - I^-}{I^+ + I^-}$	$r^0 - r^1$ [a]
b	$-3d/2$	$27\,000 \pm 400$	3.65	−1.00	−0.066 (0.22)
b'	$3d/2$	···	~0		
a	$-3d$	$27\,100 \pm 2400$	0.50	−2.57	−0.168 (0.592)
a'	$3d$	···	−0.22		

[a] Evaluated from Eq. (4.1) using $R = 0.1\%/\text{h}$, and a value of W_1 derived from the measured T_1: $W_1 = (3T_1)^{-1}$. The quantities in parenthesis are the experimental values of $r^0 - r^1$ in ortho-H_2.

the line center. If one assumes the angular dependence of the enhancement to be similar to that in hydrogen, one would predict a line that is nearly antisymmetric for large enhancements, with the center of the line having the normal unenhanced value. The observed negative enhancement at the line center is very difficult to explain and attempts to attribute it to errors in the integration or a saturation effect have been unsuccessful. Near the line center, spin exchange will certainly become

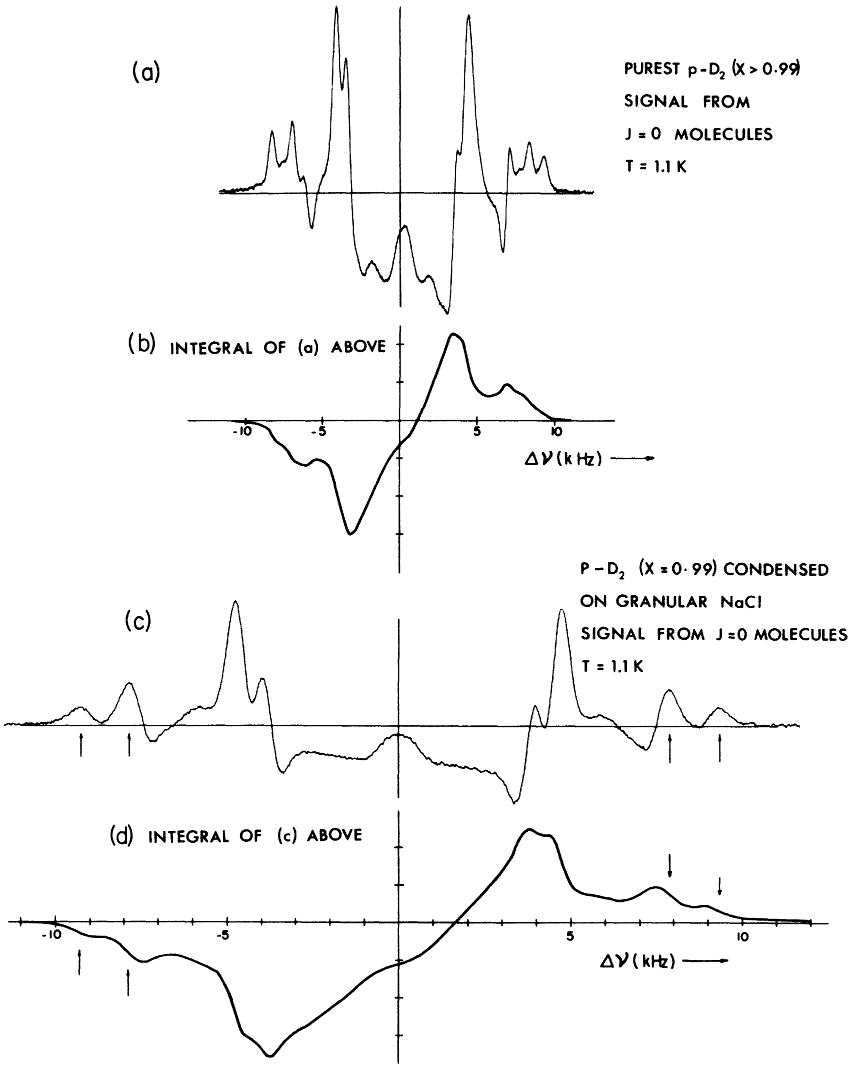

FIG. 6. Absorption spectra of the $J=0$ molecules in high-purity para-D_2. Derivative traces (a) and (c) correspond to the central regions of Figs. 5(a) and 5(c), respectively, but are taken with the magnetic field modulation reduced by a factor of 2. The arrows in traces (c) and (d) indicate the features assigned to the outer edges of the two Pake doublets predicted for the $J=0$ molecules.

effective in reducing the spin temperature gradient, but there is no reason why this should lead to a net negative spin temperature.

There is also a discrepancy in the relative strengths of the positively and negatively enhanced signals away from the central region. One would expect the amplitude of the positively enhanced signals to be everywhere stronger than the corresponding negative ones, which conflicts with experiment. This might be explained in part by nonlinear detection caused by substantial changes in the Q of the sample coil due to nuclear absorption (or emission). It has already been noted in Sec. III that because of the high Q of the resonant circuit, frequency-pulling effects (which accompany changes in Q) were large for strong signals.

We now turn to a comparison of the observed spectrum of the $J=0$ molecules to Harris's theory.[13] Making allowance for the inversion of the left half of the spectrum due to conversion enhancement, the two Pake doublets predicted by Harris[13] are clearly visible in Fig. 6(d). The extremities of the two doublets are marked with arrows. The frequency separation of the features as determined from the peaks of the derivative spectrum [Fig. 6(c)] are given in Table IV along with the assignments. For the outer features of the Pake doublets, the positions of the derivative peaks are only weakly affected by intermolecular dipolar broadening and can be used without corrections. The theoretical values of the splittings given in Table IV were computed from Eqs. (2.24) and (2.25) using a recent value of $\Gamma_{eff}=0.82$ cm^{-1} obtained from a fit of libron frequencies[23] to the anharmonic theory of Coll and Harris.[7] Also, following the suggestion of Harris,[13] Γ_{eff} was multiplied by 1.1 to account for the effects of further neighbors. The resulting values are about 15% larger than the experimental ones.

The discrepancy can be attributed almost entirely to the value of C, since the experimental *ratio* of the outer Pake splittings, $18.63/15.75=1.183$, is in excellent agreement with the theoretical value, $(15d_Q+5d_M)/(15d_Q-15d_M)=1.185$, which is independent of C. For the inner peaks of the Pake doublets, the experimental ratio is 1.200, which is in quite satisfactory agreement with the theoretical, considering the substantial shifts caused by broadening and overlapping of these features. The relative intensities of the two Pake doublets as determined by the outer features in the integrated spectrum of Fig. 6(d) are about equal, in agreement with the results given in Table I. However, the corresponding peaks in the derivative spectrum are about a factor of 2 more intense for the narrower of the doublets. This seems to imply that they have a different broadening parameter, but at present this remains unexplained.

TABLE IV. Pake splittings of $J=0$ molecules in ordered para-D_2. The experimental values are taken from derivative peaks in Fig. 6(c).

Features	Separation (kHz) Theory[a]	Expt.
$a\pm\frac{1}{4}C(15d_Q+5d_M)$	21.44	18.63
$a\pm\frac{1}{4}C(15d_Q-d_M)$	18.09	15.75
$a\pm\frac{1}{8}C(15d_Q+5d_M)$	10.72	9.53
$a\pm\frac{1}{8}C(15d_Q-d_M)$	9.04	7.95

[a] Computed from the thory of Harris (Ref. 13) using $\Gamma_{eff}=0.802$ cm^{-1} and $x=0.98$.

Meyer *et al.*[18] have also studied the nuclear magnetic resonance of the $J=0$ molecules. Although they did not resolve the two doublets, they measured the low-temperature value of the average Pake splitting for a range of concentrations extending up to about 96%. They extrapolated their results to $x=1.0$ and obtained a limiting value of 9.0 ± 0.7 kHz for the average splitting which, to within experimental error, agrees with the present results.

One can think of several reasons why the theoretical value of C does not agree with experiment, such as the effect of admixtures of states higher than $J=2$, the effect of virtual $J=1\rightarrow3$ transitions on the determination of Γ_{eff} from libron frequencies,[26] and the effects of the extra (librational) zero-point motion caused by the weak coupling of the $J=0$ molecule to its neighbors. It is clear, however, that the Pake splitting of the $J=0$ molecules is a very sensitive probe of the local crystal field. With refinements in the theory, one should be able to study, for example, the canting of the $J=1$ molecules adjacent to a $J=0$ impurity.

C. Spin-Lattice Relaxation

Figure 7 shows some measured values of T_1 in para-D_2 plotted as a function of $1/T$. The solid points are for a powder sample with $x\simeq0.96$ and were obtained by a pulse method: the magnetization $\vec{M}$ was first destroyed by a succession of pulses and then monitored throughout its recovery by periodic application of an intense but very short rf pulse (each pulse rotated $\vec{M}$ by only 1° and this allowed frequent sampling). The spectrometer operated at a frequency of 10.7 MHz and the field was adjusted to either of the main peaks in the Pake doublet [at frequency $(a\pm\frac{3}{2}d)$]. All of the recovery profiles showed deviations from a single time constant and the values in Fig. 8 correspond to the initial slope. A distribution of relaxation times may be a result of the expected anisotropy of T_1, which would result in a gradient of spin temperature

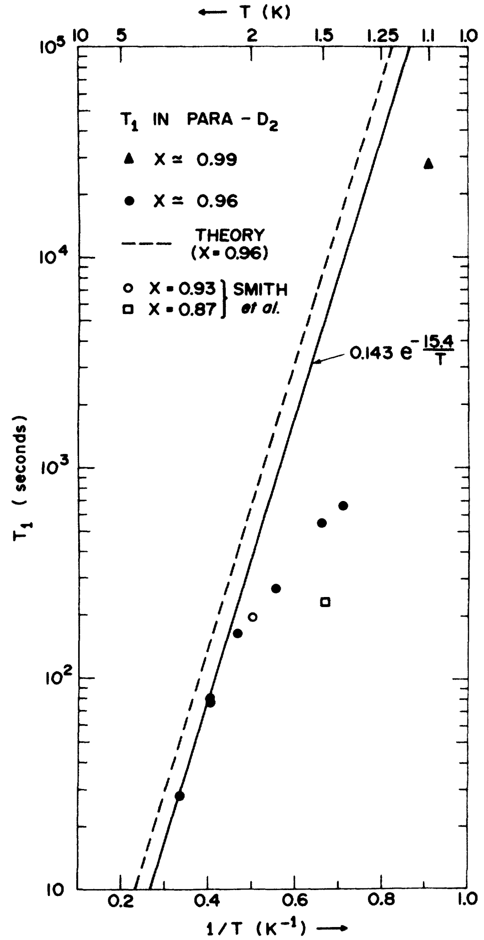

FIG. 7. T_1 vs $1/T$ in ordered para-D_2. For the sample with $x \simeq 0.96$ the measurements were made using a pulse spectrometer with its center frequency at one of the strong features of the Pake line shape [e.g., feature (b) in Fig. 5(a)]. A single exponential was not observed, possibly due to incomplete saturation of the whole Pake line. The value of T_1 was taken from the initial recovery rate. For the sample with $x \simeq 0.99$, a steady-state method was used in which the recovery of feature (b) in Fig. 5(a) was monitored after the whole Pake line had been completely saturated. The open circle and square are taken from Smith *et al.* (Ref. 27).

throughout the line, or it may be due to incomplete saturation of parts of the extremely broad and inhomogeneous line. The solid triangle was obtained from the steady-state measurements described in Sec. IVA and is for the feature at $(a - \frac{3}{2}d)$.

The dashed line is derived from the results of Harris[13] [the isotropic part of our Eq. (2.34 b)]. In evaluating $I = \int \rho^2(E) n(E)\, dE$ we have used the anharmonic single-libron density of states of Berlinsky and Coll.[28] To account for the effect of $J=0$ impurities which lower the average libron energy, we have used the expression of Harris *et al.*[26] for the concentration dependence of the average libron energy

$$E_L(x)/E_L(1) = 1 - 1.8(1-x) . \tag{4.6}$$

The coefficient 1.8 in Eq. (4.6) and the value of $E_L(1) = 12.4\ \mathrm{cm}^{-1}$ was derived from $(\partial P/\partial T)_V$ data.[29] In order to account for the fact that anharmonicity shifts some of the single-libron spectral weight into the two-libron band,[26] $\rho(E)$ has been multiplied by 0.83. Also, the factor $\frac{1}{2}$ in Harris's expression for $\rho(E)$ [Ref. 13, Eq. (8.7)] seemed to be in error and was deleted. The results for several values of the temperature and concentration are given in Table V. For $x = 0.96$ there is fair agreement with experiment at the higher temperatures, but below 2 K the agreement becomes progressively worse. The single point for the higher-purity sample is much closer to the theoretical curve and one immediately suspects that at low temperatures the relaxation is dominated by some mechanism involving the $J=0$ impurities.

We have not compared our results to the theory of Homma,[21] since his numerical results are based on an incorrect density of states.[30] It is presumed that the two theories are identical, although there seems to be a slight discrepancy in the value of $T_1(D_2)/T_1(H_2)$ at equivalent values of kT/Γ. Hom-

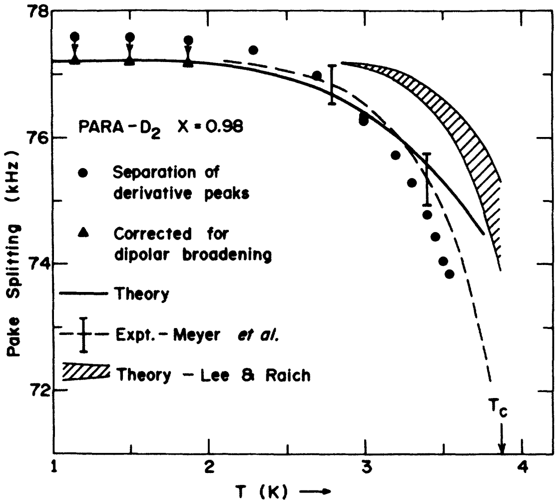

FIG. 8. Width of the Pake doublet in 98% $J=1$ para-D_2 as a function of temperature. The solid circles correspond to the difference in frequency between the peaks of features *b* and *b′* of Fig. 5 under conditions of small enhancements. The solid triangles result when corrections for intermolecular dipolar broadening are included. Above 2 K the correction cannot be made since the shape no longer corresponds to a Gaussian-broadened Pake line shape (see text). The solid line is the theory developed in this paper and the shaded area is derived from the results of Lee and Raich (Ref. 34). The dashed line with error bars is taken from Meyer *et al.* (Ref. 18).

TABLE V. Theoretical values of T_1 in the ordered state of para-D_2 as a function of temperature and concentration x of $J=1$ species. See text for details.

T (K)	$1/T$ (K^{-1})	T_1 (sec) $x=0.96$	 $x=0.98$	 $x=1.00$
1.0	1.000	1.41×10^6	2.58×10^6	4.72×10^6
1.5	0.667	8.73×10^3	1.31×10^4	1.95×10^4
2.0	0.500	670	907	1.23×10^3
2.5	0.400	142	181	231
3.0	0.333	50.1	61.4	75.2
3.5	0.286	23.7	28.2	33.6

ma[21] quotes a value 5.1, whereas the formulas of Harris[13] give 5.8.

D. Order Parameter in Para-D_2

In this section we present some precision measurements of the splitting of the $I=1$ Pake doublet as a function of temperature. On lowering the temperature, the sample went through the ordering transition at 3.65 K which, using the results of Schuch *et al.*,[31] implies that $x\approx0.975$ and that the upper transition temperature is 3.85 K. The solid circles in Fig. 8 give the separation of the features occurring at $\pm\frac{3}{2}d$ as measured from the centers of the peaks in the derivative spectrum.

At the lower temperatures the line shape was reasonably well approximated by the derivative of the convolution of a Gaussian line shape with the usual Pake shape for a powder [see Fig. 9(a)]. Based on such a fit the splitting was corrected for the effect of broadening and the results are shown as solid triangles in Fig. 8. At higher temperatures, however, the second peak in the derivative feature became weaker until at 3.5 K it had the shape shown in Fig. 9(b). The only plausible explanation of such a change in shape is that there is a distribution of Pake splittings, reflecting a distribution of local environments due to the 2% impurity of $J=0$ molecules. Undoubtedly the 2% impurity introduces a distribution of Pake splittings at the low temperatures also, but this is a relatively weak effect compared to the modification of the exponential thermal population factors.

Harris's prediction[13] for the $T=0$ Pake splitting [Eq. (2.26)] can be written

$$\Delta\nu_{D_2}=75.25\xi(1+0.06x-0.02x^{-1})\text{ kHz}$$
$$=79.13\xi\text{ kHz}\quad\text{for } x=0.98\,. \tag{4.7}$$

Experimentally we have

$$\Delta\nu_{D_2}=77.19\pm0.06\text{ kHz}\,, \tag{4.8}$$

which gives

$$\xi=0.985 \tag{4.9}$$

in good agreement with Harris,[13] and with the value 0.984 obtained by Meyer *et al.*[18] by extrapolation of measurements over a wide range of concentrations extending to $x=0.96$. The experimental error given above encompasses the total variation seen when the sample was rotated about an axis perpendicular to the magnetic field. Its value is some indication of how randomly the crystallites are oriented.

A comparison of the experimental temperature dependence of the splitting to theories for the order parameter is necessarily ambiguous because of the distribution of Pake splittings. Although $\sigma=\langle3\cos^2\theta-1\rangle_T$ is still well defined theoretically (since an ensemble average is implied), it is not possible to accurately deduce σ from experiment unless the form of the distribution is known.

The solid curve in Fig. 8 is calculated from the libron density of states. From Eq. (2.10)

$$\sigma=\tfrac{4}{5}\langle1-\tfrac{3}{2}J_z^2\rangle_T=\tfrac{4}{5}\langle1-\tfrac{3}{2}n_i\rangle_T\,, \tag{4.10}$$

where, in terms of the $c_{im}^\dagger$ Bose operators of Coll and Harris,[7]

$$n_i=c_{i,1}^\dagger c_{i,1}+c_{i,-1}^\dagger c_{i,-1}\,. \tag{4.11}$$

We can put

$$\langle n_i\rangle_T=n(T)+n(0)\,, \tag{4.12}$$

with

$$n(T)\approx2\alpha\int_0^\infty d\epsilon\rho(E)(e^{\beta\epsilon}-1)^{-1}\,, \tag{4.13}$$

where $\rho(E)$ is the single-libron density of states normalized to unity and $\alpha=0.83$ (Ref. 26) is a factor to compensate for cubic anharmonicity which shifts spectral weight from the single-libron states up into the two-libron band. The value of $n(0)$, which describes the zero-point motion of the librons, is about 0.013 (Refs. 32 and 33), so that

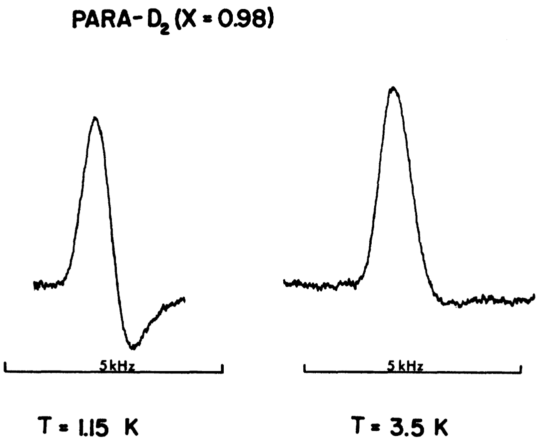

FIG. 9. Shape of one of the main Pake features in 98% $J=1$ para-D_2 at 1.15 and 3.5 K. At 1.15 K the shape is close to that of a Gaussian-broadened Pake line shape.

$$\frac{\sigma(T)}{\sigma(0)}=1-\frac{3}{2}\,\frac{n(T)}{1-\frac{3}{2}n(0)}=1-1.53n(T)\ . \qquad (4.14)$$

To compute $n(T)$, the anharmonic density of states of Berlinsky and Coll[28] was used, shifted to lower energy by an amount $0.034E_L$ to account for the 2% $J=0$ impurity {see Harris, Berlinsky, and Meyer[26] for the result $E_L(x)=E_L(0)[1-1.8(1-x)]$}. Here $E_L=16\Gamma$ is the average anharmonic single-libron energy. In order to take into account the temperature dependence of the libron energies, the order parameter σ was used to renormalize Γ. The calculation was then performed self-consistently by iteration, assuming the same value of $E_L(1)$, as in Eq. (4.6). Plotted in Fig. 8 is the quantity $77.19\sigma(T)/\sigma(0)$.

Lee and Raich[34] have calculated the temperature dependence of $n(T)$ by a cluster variation method and their results for $\sigma(T)/\sigma(0)$ multiplied by 77.19 kHz are shown in Fig. 8 with the temperature scaled so that the experimental and theoretical T_c's agree. The range of theoretical values is due to the fact that near the transition there are several structures having very nearly the same free energy and it is difficult to assign a transition temperature.

The present results agree quite well with the extrapolated NMR results of Meyer *et al.*[17] (the dashed line in Fig. 8) provided allowance is made for the fact that $x=0.98$. Theoretical values based on the libron density of states agree reasonably well up to $T=3$ K, but give too weak a temperature dependence thereafter. This is perhaps not unexpected since this type of theory is only rigorous at small value of T/T_c. The cluster variation results of Lee and Raich[34] give a temperature dependence this is considerably weaker and more abrupt than the experimental one.

V. DISCUSSION

In gross, the observed intensity anomalies seem to be quite well explained by the ortho-para pumping mechanism described in this and the following paper. However, in the case of H_2 for which a quantitative theory exists, the comparison between experiment and theory is restricted to two narrow regions of the line, and the numerical agreement is not as good as one would like. We believe the weakest link in the comparison to be the determination of W_1 from T_1. The bounds on the parameter $\alpha=3W_1T_1$ are somewhat uncertain due to the small number of points in the relaxation curves. By appropriate preparation of the spin system, W_1 can be measured in a more direct way. Experiments are planned in which both W_1 and the conversion enhancement are determined for all parts of the line. This will provide a detailed check of the theory especially with respect to the anisotropy of the conversion.

It has been established in this paper that T_1 in the ordered phase is very strongly dependent on the $J=0$ impurity concentration. In deuterium the results suggest that the current theories for nuclear spin relaxation via the Raman effect may agree with experiment in the limit of $x\rightarrow 1$. To check this and to investigate the impurity-relaxation mechanism, it is important to have a systematic study of T_1 vs temperature, concentration, and position within the Pake line shape.

The experimental situation with regard to the temperature dependence of the order parameter is still unsatisfactory due to the problem of the distribution of Pake doublets when $x\neq 1$. Although the results of Meyer *et al.*[17] were extrapolated to $x=1$, which in principle avoids this difficulty, the accuracy is not high enough to provide a critical check of the low-temperature-libron theory. The present data, although more precise, were only taken at a single concentration ($x=0.98$), which leaves the correction uncertain. Again, a systematic study at very high concentrations seems to be in order.

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[1] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U.P., Oxford, England, 1961).

[2] F. Reif and E. M. Purcell, Phys. Rev. **91**, 63 (1953).

[3] A. B. Harris, J. Appl. Phys. **42**, 1574 (1971).

[4] W. N. Hardy, I. F. Silvera, and J. P. McTague, Phys. Rev. Lett. **26**, 127 (1971).

[5] S. A. Boggs, M. J. Clouter, and H. L. Welsh, Can. J. Phys. **50**, 2063 (1972).

[6] H. M. James and J. C. Raich, Phys. Rev. **162**, 649 (1967); H. M. James, Phys. Rev. B **2**, 2213 (1970); Phys. Rev. Lett. **24**, 815 (1970); Phys. Rev. Lett. **24**, 970(E) (1970).

[7] C. F. Coll, III and A. B. Harris, Phys. Rev. B **4**, 2781 (1971).

[8] A. J. Berlinsky and A. B. Harris, Phys. Rev. B **4**, 2808 (1971); A. J. Berlinsky, Ph.D. thesis (University of Pennsylvania, 1972) (unpublished).

[9] R. L. Mills, J. L. Yarnell, and A. F. Schuch, in *Proceedings of the Thirteenth International Conference of Low Temperature Physics, Boulder, Colo., 1972*, edited by R. H. Kropschot and K. D. Timmerhaus (University of Colorado Press, Boulder, Colo., 1973). It would appear that earlier neutron data [K. F. Mucker, P. M. Harris, D. White, and R. A. Erickson, J. Chem. Phys.

49, 1922 (1968)] were not decisive due to a large background peak in the positions of the weak reflections.

[10] L. I. Amstutz, H. Meyer, S. M. Myers, and D. C. Rorer, Phys. Rev. **81,** 589 (1969).

[11] J. R. Gaines, E. M. de Castro, and D. White, Phys. Rev. Lett. **13,** 425 (1964).

[12] B. Maraviglia, F. Weinhaus, H. Meyer, and R. L. Mills, Solid State Commun. **8,** 815 (1970); Solid State Commun. **8,** 1683 (1970).

[13] A. B. Harris, Phys. Rev. B **2,** 3495 (1970).

[14] K. Motizuki and T. Nagamiya, J. Phys. Soc. Jap. **11,** 93 (1956); K. Motizuki, J. Phys. Soc. Jap. **12,** 163 (1957); J. Phys. Soc. Jap. **17,** 1192 (1962).

[15] Very recently we have been informed privately by H. Meyer and F. Weinhaus that in a sample of 96% para-D_2 they have also observed an anomalous negative absorption in the NMR spectrum of the $J = 0$ molecules.

[16] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

[17] The intensities given in Ref. (13) (2/5 and 3/5, respectively) were mistakenly interchanged [A. B. Harris (private communication)].

[18] H. Meyer, F. Weinhaus, B. Maraviglia, and R. L. Mills, Phys. Rev. B **6,** 1112 (1972).

[19] A. B. Harris, Solid State Commun. **10,** 329 (1972).

[20] A. B. Harris, Phys. Rev. B **1,** 1881 (1970).

[21] S. Homma, Prog. Theor. Phys. **40,** 1 (1968); Prog. Theor. Phys. **43,** 851 (1970).

[22] D. A. Depatie and R. L. Mills, Rev. Sci. Instrum. **39,** 105 (1968).

[23] W. N. Hardy, I. F. Silvera, and J. P. McTague (unpublished).

[24] K. W. Gray and W. N. Hardy, North American Rockwell Science Center Technical Report, 1969 (unpublished); W. N. Hardy and K. W. Gray (unpublished).

[25] F. N. H. Robinson, J. Sci. Instrum. **36,** 481 (1959).

[26] A. B. Harris, A. J. Berlinsky, and H. Meyer, Phys. Rev. B **7,** 4720 (1973).

[27] M. J. Smith, D. White, and J. R. Gaines, in *Proceedings of the Eleventh International Conference on Low Temperature Physics*, edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (University of St. Andrews, Scotland, 1969), Vol. I, p. 635; M. J. Smith, D. White, and J. R. Gaines, J. Chem. Phys. **49,** 3317 (1968).

[28] A. J. Berlinsky and C. F. Coll, III, Phys. Rev. B **4,** 1587 (1972).

[29] D. Ramm, H. Meyer, and R. L. Mills, Phys. Rev. B **1,** 2763 (1970).

[30] S. Homma and H. Matsuda, in *Proceedings of the Twelfth International Conference on Low Temperature Physics*, edited by Eizo Kanda (Academic of Japan, Kyoto, 1970) p. 841.

[31] A. F. Schuch, R. L. Mills, and D. A. Depatie, Phys. Rev. **165,** 1032 (1968).

[32] T. Nakamura and H. Miyagi, Prog. Theor. Phys. **44,** 833 (1970).

[33] C. F. Coll, III, Ph.D. thesis (University of Pennsylvania, 1972) (unpublished).

[34] R. J. Lee and J. C. Raich, Phys. Rev. Lett. **27,** 1137 (1971). A table of $n(T)$ was supplied by J. C. Raich.