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# Theory of Ortho-Para Conversion and its Effect on the NMR Spectrum of Ordered Solid Ortho-Hydrogen*

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The NMR spectrum of a system of nuclear spins in thermal equilibrium is directly proportional to $\mu H_0/kT$, where $\mu H_0$ is the difference in Zeeman energy between adjacent nuclear magnetic states and $T$ is the temperature. The metastable system, solid ortho-hydrogen, is far from thermal equilibrium because of the large rotational energy of the $(J = 1)$ molecules. Thus the populations of the three magnetic states of the $(I = 1)$ total-nuclear-spin wave functions are affected not only by the magnetic field and the temperature but also by the rate of ortho-para conversion from each of the three states. In this paper we calculate the difference $D$ between the ortho-para conversion rates from the $m_I = 0$ and the $m_I = \pm 1$ states for a crystal of ortho-hydrogen in the ordered state. It is found that $D$ depends on $(3\cos^2\beta - 1)$, where $\beta$ is the angle between the magnetic field and the symmetry axis of the molecular wave function. We then compute the steady-state populations of the nuclear-spin states as a function of $\mu H_0/kT$, $D$, and the nuclear spin-lattice relaxation time $T_1$. These are used to calculate the shape of the NMR spectrum of a powder sample for values of $T_1$ which are appropriate to the ordered state. The result is that the usual Pake line shape is distorted by an enhancement which is linear in frequency shift and proportional to $T_1D$. An expression is also derived for the average ortho-para conversion rate as a function of molar volume and the Debye energy which shows that the conversion rate, which we have calculated for the two-phonon process, is negligible below 20 cm$^3$/mole. By contrast, experiments show that at this molar volume the rate increases sharply with $1/V$. Our conclusion is that the increasing rate is due to a one-phonon process which is only effective for $V$ less than about 22 cm$^3$/mole.

## I. INTRODUCTION

The theory of ortho-para conversion in solid hydrogen was first treated by Motizuki and Nagamiya[1] in 1956. They found that the dominant mechanism for conversion is the interaction of the magnetic moments of the nuclei of an ortho-molecule with the inhomogeneous magnetic field due to the rotational and spin magnetic moments of its neighbors. They also pointed out that since the energy released in ortho-para conversion ($\Delta E = 171$ K for the free molecule) is larger than the largest phonon energy ($\Theta_D \cong 120$ K),[2-4] the interaction which causes this transition must simultaneously create at least two phonons in order to conserve energy. Their numerical calculations, based on this theory and using a Debye model to describe the phonons, gave a conversion rate of 1.94%/h in excellent agreement with the experimental value of Cremer and Polanyi[5,6] of 1.75%/h. However, it is difficult to interpret the significance of this agreement, since they took $\Theta_D$ to be 91 K, which is considerably smaller than the accepted value.

Later Motizuki[7] performed a similar calculation of the para-ortho conversion rate in solid $D_2$, which differs from solid $H_2$ in a number of significant respects. First, in $D_2$ the change of rotational energy in going from the $J=1$ to the $J=0$ state is half of that in $H_2$, while the Debye energy $\Theta_D = 115$ K[4] is nearly the same. Thus the one-phonon process is an allowed mechanism for conversion in solid $D_2$. Second, the deuterium nucleus has a nonzero quadrupole moment. The interaction of this quadrupole moment with electric field gradients due to neighboring molecules provides another mechanism for conversion in addition to dipolar interactions. Also, the final state of the $J=0$ $D_2$ molecule may be any of the six nuclear states corresponding to $I = 0$ or 2. If the final nuclear state is $I=2$, then this molecule will cause magnetic field gradients at neighboring molecules, and thus it may still contribute to the conversion process. This is in contrast to the case of solid $H_2$ where the para-molecules have $J = I = 0$ and thus do not contribute to further conversion. Motizuki's calculation of the conversion rate in $D_2$ included all of these effects and she again treated the phonons by means of the Debye approximation, taking $\Theta_D = 105$ K. Her results agree quite well with experiment[8] over a range of para-concentrations. For 100% para-$D_2$, she predicts a conversion rate of about 0.13%/h.

Despite the uncertainty which results from their use of an incorrect value of $\Theta_D$ for $H_2$, the agreement between theory and experiment for both solid $H_2$ and $D_2$ provides strong evidence for the correctness of the theoretical approach of Motizuki and Nagamiya. The situation is not entirely satisfactory, however, since it would be interesting to see if their theory gave the correct answer for $H_2$ when a reasonable value of $\Theta_D$ was used. Also, one would like to be able to test their theory in more detail by varying some of the physical parameters to see if the correct functional behavior is predicted. One step in this direction was taken by Ahlers,[9] who measured the conversion rate in $H_2$ as a function of molar volume. His results indicated a $V^{-8/3}$ dependence of the conversion rate on the volume, but he was not able to interpret this result theoretically since the volume dependence of the Motizuki-Nagamiya theory is not transparent. In this paper we have derived an analytic expression for the average two-phonon ortho-para conversion rate, using the same approximation as did Motizuki and Nagamiya. Our result does not agree with that of Motizuki and Nagamiya when evaluated using their value of $\Theta_D$. However, it is in good agreement with zero-pressure data when a realistic value of $\Theta_D$, namely, $\Theta_D = 120$ K, is used. In addition we have used the measurement of Ahlers[10] of $\Theta_D$ as a function of molar volume to estimate the dependence of the two-phonon conversion rate upon the volume.

The possibility of a more stringent test of the theory has arisen as the result of recent nuclear-magnetic-resonance (NMR) experiments in samples of high-purity ortho-$H_2$ and para-$D_2$, in their orientationally ordered phases. These experiments seem to provide much more detailed information about the conversion process. In particular they apparently enable us to determine the dependence of the conversion rate upon the initial and final nuclear-spin states of the molecule. The experimental results appear in the preceding paper,[11] which we will refer to as I. Also included in I is a detailed description of the theory of the NMR line shape in solid ortho-hydrogen and para-deuterium. Thus in this section we will restrict ourselves to a brief review of the NMR theory and refer the reader to I for further details. Also, in this paper we will confine our attention to the study of ortho-para conversion in solid $H_2$. A similar, but unfortunately more complicated, calculation for solid $D_2$ will appear in a later publication.

Pure ortho-$H_2$ undergoes an orientational order-disorder transition at about 2.8 K. Below this temperature the $J = 1$ molecules are in $m_J = 0$ orbitals oriented along certain local symmetry directions with the over-all space-group symmetry being $Pa3$. Detailed descriptions of this ordered state are given in a number of references.[12,13] The total nuclear spin of the ortho-molecules is $I = 1$, and in the presence of a magnetic field $H_0$, the Zeeman energies of the three nuclear-spin states are given by $E(m_I) = -2\mu_p H_0 m_I$, where $\mu_p$ is the magnetic moment of the proton. In addition, the two protons interact via their magnetic dipole moments. When this interaction is included, the energies of the nuclear spins are (in a high-field approximation)

$$E(m_I) = -2\mu_p H_0 m_I + hd\,(1 - \tfrac{3}{2} m_I^2)\,(3\cos^2\beta - 1), \quad (1.1\text{a})$$

where $h$ is Planck's constant,

$$d = \tfrac{4}{5}\,\mu_p^2 \langle r^{-3} \rangle / h = 57.68 \text{ kHz}, \quad (1.1\text{b})$$

$r$ is the separation between the protons, $\beta$ is the angle between the $m_J = 0$ orbital and the external field, and where we have ignored small corrections due to zero-point and thermal motion of the molecular wave function. In a magnetic-resonance experiment, transitions are induced between levels $m_I$ and $m_I \pm 1$. From Eq. (1.1a) we see that these transitions will occur at frequencies $\nu_\pm$ given by

$$h\nu_\pm = 2\mu_p H_0 \pm \tfrac{3}{2} hd(\langle 3\cos^2\beta - 1 \rangle). \quad (1.2)$$

The intensity of power absorbed in these transitions is proportional to the difference in populations of neighboring spin levels. In the usual case, when the three levels are in thermal equilibrium, this population difference is simply given by $2\mu_p H_0 / 3kT$ times the number of molecules (in the high-temperature approximation). On the other hand, if there were some process such as ortho-para conversion, which selectively depleted, for example, the $m_I = 0$ state faster than thermal equilibrium could be restored, then we would expect the absorption at $\nu_+$ to be enhanced and that at $\nu_-$ to be reduced. In fact if the depletion of the $m_I = 0$ state were sufficiently fast, then a population inversion would occur with a resulting emission of power at the frequency $\nu_-$.

In the calculation of Sec. II we show that the rate of ortho-para conversion from the state $m_I = 0$ does indeed differ from the conversion rate from the states $m_I = \pm 1$, and that in fact the difference in the rates depends upon the quantity $\langle 3\cos^2\beta - 1 \rangle$ as does the dipolar splitting. A byproduct of this calculation is an explicit expression for the average conversion rate as a function of the volume and the Debye energy. In Sec. III we calculate the effect of the $m_I$ dependence of the conversion rate upon the populations of the nuclear-spin levels. Finally, in Sec. IV we compute the theoretical shape of the Pake absorption line when it is distorted by ortho-para conversion and compare it to the experimental data given in I.

## II. THEORY OF ORTHO-PARA CONVERSION

As has already been discussed, ortho-para conversion in solid $H_2$ is caused by the interaction of the magnetic dipole moment of the nuclei of a molecule with the magnetic fields of its neighbors. This interaction has two parts, which we call $H_{ss}$ and $H_{rs}$, which describe interactions with neighboring spins and rotational magnetic moments, respectively. They are given by

$$H_{ss} = \left( \frac{24\pi}{5} \right)^{1/2} \sum_{p,\delta,s} \frac{4\mu_p^2}{|\vec{r}_\delta + \vec{r}_s - \vec{r}_p|^3}$$

$$\times \sum_{m,n} C(112;m,n)\, i_{\delta,s}^{m}\, i_{p}^{n}[Y_2^{m+n}(\Omega_{\delta,s,p})]^{*}, \tag{2.1a}$$

$$H_{rs} = \left(\frac{24\pi}{5}\right)^{1/2} \sum_{p,\delta} \frac{2\mu_r \mu_p}{|\vec{r}_\delta - \vec{r}_p|^3} \times \sum_{m,n} C(112;m,n)\, J_\delta^m\, i_p^n [Y_2^{m+n}(\Omega_{\delta,p})]^{*}. \tag{2.1b}$$

In Eq. (2.1a) $\mu_p$ is the proton magnetic moment, $\delta$ labels a neighboring molecule, and $s = 1, 2$ labels its two protons. The two protons of the central molecule, which is to undergo the transition, are labeled by $p = 1, 2$. We take our origin at the center of mass of the central molecule. Then $\vec{r}_p$ are the positions of the two protons of the central molecule, and $\vec{r}_\delta + \vec{r}_s$ is the position of proton $s$ of neighboring molecule $\delta$; $i_{\delta,s}^m$ is the $m$th spherical component of the nuclear spin of proton $s$ on molecule $\delta$. In Eq. (2.1b) $\mu_R$ is the rotational magnetic moment of the $H_2$ molecule. $\Omega_{\delta,s,p}$ and $\Omega_{\delta,p}$ denote the directions of the vectors $\vec{r}_\delta + \vec{r}_s - \vec{r}_p$ and $\vec{r}_\delta - \vec{r}_p$, respectively, and $J_\delta^m$ is the $m$th spherical component of the angular momentum of molecule $\delta$. The labeling of the various vectors and nuclear spins is illustrated in Fig. 1. The coefficients $C(112; m,n)$ are Clebsch-Gordan coefficients and $Y_L^M(\Omega)$ is a spherical harmonic using the phase convention of Rose.[14]

Since ortho-para conversion involves a change of the orientational coordinates of the central molecule, and to conserve energy it must also involve the creation of at least two phonons, we must expand the functions

$$\frac{[Y_2^{m+n}(\Omega_{\delta,s,p})]^{*}}{|\vec{r}_\delta + \vec{r}_s - \vec{r}_p|^3} \quad \text{and} \quad \frac{[Y_2^{m+n}(\Omega_{\delta,p})]^{*}}{|\vec{r}_\delta - \vec{r}_p|^3} \tag{2.2}$$

to first order in $\vec{r}_p$ and to second order in displacements of $\vec{r}_\delta$. In the expansion of Eq. (2.1a) we will make the approximation that $|\vec{r}_s| \approx 0$ so that $H_{ss}$ does not depend on the orientation of molecule $\delta$ but only on its nuclear spin. Also, we write

$$\vec{r}_\delta = \vec{R}_\delta + \vec{U}_\delta, \tag{2.3}$$

where $\vec{R}_\delta$ is the equilibrium position of molecule $\delta$ and $\vec{U}_\delta$ is a small displacement which may be written in terms of phonon operators.

The term in the expansion of Eqs. (2.1) which is first order in $\vec{r}_p$ and second order in $\vec{U}_\delta$ depends upon

$$\frac{T_2^M(\Omega_\delta)}{R_0^3} = -\tfrac{1}{2}[(\vec{U}_\delta \cdot \vec{\nabla})^2 (\vec{r}_p \cdot \vec{\nabla})] \frac{[Y_2^M(\Omega)]^{*}}{|\vec{R}|^3}, \tag{2.4}$$

where the derivatives are evaluated at

$$|\vec{R}| = R_0, \tag{2.5a}$$

$$\Omega = \Omega_\delta. \tag{2.5b}$$

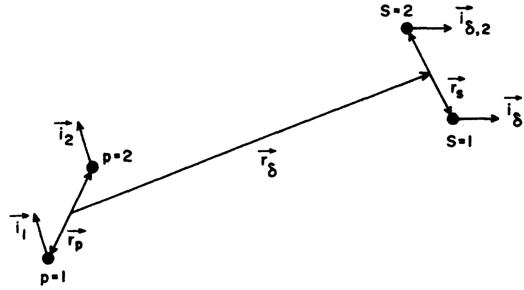

FIG. 1. Vectors that define the positions of the protons for two $H_2$ molecules. In Sec. II we calculate the probability that the molecule on the left converts from ortho to para. The molecule on the right at $\vec{r}_\delta$ is one of its 12 nearest neighbors.

$R_0$ in Eqs. (2.4) and (2.5a) is the equilibrium nearest-neighbor lattice spacing ($R_0 = 3.755$ Å) and $\Omega_\delta$ represents the direction of $\vec{R}_\delta$.

We may evaluate $T_2^M(\Omega_\delta)$ by repeated use of a formula which is easily derived from Eqs. (6.42) and (6.43) in Rose.[14] If $\vec{V}$ is an arbitrary vector, then

$$\vec{V} \cdot \nabla \frac{Y_J^M}{R^{J+1}} = -(2J+1)\left(\frac{J+1}{2J+3}\right)^{1/2} \times \sum_m C(J,1,J+1;M,m) \frac{Y_{J+1}^{M+m}}{R^{J+2}} V^{m*}. \tag{2.6}$$

The expression for $T_2^M(\Omega_\delta)$ which results from the use of Eq. (2.6) in Eq. (2.4) may be written in the form

$$\frac{T_2^M(\Omega_\delta)}{R_0^3} = 525\left(\frac{3}{385}\right)^{1/2} \sum_{m,m',m''} C(112;m,m') \times C(213;m+m,m'')\, C(325;m+m'+m'',M) \times U_\delta^m U_\delta^{m'} r_p^{m''} \frac{[Y_5^{M+m+m'+m''}(\Omega_\delta)]^{*}}{R_0^6}. \tag{2.7}$$

In deriving this expression, we have used an equation from Rose,[14] Eq. (6.4b), to recouple the various angular momenta so that the phonon coordinates appear in a symmetrical form. (See also Appendix B for the values of the required Racah coefficients.)

We can write components of $\vec{r}_p$ as

$$r_p^m = \frac{\rho}{2}\left(\frac{4\pi}{3}\right)^{1/2} Y_1^m(\Omega_p), \tag{2.8}$$

where $\rho = 0.75$ Å is the internuclear separation. We also note that

$$\vec{r}_1 = -\vec{r}_2. \tag{2.9}$$

Then the parts of $H_{ss}$ and $H_{rs}$ corresponding to ortho-para conversion plus two-phonon creation may be written as

$$H_{ss}=2A\gamma_{ss}\left(\frac{\rho}{R_0}\right)\sum_{\delta}\sum_{\substack{\mu,\nu\\ m,m',m''}}C(112;\mu,\nu)C(112;m,m')C(213;m+m',m'')C(325;m+m'+m'',\mu+\nu)$$

$$\times\frac{U_\delta^m U_\delta^{m'}}{R_0^2}Y_1^{m''}(\Omega)(i_1^\mu-i_2^\mu)I_\delta^\nu[Y_5^{\mu+\nu+m+m'+m''}(\Omega_\delta)]^*, \tag{2.10}$$

where

$$A=1260\pi\left(\frac{2}{231}\right)^{1/2}, \tag{2.11a}$$

$$\gamma_{ss}=\mu_p^2/R_0^3, \tag{2.11b}$$

$$I_\delta^\nu=(i_{1\delta}^\nu+i_{2\delta}^\nu), \tag{2.11c}$$

and $\Omega$ is the orientation of the central molecule. Similarly $H_{rs}$ is given by

$$H_{rs}=A\gamma_{rs}\left(\frac{\rho}{R_0}\right)\sum_{\delta}\sum_{\substack{\mu,\nu\\ m,m',m''}}C(112;\mu,\nu)C(112;m,m')C(213;m+m',m'')C(325;m+m'+m'',\mu+\nu)$$

$$\times\frac{U_\delta^m U_\delta^{m'}}{R_0^2}Y_1^{m''}(\Omega)(i_1^\mu-i_2^\mu)J_\delta^\nu[Y_5^{\mu+\nu+m+m'+m''}(\Omega_\delta)]^*, \tag{2.12}$$

where

$$\gamma_{rs}=\mu_p\mu_r/R_0^3. \tag{2.13}$$

Motizuki and Nagamiya[1] have shown that, in the rotationally disordered phase, the ortho-para conversion rate for the disordered system ($T>3$ K) may be written as

$$R=R_{ss}[1+\tfrac{1}{4}(\mu_r^2/\mu_p^2)], \tag{2.14}$$

where the second term corresponds to processes involving $H_{rs}$. Since

$$\mu_p^2\approx 10\mu_r^2, \tag{2.15}$$

these processes account for about 2.5% of the total rate. Strictly speaking, this ratio of spin-rotation to spin-spin conversion rates will be different in the ordered phase because of coherent effects involving the propagation of librons. However, the change will probably be a small fraction of the spin-rotation conversion rate, which is itself small. Consequently we will perform a detailed calculation only for conversion due to spin-spin interactions and include the effect of spin-rotation interactions perturbatively by means of Eq. (2.14).

The ortho-para conversion rate for a hydrogen molecule with initial nuclear state $M$ is

$$R_{ss}^M=\frac{2\pi}{\hbar}\sum_{i,f}{}'P_i|\langle f|H_{ss}|i\rangle|^2\delta(E_i-E_f), \tag{2.16}$$

where the prime on $\sum$ restricts the sum over initial states $i$ to states in which the molecule has $I_z=M$, and $P_i$ is the probability that the system is initially in the state $i$.

The matrix element for the nuclear spin of the central molecule is

$$\langle I=0,\ m_I=0|i_1^\mu-i_2^\mu|I=1,\ m_I=M\rangle=\delta_{\mu,-M}. \tag{2.17}$$

The operator $I_\delta^\nu$ has matrix elements

$$\langle m_\delta'|I_\delta^\nu|m_\delta\rangle=\sqrt{2}\,C(111;m_\delta,m_\delta'-m_\delta)\delta_{\nu,m_\delta'-m_\delta}. \tag{2.18}$$

The operator $Y_1^{m''}(\Omega)$ causes the central molecule to convert from $J=1$ to $J=0$. Since we are treating the crystal in its ordered state, this molecule will be in an $m_J=0$ state with respect to its local equilibrium axis. Thus it is convenient to write $Y_1^{m''}(\Omega)$ as

$$Y_1^{m''}(\Omega)=\sum_{m'''}[D_{m'',m'''}^{(1)}(\chi)]^*Y_1^{m'''}(\omega), \tag{2.19}$$

where $\omega$ measures the orientation of the molecule with respect to its local equilibrium axis and $\chi$ is the set of Euler angles $(\alpha,\beta,\gamma)$ relating the equilibrium axis to the lab frame. Using Eq. (2.19) we find that

$$\langle J=0,\ m_J=0|Y_1^{m''}(\Omega)|J=1,\ m_J=0\rangle$$

$$=\frac{1}{\sqrt{(4\pi)}}[D_{m'',0}^{(1)}(\chi)]^*. \tag{2.20}$$

To write the sum over final phonon states of the displacement operators it is necessary to expand them in terms of phonon operators:

$$\frac{U_\delta^m}{R_0}=\frac{1}{\sqrt{N}}\sum_{\vec{k},\tau}(1-e^{i\vec{k}\cdot\vec{R}_\delta})\left(\frac{\hbar^2}{2MR_0^2\epsilon_{\vec{k}\tau}}\right)^{1/2}$$

$$\times(a_{\vec{k},\tau}^\dagger+a_{-\vec{k},\tau})\eta_\tau^m(\vec{k}), \tag{2.21}$$

where $\vec{k}$ is a wave vector; $\tau$ labels the polarization; $\epsilon_{\vec{k}\tau}$ is a phonon energy; $a_{\vec{k}\tau}^\dagger$ is a phonon creation operator; and $\eta_\tau^m(\vec{k})$ is the $m$th spherical component of the unit polarization vector.

If we make the reasonable assumptions that the energies of the nuclear-spin states can be neglected when compared to the phonon and ortho-para conversion energies and that the nuclear spins are uncorrelated, then the transition rate depends upon the part of the two-phonon spectral density which is diagonal in the site indices:

$$G_\delta(m, m'; n, n'; E_{10}) \equiv R_0^{-4} \sum_{|2\rangle} \langle 0 | [U_\delta^n]^* [U_\delta^{n'}]^* | 2 \rangle \times \langle 2 | U_\delta^m U_\delta^{m'} | 0 \rangle \delta(E_{10} - E_2), \tag{2.22}$$

where $|2\rangle$ is summed over all two-phonon states, $E_2$ is the energy of the two phonons, and $E_{10}$ is the energy released in ortho-para conversion.

Using Eq. (2.21) in Eq. (2.22) we find that

$$G_\delta(m, m'; n, n'; E_{10}) = \left(\frac{\hbar^2}{2MR_0^2 E_D}\right)^2 \frac{1}{N^2} \sum_{\vec{k}, \vec{k}'} \sum_{\tau, \tau'} \frac{E_D^2}{\epsilon_{\vec{k},\tau} \epsilon_{\vec{k}',\tau'}} \left| (1 - e^{i\vec{k}\cdot\vec{R}_\delta})(1 - e^{i\vec{k}'\cdot\vec{R}_\delta}) \right|^2 \delta(E_{10} - \epsilon_{\vec{k}\tau} - \epsilon_{\vec{k}',\tau'})$$
$$\times \{ \eta_\tau^m(\vec{k}) \eta_{\tau'}^{m'}(\vec{k}') [\eta_\tau^n(\vec{k})]^* [\eta_{\tau'}^{n'}(\vec{k}')]^* + \eta_\tau^m(\vec{k}) \eta_{\tau'}^{m'}(\vec{k}') [\eta_{\tau'}^n(\vec{k}')]^* [\eta_\tau^{n'}(\vec{k})]^* \}, \tag{2.23}$$

where we have multiplied and divided by the square of the Debye energy $E_D$.

We define the quantum numbers

$$N = m + m', \quad N' = n + n', \tag{2.24}$$

which represent the $z$ component of the total angular momentum of the two phonons. Then, holding $N$ and $N'$ fixed, we define the spectral function

$$G_\delta^{(2)}(N, N'; E_{10}) = \sum_{m,n} C(112; m, N - m) C(112; n, N' - n) G_\delta(m, N - m; n, N' - n; E_{10}). \tag{2.25}$$

Finally, we can write the transition rate, using Eqs. (2.17), (2.18), (2.20), and (2.25) in Eq. (2.16). The result is

$$R_{ss}^M = \frac{4}{3} \frac{\gamma_{ss}^2}{\hbar} A^2 \left(\frac{\rho}{R_0}\right)^2 \sum_\delta \sum_{m_\delta m_\delta'} \sum_{\substack{NN',\\ m_J, m_J'}} C^2(112; M, m_\delta - m_\delta')$$
$$\times C^2(111; m_\delta, m_\delta' - m_\delta) C(213; N, m_J) C(213; N', m_J') C(325; N + m_J, m_\delta' - m_\delta - M) C(325; N' + m_J', m_\delta' - m_\delta - M)$$
$$\times [D_{m_J,0}^{(1)}(\chi)]^* D_{m_J',0}^{(1)}(\chi) G_\delta^{(2)}(N, N'; E_{10}) [Y_5^{N+m_J+m_\delta'-m_\delta-M}(\Omega_\delta)]^* Y_5^{N'+m_J'+m_\delta'-m_\delta-M}(\Omega_\delta). \tag{2.26}$$

In Eq. (2.26) the factor $\frac{1}{3}$ corresponds to $P_i$ in Eq. (2.16). It is the inverse of the number of nuclear magnetic states of the neighboring ortho-molecule. Then the total ortho-para conversion rate will be given by

$$R_{ss} = \frac{1}{3} \sum_M R_{ss}^M. \tag{2.27}$$

In deriving Eq. (2.26) the only approximation that we have made is that the nuclear-spin energies are small compared to the phonon energies and the temperature. However, in order to evaluate Eq. (2.26) explicitly, it will be necessary to make two assumptions.

The first assumption we will make is that the solid is in the form of a powder of randomly oriented crystallites. Such an ideal powder is possible, although difficult, to achieve experimentally. The fact that we have assumed a powder does not mean that we can average $R_{ss}^M$ over all orientations of the crystal, however, because the NMR experiment, which we would like to interpret, distinguishes between molecules on the basis of $P_2(\cos\beta) = (3\cos^2\beta - 1)/2$ of the molecule, where $\beta$ is the angle between the molecular symmetry axis and the external magnetic field. Thus molecules with different values of $P_2(\cos\beta)$ appear in different places in the NMR spectrum. Consequently our powder average will consist of an average over all orientations of the molecule while holding the angle between the molecular axis and the lab $z$ axis fixed. Also from now on we will take the lab $z$ axis to be the direction of the magnetic field.

The second approximation, which we are more or less forced to make because of the complexity of the problem, but which is most difficult to justify on physical grounds, is that the phonons may be described by a Debye dispersion relation

$$\epsilon_{\vec{k}\tau} = v\hbar |\vec{k}|, \tag{2.28}$$

with a single velocity of sound $v$ for both transverse and longitudinal modes. This assumption provides a great simplification of the calculation, since it decouples the phonon portion of the calculation from the Clebsch-Gordan coefficient and lattice sums.

In defense of our use of the Debye spectrum we note that, although the Debye density of states

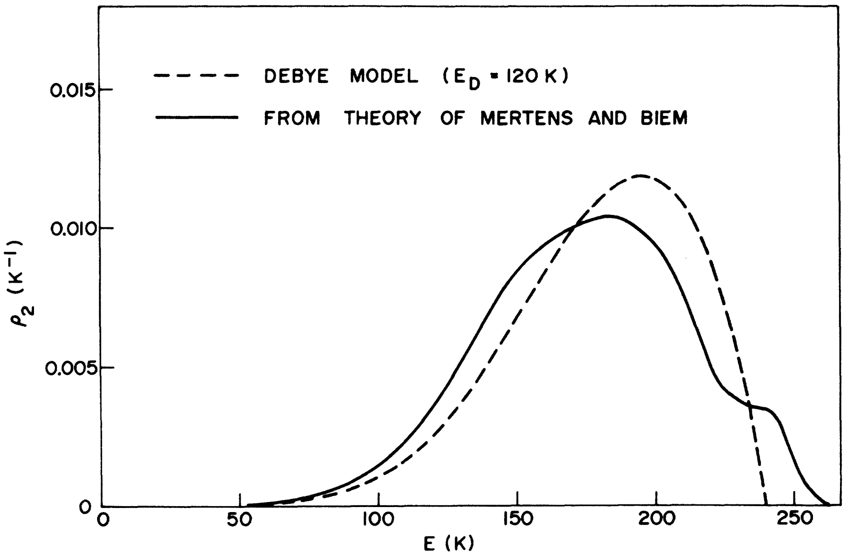

FIG. 2. Comparison of the two-phonon density of states $\rho_2(E)$ computed from the Debye model with $E_D/k = \Theta_D = 120$ K (dashed curve) to $\rho_2(E)$, computed using the phonon density of states from Ref. (15) (solid curve).

looks very different from the phonon density of states of solid $H_2$ as calculated, for example, by Mertens and Biem,[15] the two-phonon densities of states for the two theories are quite similar. This is shown in Fig. 2, where the solid curve represents the function

$$\rho_2(E) = \int_0^\infty d\epsilon\, g(\epsilon) g(E-\epsilon)\,, \tag{2.29}$$

and $g(E)$ is Mertens and Biem's density of states with the energy scale renormalized by a factor of 0.794, to bring it into agreement with optical-phonon data.[16] The dashed curve is the function $\rho_2(E)$ calculated using the Debye density of states

$$g_D(\epsilon) = 3\epsilon^2/E_D^3\,, \tag{2.30}$$

where $E_D = k\Theta_D$, and we have taken $E_D/k = 120$ K. The similarity of the two curves is quite suggestive. On the other hand, this argument is not compelling since the conversion rate depends not only on the density of states but also upon wave-vector- and polarization-dependent matrix elements whose effect is difficult to estimate. What one can safely say is that the Debye approximation may be reasonable for this calculation, whereas for the analogous one-phonon process it would almost certainly give rise to spurious effects.

The explicit calculation of the two-phonon spectral function is given in Appendix A. Here we merely quote the result

$$G_6^{(2)}(N, N'; E_{10}) = \delta_{NN'} g^{(2)}(E_{10})\,, \tag{2.31}$$

where $g^{(2)}(E_{10})$ depends only on $E_{10}$, $R_0$, and the Debye energy $E_D$ and not on $N$, $N'$, or $\delta$. We begin our evaluation of Eq. (2.26) by performing the powder average, which was described above. First, we write the $Y_5$'s in terms of rotation matrices and spherical harmonics referred to the molecular symmetry axis. That is,

$$[Y_5(\Omega_6)]^* = \sum_\nu D^{(5)}_{M,\nu}(\chi)[Y_5^\nu(\omega_6)]^*\,, \tag{2.32}$$

where $\chi$ is the same set of Euler angles as in Eq. (2.19). The powder average of the transition rate thus involves the quantity

$$\langle [D^{(1)}_{m_J,0}(\chi)]^* D^{(1)}_{m_J',0}(\chi) D^{(5)}_{\eta,\nu}(\chi) [D^{(5)}_{\eta',\nu'}(\chi)]^* \rangle_{\alpha,\gamma}\,, \tag{2.33}$$

where

$$\eta = N + m_J + m_6' - m_6 - M\,, \tag{2.34a}$$

$$\eta' = \eta - m_J + m_J'\,, \tag{2.34b}$$

and the average is over the Euler angles $\alpha$ and $\gamma$ holding $\beta$ fixed. The result is

$$\begin{aligned}\langle [D^{(1)}_{m_J,0}(\chi)]^* D^{(1)}_{m_J',0}(\chi) D^{(5)}_{\eta,\nu}(\chi) [D^{(5)}_{\eta',\nu'}(\chi)]^* \rangle_{\alpha,\gamma} &= (-1)^{m_J+\eta'-\nu'} \delta_{\nu,\nu'} \sum_{l,j,k} C(11l;0,0)\, C(11l;-m_J, m_J') \\ &\quad \times C(55j;\eta,-\eta')\, C(55j;\nu,-\nu)\, C(jlk;\eta-\eta', m_J'-m_J)\, C(jlk;0,0) P_k(\cos\beta)\,. \end{aligned} \tag{2.35}$$

Before substituting from Eqs. (2.35) and (2.31) into the equation for the conversion rate, Eq. (2.26), we should make two trivial simplifications. First, we note that if we define the index

$$L = m_6 - m_6'\,, \tag{2.36}$$

which represents the change in the magnetic quantum number of the nuclear spin at $\vec{R}_\delta$, then the sum over $m_\delta$ is easily done holding $L$ fixed. This sum involves only

$$\sum_{m_\delta} C^2(111;m_\delta, -L)=1\,. \tag{2.37}$$

The second simplification is to define the coefficients

$$d^j(\delta)=\sum_\nu C(55j;\nu,-\nu)\,Y_5^\nu(\omega_\delta)\,Y_5^{-\nu}(\omega_\delta) \tag{2.38a}$$

$$=\frac{11C(55j;0,0)\,Y_j^0(\omega_\delta)}{[4\pi(2j+1)]^{1/2}}\,. \tag{2.38b}$$

Finally, we may write the conversion rate as

$$R_{ss}^M=\frac{4}{3}\frac{\gamma_{ss}^2}{\hbar}A^2\left(\frac{\rho}{R_0}\right)^2 g^{(2)}(E_{10})\sum_{l,j,k} C(11l;0,0)\,C(jlk;0,0)$$
$$\times\Bigg\{\sum_{L,N,m_J,m_J'}(-1)^{m_J+m_J'+N-L-M}\,C^2(112;L,M)\,C(213;N,m_J)\,C(213;N,m_J')\,C(325;N+m_J,-L-M)$$
$$\times C(325;N+m_J',-L-M)\,C(11l;-m_J,m_J')\,C(55j;N+m_J-L-M,L+M-N-m_J')\,C(jlk;m_J-m_J',m_J'-m_J)\Bigg\}$$
$$\times\sum_\delta d^j(\delta)\,P_k(\cos\beta)\,. \tag{2.39}$$

The expression in curly brackets is a sum over four indices of a product of nine Clebsch-Gordan coefficients. It may be performed by repeated applications of Eq. (6.5b) in Rose[14] plus a single application of his Eq. (11.31), which involves an $X$ coefficient (9-$j$ symbol). The process is both lengthy and uninteresting, so we will simply quote the result:

$$\{\cdots\}=(-1)^l\frac{385}{\sqrt{3}}[(2l+1)(2j+1)(2k+1)]^{1/2}$$
$$\times W(3131;2,l)\,W(1212;1,k)\,X(532;532;j,l,k)$$
$$\times C(1k1;M,0)\,. \tag{2.40}$$

This expression was checked by performing the Clebsch-Gordan sums numerically on a computer. When Eq. (2.40) is inserted in Eq. (2.39) we find that

$$R_{ss}^M=\frac{1540}{3\sqrt{3}}A^2\frac{\gamma_{ss}^2}{h}\left(\frac{\rho}{R_0}\right)^2 g^{(2)}(E_{10})\sum_{l,j,k}(-1)^l[(2l+1)(2j+1)(2k+1)]^{1/2}$$
$$\times C(11l;0,0)\,C(jlk;0,0)\,W(3131;2,l)\,W(1212;1,k)\,X(532;532;j,l,k)\sum_\delta d^j(\delta)\,C(1k1;M,0)\,P_k(\cos\beta)\,. \tag{2.41}$$

Thus the coefficient of the Legendre polynomial $P_k(\cos\beta)$ is a Clebsch-Gordan coefficient times the sum over $j$ and $l$ of a product of various factors, most of which look rather complicated. Things are not as bad as they look, however; and, in fact, the number of nonvanishing terms in the triple sum over $l$, $j$, and $k$ is extremely small.

The coefficient $C(11l;0,0)$ vanishes except when $l=0$ or 2. The coefficient $C(1k1;M,0)$ vanishes for $k>2$. The lattice sum over $\delta$ vanishes when $j$ is odd and, for a close-packed lattice, when $j=2$. The coefficient $C(jlk;0,0)$ vanishes when $j+l+k$ is odd or when the three indices violate the triangle inequality.[14] The net result of all these restrictions is that the triple sum contains only three nonvanishing terms. These are

$$(A)\quad k=j=l=0\,, \tag{2.42a}$$

$$(B)\quad k=2,\ j=0,\ l=2\,, \tag{2.42b}$$

$$(C)\quad k=2,\ j=4,\ l=2\,, \tag{2.42c}$$

and we will refer to the transition rates associated with these terms as $R_{ss}^M(A)$, $R_{ss}^M(B)$, and $R_{ss}^M(C)$.

In order to complete our evaluation of the conversion rates, we need the lattice sum in Eq. (2.41). That is, we must evaluate the coefficients

$$S^j\equiv\sum_\delta d^j(\delta)\,. \tag{2.43}$$

For $j<6$ the only nonzero coefficients are

$$S^0=-\frac{3}{\pi}\sqrt{11}, \tag{2.44a}$$

$$S^4=-\frac{77}{8\pi}\sqrt{\frac{2}{143}}\,, \tag{2.44b}$$

Finally, we must also evaluate the spectral function $g^{(2)}(E_{10})$. We see from Appendix A that this has the value

$$g^{(2)}(E_{10})=\frac{18}{E_D}\left(\frac{\hbar^2}{2MR_0^2E_D}\right)^2\eta\,, \tag{2.45}$$

where $\eta$ is the sum of trigonometric functions given in Eq. (A.14). For $E_{10}=159$ K, which is the value measured by neutron scattering[17] for the ordered state, and for $E_D=120$ K we find that

$$\eta=0.7331 \tag{2.46}$$

For convenience we also define the rate

$$\gamma\equiv\frac{\gamma_{ss}^2}{\hbar E_D}\left(\frac{\rho}{R_0}\right)^2\left|\frac{\hbar^2}{2MR_0^2E_D}\right|^2, \tag{2.47a}$$

$$=0.585\times10^{-6}\%/\text{h}. \qquad (2.47\text{b})$$

Then, using the values of coefficients listed in Appendix B, we find that the three contributions to the conversion rate are

$$R_{ss}^{M}(A)=1\,209\,600\ \pi r\eta\,, \qquad (2.48\text{a})$$

$$R_{ss}^{M}(B)=-1\,209\,600\ \pi r\eta \times\frac{1}{\sqrt{10}}C(121;M,0)\,P_2(\cos\beta)\,, \qquad (2.48\text{b})$$

$$R_{ss}^{M}(C)=-302\,400\ \pi r\eta \times\frac{1}{\sqrt{10}}C(121;M,0)\,P_2(\cos\beta)\,. \qquad (2.48\text{c})$$

Inserting numerical values for $r$ and $\eta$ we find that

$$R_{ss}^{M}(A)=1.63\%/\text{h} \qquad (2.49)$$

and

$$R_{ss}^{M}(A)+R_{ss}^{M}(B)+R_{ss}^{M}(C) =1.63\left(1-\frac{\sqrt{10}}{8}\,C(121;M,0)\,P_2(\cos\beta)\right)\%/\text{h}\,. \qquad (2.50)$$

The average ortho-para conversion rate, which we call $R$, is simply equal to $R_{ss}^{M}(A)$ since the remaining terms, which are proportional to $C(121;M,0)P_2(\cos\beta)$, vanish when averaged over $M$ or over orientations of the crystal. This expression for the average rate is valid for either the ordered or disordered phases since it is independent of the molecular orientation. However, we must also include in $R$ a correction, owing to the spin-rotation interaction. Using Eq. (2.14) we find that

$$R=1.025\,R_{ss}^{M}(A)=1.67\%/\text{h}\,. \qquad (2.51)$$

This figure should be compared with the results of Cremer and Polanyi,[5,6] who found $R=1.75\%$/h, and of Ahlers,[9] who found $R=1.82\%$/h.

Inserting the values of the Clebsch-Gordan coefficients, we find that the final expression for the conversion rate from the state $M$ is $R_{ss}^{M}$, where

$$R_{ss}^{\pm1}=1.67\left[1-\tfrac{1}{8}P_2(\cos\beta)\right]\%/\text{h}\,, \qquad (2.52\text{a})$$

$$R_{ss}^{0}=1.67\left[1+\tfrac{1}{4}P_2(\cos\beta)\right]\%/\text{h}\,. \qquad (2.52\text{b})$$

Motizuki and Nagamiya[1] included an additional contribution to the ortho-para conversion rate due to three-phonon processes, which they found to be about 0.20%/h. We will not attempt to repeat their calculation. Instead we simply note that the contribution due to three-phonon processes for $E_D=120$ K should be considerably smaller than that for $E_D=91$ K, which they considered. To illustrate this point, we show in Fig. 3 the behavior of the two-phonon conversion rate as a function of $E_D$, taking $E_{10}=159$ K for the nearly pure ordered system. The figure shows that the two-phonon conversion rate is a sharply decreasing function of $E_D$ for $E_D$ larger than 95 K. There are three reasons why $R$ decreases as it does. First, since the total number of phonon modes is fixed, the phonon density of states scales inversely with $E_D$. Second, as $E_D$ increases the conversion process increasingly samples the longer-wavelength phonons. Since the number of these phonons scales like $k^2$, there are fewer phonon states available. Third, long-wavelength phonons are less efficient in causing conversion since they do not cause large magnetic field gradients. This information is carried in the factors $[1-j_0(x)]$ in Eq. (A7). Exactly the same arguments apply to the behavior of the three-phonon conversion rate as a function of $E_D$, and thus we conclude that if the calculation of Motizuki and Nagamiya for $E_D=91$ K did not contain any errors, then for $E_D=120$ K the three-phonon conversion rate is probably between 0.01 and 0.05%/h.

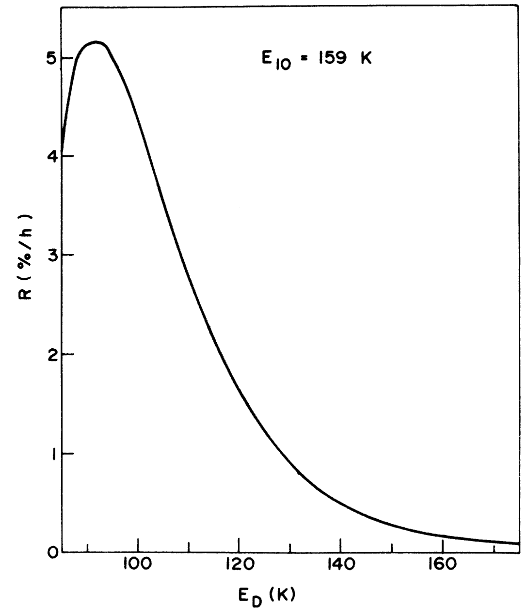

FIG. 3. Dependence of the average conversion rate $R$ upon the Debye energy for fixed molar volume ($V=22.55$ cm$^3$) using Eq. (2.51) and taking the ortho-para conversion energy $E_{10}=159$ K.

Since we have an expression for the two-phonon conversion rate as a function of the Debye energy $E_D$ and the nearest-neighbor separation $R_0$, it is a simple matter to compute the volume dependence of $R$ using the measurements of Ahlers[10] to relate $E_D$ to the molar volume $V$. These measurements are plotted in Fig. 4(a), where we have also drawn a smooth curve to interpolate between the three data points. Following the suggestion of Jarvis *et al.*,[18] we have shifted the lowest-pressure data points from $V=22.55$ cc/mole to $V=22.05$ cc/mole, which corresponds to a pressure of 55 bar at which

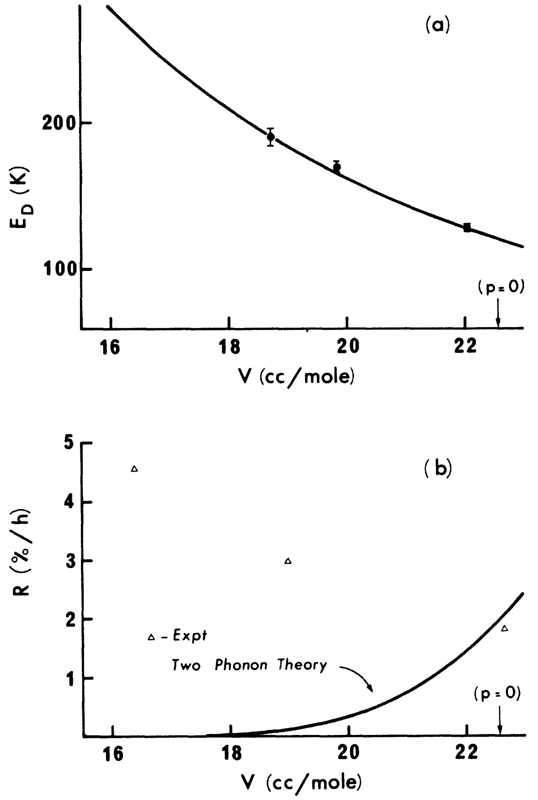

FIG. 4. Dependence of the Debye energy $E_D$ and the ortho-para conversion rate upon molar volume $V$. In (a) the dots with error bars are experimental values of $E_D$ taken from Ref. 10. The solid curve has been used to interpolate between the three points. In (b) the triangles are experimental measurements of $R$ from Ref. 9, and the solid curve is the prediction of theory for two-phonon conversion processes.

the measurement was made. In Fig. 4(b) the triangles correspond to Ahlers's measurements of the conversion rate in solid $H_2$ with the concentration of $J=1$ molecules $x \approx 0.75$. For this value of $x$, neutron scattering measurements[17] show that $E_{10} \approx 166$ K. Using this value of $E_{10}$ and the values of $E_D$ taken from the solid curve in Fig. 4(a), we have computed the theoretical value of $R$ vs molar volume, and the result is shown by the solid curve in Fig. 4(b). The immediate conclusion that one draws from the figure is that the two-phonon process does not account for the ortho-para conversion rate except perhaps at zero pressure. The agreement at zero pressure ($V=22.55$ cc/mole) is fairly good, but at any significant pressure it would appear that the one-phonon process becomes energetically possible (possibly because anharmonicity adds a long tail onto the phonon density of states); and, as the pressure is increased, this process takes over completely.

## III. EFFECT OF ORTHO-PARA CONVERSION UPON THE NUCLEAR-SPIN POPULATIONS

Having established the fact that ortho-para conversion proceeds at different rates for the different nuclear-magnetic states the next question of interest is what effect this has upon the relative populations of these states when they are split in energy by an external magnetic field. To answer this question we examine the time evolution of the populations of the various states of the four-level system which is shown schematically in Fig. 5. The three magnetic sublevels of the $I=1$ state are split by the energy $\Delta = 2\mu_p H_0$. The $I=0$ level is at an energy $-2B$, where $2B$ ($=171$ K) is the rotational kinetic energy of an $H_2$ molecule in a $J=1$ angular momentum state. The various constants $W_{m,m'}$, $R^0$, and $R^1$ are the rates of transitions between the various states. In the absence of ortho-para conversion, the $W_{m,m'}$ bring about thermal equilibrium within the $I=1$ manifold. $R^1$ and $R^0$ are the rates of ortho-para conversion which we have calculated in the previous section [see Eqs. (2.52)].

Because the lattice is assumed to be in thermal equilibrium, the six rate constants $W_{m,m'}$ are not all independent and, in fact, are related in the following way:

$$W_{-1,0} = W_{0,1} = W_1 , \tag{3.1a}$$

$$W_{0,-1} = W_{1,0} = \gamma W_1 , \tag{3.1b}$$

$$W_{-1,1} = W_2 , \tag{3.1c}$$

$$W_{1,-1} = \gamma^2 W_2 , \tag{3.1d}$$

where

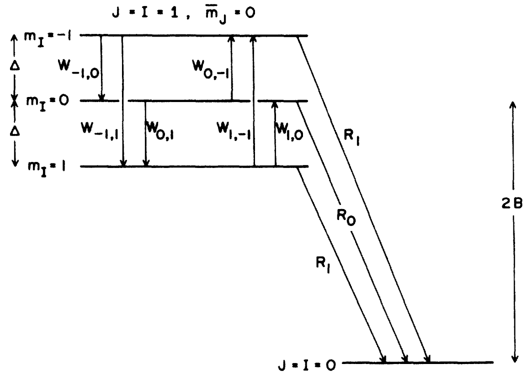

FIG. 5. Nuclear energy levels of ortho- and para-molecules in the solid. The three $I=1$ states are split an amount Δ by the external field. Transitions from level $m$ to $m'$ proceed at a rate $W_{m,m'}$. Ortho-para conversion from the state $m$ occurs with a rate $R_{|m|}$, into the state ($J=I=0$) which is at an energy $E_{10} \approx 2B$ below the ortho states.

$$\gamma = e^{-\Delta/kT} . \tag{3.2}$$

The time-dependent populations of the four states may be determined from the coupled differential equations:

$$\frac{dp_{-1}}{dt} = -(R^1 + W_1 + W_2)p_{-1} + \gamma W_1 p_0 + \gamma^2 W_2 p_1 , \tag{3.3a}$$

$$\frac{dp_0}{dt} = W_1 p_{-1} - (R^0 + W_1 + \gamma W_1)p_0 + \gamma W_1 p_1 , \tag{3.3b}$$

$$\frac{dp_1}{dt} = W_2 p_{-1} + W_1 p_0 - (R^1 + \gamma W_1 + \gamma^2 W_2)p_1 , \tag{3.3c}$$

$$\frac{dq}{dt} = R^1 p_{-1} + R^0 p_0 + R^1 p_1 , \tag{3.3d}$$

where $p_m$ is the population of the state $I=1$, $m_I = m$, and $q$ is the population of the $I=0$ state. In addition we require certain boundary conditions, namely, the initial values of the $p_m$ and $q$, and for convenience we normalize the total population to unity. That is

$$q + \sum_m p_m = 1 . \tag{3.4}$$

Equations (3.3a)–(3.3c) do not involve $q$ and may be solved separately from Eq. (3.3d). To do this we make the ansatz that

$$p_m(t) = \sum_{i=1}^{3} U^i_m a_i e^{-\lambda_i t} . \tag{3.5}$$

Inserting this into Eqs. (3.3a)–(3.3c) we obtain the algebraic equations

$$\begin{bmatrix} R^1 + W_1 + W_2 & -\gamma W_1 & -\gamma^2 W_2 \\ -W_1 & R^0 + W_1(1+\gamma) & -\gamma W_1 \\ -W_2 & -W_1 & R^1 + \gamma(W_1 + \gamma W_2) \end{bmatrix} \begin{bmatrix} U^i_{-1} \\ U^i_0 \\ U^i_1 \end{bmatrix} = \lambda_i \begin{bmatrix} U^i_{-1} \\ U^i_0 \\ U^i_1 \end{bmatrix} . \tag{3.6}$$

Next we make a high-temperature approximation by writing $\gamma$ as

$$\gamma = 1 - 2\delta , \tag{3.7}$$

where

$$\delta = \mu_p H_0 / kT , \tag{3.8}$$

and we also define the dimensionless variables

$$y = W_2/W_1 , \tag{3.9a}$$

$$c = R^1/W_1 , \tag{3.9b}$$

$$d = (R^0 - R^1)/W_1 , \tag{3.9c}$$

$$\eta_i = (\lambda_i / W_1) - c . \tag{3.9d}$$

Then the eigenvalue Eq. (3.6) has the form

$$\underline{\mathrm{M}}\vec{\mathrm{U}}^i = \eta_i \vec{\mathrm{U}}^i , \tag{3.10}$$

where the matrix $\underline{\mathrm{M}}$ is given by

$$\underline{\mathrm{M}} = \begin{bmatrix} 1+y & -1+2\delta & -y+4\delta y \\ -1 & 2+d-2\delta & -1+2\delta \\ -y & -1 & 1+y-2\delta(1+2y) \end{bmatrix} . \tag{3.11}$$

The matrix $\underline{\mathrm{M}}$ may be written as a sum of two terms:

$$\underline{\mathrm{M}} = \underline{\mathrm{M}}^0 + \underline{\mathrm{m}} , \tag{3.12}$$

where $\underline{\mathrm{M}}^0$ has matrix elements that are all of order unity while the matrix elements of $\underline{\mathrm{m}}$ are all of order of $d$ or $\delta$, which are presumed to be much less than 1.

$$\underline{\mathrm{M}}^0 = \begin{bmatrix} 1+y & -1 & -y \\ -1 & 2 & -1 \\ -y & -1 & 1+y \end{bmatrix} , \tag{3.13a}$$

$$\underline{\mathrm{m}} = \begin{bmatrix} 0 & 2\delta & 4\delta y \\ 0 & d-2\delta & 2\delta \\ 0 & 0 & -2\delta(1+2y) \end{bmatrix} . \tag{3.13b}$$

The matrix $\underline{\mathrm{M}}^0$ is diagonalized trivially and its eigenvectors and eigenvalues are well known. They are

$$\vec{\mathrm{V}}_s = \frac{1}{\sqrt{3}} \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} , \quad \eta^0_s = 0 \tag{3.14a}$$

$$\vec{\mathrm{V}}_v = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} , \quad \eta^0_v = 1+2y \tag{3.14b}$$

$$\vec{\mathrm{V}}_t = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 \\ -2 \\ 1 \end{bmatrix} , \quad \eta^0_t = 3 \tag{3.14c}$$

where the subscripts $s$, $v$, and $t$ refer to scalar, vector, and tensor polarizations, which these vectors represent. Using the eigenvectors and eigenvalues of $\underline{\mathrm{M}}^0$ and standard first-order perturbation theory, we can compute the effect of adding the matrix $\underline{\mathrm{m}}$ to $\underline{\mathrm{M}}^0$. Assuming that $y$ is sufficiently different from 1 that the ratios $d/(y-1)$ and $\delta/(y-1)$ are perturbative, we find that the eigenvectors of $\underline{\mathrm{M}}$ are approximately given by

$$\vec{\mathrm{U}}^{s}=\frac{1}{\sqrt{3}}\begin{bmatrix}1-2\delta+d/9\\ 1-2d/9\\ 1+2\delta+d/9\end{bmatrix}, \quad \eta_s=d/3 \tag{3.15a}$$

$$\vec{\mathrm{U}}^{v}=\frac{1}{\sqrt{2}}\begin{bmatrix}1+\delta/2(y-1)\\ -\delta/(y-1)\\ -1+\delta/2(y-1)\end{bmatrix}, \quad \eta_v=1+2y-\delta-4\delta y \tag{3.15b}$$

$$\vec{\mathrm{U}}^{t}=\frac{1}{\sqrt{6}}\begin{bmatrix}1-2d/9+\delta(1-4y)/2(y-1)\\ -2-2d/9\\ 1-2d/9-\delta(1-4y)/2(y-1)\end{bmatrix},$$

$$\eta_t=3-3\delta+\frac{2d}{3}\ . \tag{3.15c}$$

To complete our solution we must specify the initial condition of the system. Experimentally it is possible to prepare the system in a state in which the three nuclear levels are equally populated. This is done by sweeping back and forth across the line with a strong rf field. Then for a sample of pure ortho-hydrogen at $t=0$ we have

$$p_m(0)=\tfrac{1}{3}, \quad m=0, \pm 1\ . \tag{3.16}$$

The constants $a_i$ are determined by using Eq. (3.16) in Eq. (3.5),

$$\sum_i U^i_m a_i=\tfrac{1}{3}, \quad m=0, \pm 1 \tag{3.17}$$

which has the solution

$$a_s=\frac{1}{\sqrt{3}}, \tag{3.18a}$$

$$a_v=\frac{2\sqrt{2}}{3}\delta\ , \tag{3.18b}$$

$$a_t=\frac{-2d}{9\sqrt{6}}\ . \tag{3.18c}$$

Then, using Eqs. (3.5), (3.15), and (3.18), we can write down the populations of the nuclear states. We find, to first order in $d$ and $\delta$, that

$$e^{cW_1t}p_{-1}(t)=\tfrac{1}{3}(1-2\delta+d/9)e^{-\eta_s W_1 t} +\tfrac{2}{3}\delta e^{-\eta_v W_1 t}-(d/27)e^{-\eta_t W_1 t}\ , \tag{3.19a}$$

$$e^{cW_1t}p_{0}(t)=\tfrac{1}{3}(1-2d/9)e^{-\eta_s W_1 t}+(2d/27)e^{-\eta_t W_1 t}\ , \tag{3.19b}$$

$$e^{cW_1t}p_{1}(t)=\tfrac{1}{3}(1+2\delta+d/9)e^{-\eta_s W_1 t} -\tfrac{2}{3}\delta e^{-\eta_v W_1 t}-(d/27)e^{-\eta_t W_1 t}\ . \tag{3.19c}$$

The absorption signal observed in NMR is proportional to the difference in population of adjacent nuclear levels. For a single molecule the NMR signal will be a doublet, split by the intramolecular dipole-dipole interaction. The strengths of these two absorption signals may be written as

$$S^-(t)\equiv S_0[p_0(t)-p_{-1}(t)]\ , \tag{3.20a}$$

$$S^+(t)\equiv S_0[p_1(t)-p_0(t)]\ , \tag{3.20b}$$

where $S_0$ is a constant that depends on the experimental apparatus. We evaluate Eqs. (3.20) using Eqs. (3.19) and inserting the value of $\delta$, $d$, and the $\eta$'s. The result to lowest order in $\delta$ and $d$ is

$$S^{\pm}(t)=S_0e^{-Rt}\left(\frac{2\mu_pH_0}{3kT}(1-e^{-t/T_1})\pm\frac{R^0-R^1}{9W_1}(1-e^{-3W_1t})\right)\ , \tag{3.21}$$

where $R$ is the average conversion rate and the $R^M$ are the conversion rates from the states $M$. The spin-lattice relaxation time $T_1$ is related to $W_1$ and $W_2$ by

$$1/T_1=W_1+2W_2\ . \tag{3.22}$$

This is just the relaxation time for a state of vector polarization. The rate of time development and the magnitude of the tensor polarization which results from anisotropic ortho-para conversion, depend only on the probability of $\Delta M=\pm 1$ transitions—that is, on the quantity $3W_1$.

## IV. THEORETICAL NMR ABSORPTION LINE SHAPES

Using the results of Sec. II and III, we are now in a position to predict the shape of the NMR spectrum in ordered solid ortho-$H_2$. Let us first consider the case in which $T_1$ relaxation is fast compared to the ortho-para conversion rate. Then to a good approximation we can neglect ortho-para conversion. The unbroadened absorption by molecules oriented along a particular direction and which are in thermal equilibrium is

$$S(\nu)=\frac{2S_0\mu_pH_0}{3kT}[\delta(\nu-\nu_+)+\delta(\nu-\nu_-)]\ , \tag{4.1}$$

where $\nu_+$ and $\nu_-$ are defined in Eq. (1.2). The signal that is actually observed will always have a nonzero linewidth due to fluctuations in local fields at the nuclei and to instrumental effects. A good approximation for the actual observed signal is

$$S(\nu)=\frac{2S_0\mu_pH_0}{3kT}[g(\nu-\nu_+)+g(\nu-\nu_-)]\ , \tag{4.2}$$

where

$$g(\nu)\equiv\frac{1}{\sqrt{2\pi}\sigma}e^{-\nu^2/2\sigma^2} \tag{4.3}$$

is a normalized Gaussian line-shape function of width $\sigma$.

If the sample is a powder of randomly oriented crystallites, Eq. (4.2) must be averaged over all orientations of the molecule. Then the signal has the form

$$S(\nu)=\frac{S_0\mu_pH_0}{6\pi kT}\int[g(\nu-\nu_+(\beta))+g(\nu-\nu_-(\beta))]\sin\beta\, d\beta\, d\phi\,, \tag{4.4}$$

where we have explicitly noted the dependence of $\nu_+$ and $\nu_-$ on $\beta$. Unfortunately the integration of Eq. (4.4) cannot be performed analytically. However, numerical integration for a particular choice of $\sigma/d$ is rather simple. The result for $\sigma/d=0.145$[19–21] is shown by curve (a) in Fig. 6.

Next we consider the case in which the ortho-para conversion rate is nonzero. After a time long compared to $T_1$, we see from Eq. (3.21) that the signal from molecules oriented along a particular direction will have the form

$$S(\nu)=S_0\left[\left(\frac{2\mu_pH_0}{3kT}+\frac{R^0-R^1}{9W_1}\right)g(\nu-\nu_+)+\left(\frac{2\mu_pH_0}{3kT}-\frac{R^0-R^1}{9W_1}\right)g(\nu-\nu_-)\right]\,. \tag{4.5}$$

The difference $R^0-R^1=D$ may be obtained from Eq. (2.52). The result is

$$D=\tfrac{3}{8}\,RP_2(\cos\beta)\,. \tag{4.6}$$

In order to evaluate Eq. (4.5) we need the value of $W_1$, which is the rate of $\Delta m=\pm 1$ transitions. Since the NMR signal represents a linear combination of nuclear states with vector and tensor polarizations, the relaxation rates which are measured experimentally are a linear combination of $1/T_1$ and $3W_1$. In the previous paper (I), it is argued that within experimental error

$$1/T_1=3W_1\,, \tag{4.7}$$

since the relaxation rate appears to be uniform throughout the NMR line.

Referring back to the definition of $T_1$ in Eq. (3.22), we see that Eq. (4.7) is equivalent to saying that

$$W_1=W_2\,. \tag{4.8}$$

Thus we were not justified in Sec. III, where we defined $y\equiv W_1/W_2$, in assuming that quantities such as $\delta/(y-1)$ are perturbative. However, we have repeated the calculation of Sec. III for the case $y=1$. Using first-order degenerate perturbation theory, we found that the final equation, Eq. (3.21), is unchanged. Then using Eq. (4.7) and averaging over all orientations of the molecules we find that

$$S(\nu)=\frac{S_0\mu_pH_0}{6\pi kT}\int\{[1+\gamma P_2(\cos\beta)]g(\nu-\nu_+(\beta))+[(1-\gamma P_2(\cos\beta))g(\nu-\nu_-(\beta))]\}\sin\beta\, d\beta\, d\phi\,, \tag{4.9}$$

where

$$\gamma=3RT_1kT/16\mu_pH_0\,. \tag{4.10}$$

Since $\nu_+(\beta)$ and $\nu_-(\beta)$ are both linear in $P_2(\cos\theta)$ [see Eq. (1.2)], the enhancement of the signal in Eq. (4.9) will be a linear function of the frequency as measured from the center of the line with the maximum and minimum enhancements occurring at the outer edges of the line with magnitude $(1+\gamma)$

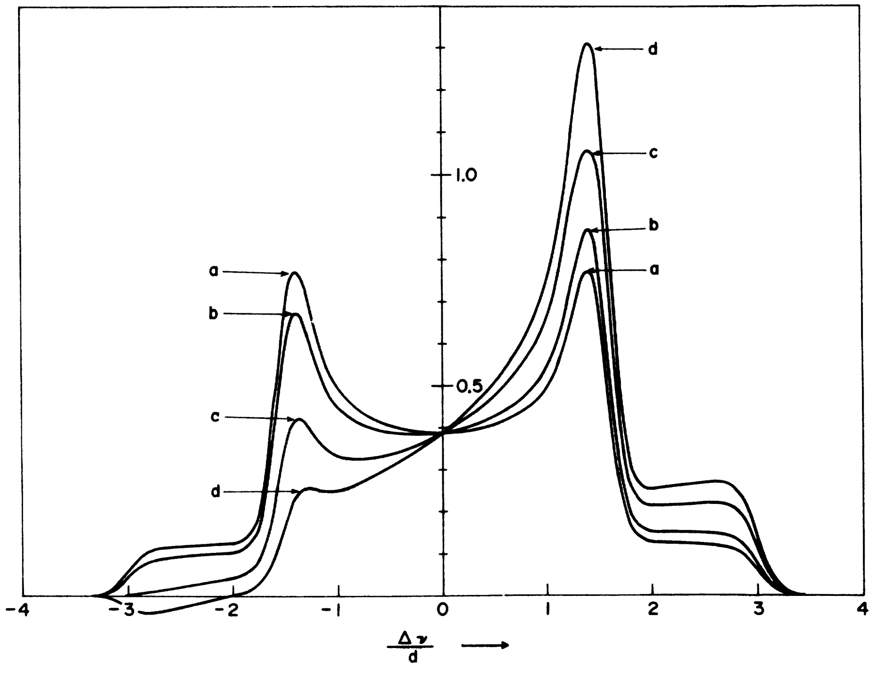

FIG. 6. Theoretical shape of the (Pake) NMR spectrum in the presence of ortho-para conversion. Curves (a), (b), (c), and (d) correspond to $\gamma=0$, 0.277, 1.0, and 1.5, respectively, where $\gamma$ is defined in Eq. (4.10). Note that for $\gamma>1$, the "absorption" becomes negative on the low-frequency side of the spectrum.

and $(1-\gamma)$, respectively. Two prominent peaks also occur in the spectrum at energies corresponding to $P_2(\cos\beta)=-\frac{1}{2}$. These peaks will be enhanced by $(1+\gamma/2)$ on the high-energy side and by $(1-\gamma/2)$ on the low-energy side.

For the experiment reported in I we have $T=1.1$ K, $T_1=75$ sec, and $H_0=2650$ G. If we take the experimentally determined value of $R=1.75\%/\mathrm{h}$, we find

$$RT_1=0.364\times10^{-3}\,, \tag{4.11a}$$

$$\frac{\mu_p H_0}{kT}=0.246\times10^{-3}\,, \tag{4.11b}$$

$$\gamma=0.277\,. \tag{4.11c}$$

In Fig. 6 curve (b) represents the absorption for this value of $\gamma$ while curves (c) and (d) correspond to $\gamma=1.0$ and 1.5, respectively. Since the Legendre polynomial $P_2(\cos\beta)$ has values between 1 and $-\frac{1}{2}$, it is clear from Eq. (4.9) and from Fig. 6 that, when $\gamma$ is greater than 1, the low-energy side of the spectrum will emit power.

The agreement between theory and the experimental data presented in I is fair. The theory predicts that the enhancement of the peaks corresponding to $P_2(\cos\beta)=-\frac{1}{2}$ should be half as much as for the shoulders which correspond to $P_2(\cos\beta)=1$. The actual experimental ratio is 0.196 : 0.518, which is somewhat less than $\frac{1}{2}$. The experimentally derived values of $\gamma$ are 0.392 and 0.518, both of which are significantly higher than the value 0.277 given in Eq. (4.11c). Thus although our theory certainly gives qualitatively correct results, it appears that the observed spectrum is more strongly enhanced than we would predict, and there may be a small deviation from the rule which says that the anisotropy in the conversion rate is proportional to $P_2(\cos\beta)$. There is certainly a need here for more experimental work, especially since the hydrogen data in I is for only one sample at a single temperature and field strength. More extensive measurements, perhaps with higher-purity ortho-hydrogen samples, would allow us to make a detailed comparison between theory and experiment.

In conclusion, we summarize the main results of this paper:

(i) We have derived an expression for the two-phonon ortho-para conversion rate, as a function of the initial nuclear-magnetic state of the molecule, for a high-purity powder of solid ortho-hydrogen in the ordered state. This expression shows that the conversion rate from the $M_I=0$ nuclear state is different from that from the $M_I=\pm1$ states and that this difference is proportional to $P_2(\cos\beta)$, where $\beta$ is the direction of the molecular symmetry axis.

(ii) A dividend which arises from the above calculation is an analytic expression for the average conversion rate which is valid for either the ordered or disordered phases. Since this expression is a simple function of the intermolecular distance and the Debye energy, it is possible to determine the density dependence of the two-phonon conversion rate using measured values of $E_D$ vs molar volume. Our conclusion is that for molar volumes of less than 20 cc/mole the two-phonon conversion rate is negligible and conversion proceeds almost completely via the one-phonon mechanism.

(iii) We have calculated the effect of the difference in ortho-para conversion rates from different nuclear states upon the populations of these states. We find that the amount that these populations are disturbed from the equilibrium Boltzman distribution is proportional to the difference in ortho-para conversion rates divided by $W_1$, which is the rate of $\Delta M_I=\pm1$ transitions.

(iv) Finally, we have compared our theory to the only available NMR data for high-purity ortho-$H_2$ in the ordered phase. We find that the asymmetry of the line does depend upon $P_2(\cos\beta)$ to a reasonable approximation. On the other hand, the magnitude of the asymmetry seems to be about 60% higher than our theory predicts.

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## APPENDIX A: EVALUATION OF THE TWO-PHONON SPECTRAL DENSITY IN THE DEBYE APPROXIMATION

We wish to evaluate the spectral function $G_\delta^{(2)}(N,N';E_{10})$, which is defined in Eq. (2.25). If we make the approximation that the crystal is isotropic and consequently that all modes with a given $|\vec{k}|$ are degenerate, then we may choose any three orthogonal unit vectors as the polarization vectors. In particular, we may take

$$\eta_\tau^m=\delta_{m,\tau}\,. \tag{A1}$$

Then the sums over $\tau, \tau', m,$ and $n$ in Eq. (2.25) are performed trivially with the result

$$\begin{aligned}G_\delta^{(2)}(N,N';E_{10})=2\delta_{NN'}\left(\frac{\hbar^2}{2MR_0^2E_D}\right)^2 &\times\frac{1}{N^2}\sum_{\vec{k},\vec{k}'}\frac{E_D^2}{\epsilon_{\vec{k}}\epsilon_{\vec{k}'}}\\ &\times\left|(1-e^{i\vec{k}\cdot\vec{R}_\delta})(1-e^{i\vec{k}'\cdot\vec{R}_\delta})\right|^2\\ &\times\delta(E_{10}-\epsilon_{\vec{k}}-\epsilon_{\vec{k}'})\,.\end{aligned} \tag{A2}$$

We may transform the sums over $\vec{k}$ to integrals over energy by making the substitution

$$\frac{1}{N}\sum_{\vec{k}}\to\frac{3}{4\pi E_D^3}\int_0^{E_D}\epsilon^2\,d\epsilon\,d\Omega_k\,. \tag{A3}$$

Then the angular integrals are easily evaluated:

$$\frac{1}{4\pi}\int |1-e^{i\vec{k}\cdot\vec{R}_0}|^2\,d\Omega = 2-2j_0(kR_0)\,, \tag{A4}$$

where $j_0(x)$ is a spherical Bessel function

$$j_0(x)=(\sin x)/x\,. \tag{A5}$$

We also define the energy $\epsilon_0$, which is the energy of a phonon with wave vector $k=2\pi/R_0$. Then

$$\epsilon_0=E_D\left(\frac{\pi}{3}\right)^{1/3}\sqrt{2}\approx 1.44E_D\,. \tag{A6}$$

Using Eqs. (A3)–(A6) in Eq. (A2), we find that

$$\begin{aligned} G_\delta^{(2)}(N,N';E_{10}) = 18\delta_{NN'}\left(\frac{\hbar^2}{2MR_0^2E_D}\right)^2 &\times\frac{4}{E_D^4}\int_0^{E_D}d\epsilon\int_0^{E_D}d\epsilon'[1-j_0(2\pi\epsilon/\epsilon_0)]\\ &\times[1-2j_0(2\pi\epsilon'/\epsilon_0)]\epsilon\epsilon'\delta(E_{10}-\epsilon-\epsilon')\,. \end{aligned} \tag{A7}$$

To perform the double integral in Eq. (A7), we change variables to

$$\epsilon_1=\epsilon+\epsilon',\quad \epsilon_2=\epsilon-\epsilon'\,. \tag{A8}$$

Then the integral over $\epsilon_1$ is trivial because of the $\delta$ function. We are left with

$$G_\delta^{(2)}(N,N';E_{10})=\frac{18}{E_D}\delta_{N,N'}\left|\frac{\hbar^2}{2MR_0^2E_D}\right|\eta\,, \tag{A9}$$

where

$$\begin{aligned}\eta=\frac{1}{E_D^3}\int_0^{2E_D-E_{10}}&[1-j_0(\pi(E_{10}+\epsilon_2)/\epsilon_0)]\\ &\times[1-j_0(\pi(E_{10}-\epsilon_2)/\epsilon_0)](E_{10}^2-\epsilon_2^2)\,d\epsilon_2\,,\end{aligned} \tag{A10}$$

and where we have made the assumption that $E_D<E_{10}$. For small molar volumes where $E_D>E_{10}$, the upper bound on the integral in Eq. (A10) is $E_D$. This integral may be performed analytically if we write the Bessel function as $(\sin x)/x$. However, first it is convenient to change to dimensionless variables

$$b=\frac{\pi}{\sqrt{2}}\left(\frac{3}{\pi}\right)^{1/3}=2.1876\,, \tag{A11a}$$

$$a=bE_{10}/E_D\,, \tag{A11b}$$

$$y=2b-a\,. \tag{A11c}$$

Then $\eta$ is given by

$$\eta=b^{-3}\int_0^y[1-j_0(a+x)][1-j_0(a-x)](a^2-x^2)dx\,. \tag{A12}$$

Using Eq. (A5) we have

$$\begin{aligned}\eta=b^{-3}\int_0^y&[(a^2-x^2)-(a-x)\sin(a+x)\\ &-(a+x)\sin(a-x)+\sin(a+x)\sin(a-x)]\,dx\,,\end{aligned} \tag{A13}$$

which is a sum of elementary integrals. The solution is

$$\begin{aligned}\eta=b^{-3}\{&(a^2y-y^3/3)+2a\cos 2b\\ &+2\cos a\,(\sin y-2b\cos y)\\ &+\tfrac{1}{2}(\sin y\cos y-y\cos 2a)\}\,.\end{aligned} \tag{A14}$$

## APPENDIX B: VALUES OF SEVERAL COEFFICIENTS

$$C(110;0,0)=-\frac{1}{\sqrt{3}}\,,$$

$$C(0,K,K;0,M)=C(K,0,K;M,0)=1\,,$$

$$C(422;0,0)=\sqrt{\tfrac{2}{7}}\,,$$

$$C(121;M,0)=\begin{cases}1/\sqrt{10}\,, & M=1\\ -2/\sqrt{10}\,, & M=0\\ 1/\sqrt{10}\,, & M=-1\,,\end{cases}$$

$$C(112;0,0)=\sqrt{\tfrac{2}{3}}\,,$$

$$W(2141;3,2)=\frac{1}{\sqrt{35}}\,,$$

$$W(2251;4,3)=\frac{1}{\sqrt{63}}\,,$$

$$W(3131;2,0)=\frac{1}{\sqrt{21}}\,,$$

$$W(3131;2,2)=\tfrac{1}{5}\sqrt{\tfrac{2}{7}}\,,$$

$$W(1212;1,0)=\frac{1}{\sqrt{15}}\,,$$

$$W(1212;12)=\tfrac{1}{10}\sqrt{\tfrac{7}{3}}\,,$$

$$X(532;532;0,0,0)=\frac{1}{\sqrt{385}}\,,$$

$$X(532;532;0,2,2)=\frac{1}{7\sqrt{330}}$$

$$X(532;532;2,2,2)=\tfrac{1}{7}\sqrt{\tfrac{13}{2310}}\,.$$

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[2] Here we compromise between the value $\Theta_D = 122$ K from Ref. 3 and $\Theta_D = 118$ K from Ref. 4. Both these values are for pure para-$H_2$. We might expect $\Theta_D$ to be a few percent higher for ortho-$H_2$ in the ordered phase since the lattice contracts slightly because of the quadrupole forces. In fact some evidence for this increase is seen in the neutron data of Ref. 17.

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