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Theory of ortho-para conversion in solid hydrogen at high densities

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An expression is derived for the ortho-para conversion rate, as a function of density ρ, of solid ortho-H_2 in its rotationally disordered state. For ρ greater than about 1.1 times the zero-pressure density ρ_0, conversion is shown to result from a one-phonon process. This rate is proportional to $(\rho/\rho_0)^{10/3-2\gamma}$, where γ is the Grüneisen constant for solid H_2, times a phonon spectral function which depends on the density as a parameter. Using the data of Pedroni *et al.* for the density dependence of the conversion rate for $1.0 \leq \rho/\rho_0 \leq 1.7$, we extract the phonon spectral function and compare it to a theoretical spectrum calculated in a simple harmonic approximation.

I. INTRODUCTION

In a recently published work[1] we derived an expression for the zero-pressure ortho-para conversion rate in a powder of solid ortho-hydrogen in its orientationally ordered phase. The method used in that calculation closely paralleled the approach of Motizuki and Nagamiya[2] who first computted the conversion rate for the disordered phase. We also pointed out that the conversion mechanism which is effective at zero pressure (conversion with emission of two phonons) becomes very inefficient at high pressures, i.e., at pressures corresponding to molar volumes of less than 20 cm^3/mole. This was at odds with the measurements of Ahlers[3] who showed the conversion rate to be a sharply increasing function of density, and we suggested that this increasing conversion rate must be attributed to a one-phonon process which becomes energetically possible at high densities because of the increased stiffness of the lattice.

Pedroni *et al.*[4] have performed extensive measurements of the conversion rate as a function of density using NMR techniques and a high-pressure cell which allows them to achieve densities ρ/ρ_0 as high as 1.7 where ρ_0 is the zero-pressure density. The results of their measurements are represented in Fig. 1 by the circles with error bars. More recently Buzerak and Meyer[5] have measured the conversion rate for $1.0 < \rho/\rho_0 < 1.2$ by determining the ortho concentration of a gas before and after holding it at constant pressure as a solid for a measured time. These results are shown by the triangles in Fig. 1. Also shown in the figure is the data of Ahlers.[3] The dotted curve in the lower left-hand corner of the figure is the two-phonon conversion rate which was computed in Ref. 1 and which clearly does not correspond to the observed rates. The most surprising features of the data of Pedroni *et al.*[4] are the two peaks in the conversion rate at $\rho/\rho_0 \approx 1.3$ and 1.5, followed by a decreasing rate for $\rho/\rho_0 > 1.5$. We infer that the conversion rate is a complicated function of the density, and that its behavior cannot be predicted simply from the volume dependence of the dipole interactions responsible for the transitions as was suggested by Ahlers.[3]

In this paper we derive an expression for the one-phonon conversion rate in terms of a one-phonon spectral function which is similar to the scattering function observed in incoherent inelastic neutron scattering. We then use this expression to extract experimental values for the spectral function from the data of Pedroni *et al.*, and compare the result to a simple model calculation based on the harmonic approximation. This comparison shows that the effect of anharmonicity is to broaden the high-energy features of the phonon spectrum into a high-energy tail which extends far above the Debye energy E_D ($E_D \approx 120$ K in solid H_2).

II. THEORY

The primary mechanism for conversion is the interaction $\mathcal{H}_{ss}$ between nuclear magnetic dipole moments of neighboring molecules. Another mechanism is the interaction of the nuclear spin of one molecule with the rotational magnetic moments of its neighbors. Motizuki and Nagamiya[2] have shown that for the disordered solid this mechanism may be included by multiplying the rate due to $\mathcal{H}_{ss}$ by a factor $\alpha = 1.025$.

For a single molecule interacting with its twelve neighbors, $\mathcal{H}_{ss}$ may be conveniently written

$$\mathcal{H}_{ss} = \left(\frac{24\pi}{5}\right)^{1/2} \sum_{p,s,\delta} \sum_{m,n} \frac{4\mu_p^2}{|\vec{r}_\delta + \vec{r}_s - \vec{r}_p|^3} \times C(112;\ m,n) i_p^m i_{\delta,s}^n Y_2^{m+n}(\Omega_{p\delta s})^* , \qquad (2.1)$$

where $C(112; m,n)$ is a Clebsch-Gordan coefficient and $Y_2^{m+n}(\Omega)$ is a spherical harmonic, both in the convention of Rose.[6] In Eq. (2.1) the protons of the central molecule are labeled by $p = 1, 2$; $\delta = 1, \ldots 12$ labels its twelve nearest neighbors and $s = 1, 2$ labels the two protons of molecule δ; the vectors $\vec{r}_p$ and $\vec{r}_s$ are the positions of the protons with re-

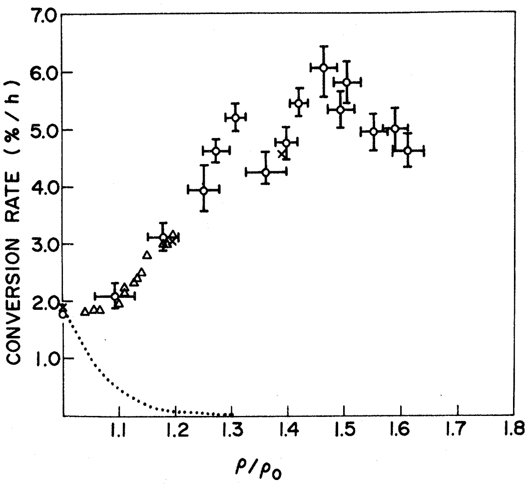

FIG. 1. Density dependence of the ortho-para conversion rate in solid ortho-H_2. The circles with error bars are from Ref. 4; the triangles are from Ref. 5; and the X's are from Ref. 3. The dotted curve is the theoretical conversion rate for the two-phonon process as computed in Ref. 1.

spect to the centers of mass of the molecules, and $\vec{r}_\delta$ connects the center of mass of the central molecule to that of molecule δ. The angular coordinates of the vector $\vec{r}_\delta + \vec{r}_s - \vec{r}_p$ are denoted $\Omega_{p\delta s}$. i_p^m is the mth spherical component of the spin of proton p, and $i_{\delta,s}^n$ refers to nuclear spin s of molecule δ. The relationship between the various vectors and nuclear spins is illustrated in Fig. 2.

If we perform a Taylor-series expansion of $\mathcal{H}_{ss}$ in terms of the internuclear separation of the central molecule and of small displacements of the lattice vectors, then the term responsible for the one-phonon conversion process is

$$\mathcal{H}_{ss}^{(1)} = \sum_{\delta,p} (\vec{U}_\delta \cdot \vec{\nabla})(\vec{r}_p \cdot \vec{\nabla})\mathcal{H}_{ss} , \qquad (2.2)$$

where $\vec{U}_\delta$ represents a small displacement of the center of mass of molecule δ with respect to the center of mass of the central molecule which we take as our origin. Also since the internuclear separation is about $\frac{1}{5}$ of the distance between molecules, it is appropriate in this approximation to take $\vec{r}_s \approx 0$. Thus the interaction $\mathcal{H}_{ss}^{(1)}$ is a function of the total nuclear spin of molecule δ and does not depend upon the direction of its internuclear axis.

Eq. (2.2) may be evaluated in terms of Clebsch-Gordon coefficients and fourth-rank spherical harmonics. If we write the vectors $\vec{r}_p$ in the terms of spherical harmonics as

$$r_p^\nu = \left(\frac{4\pi}{3}\right)^{1/2} (\tfrac{1}{2}d) Y_1^\nu(\Omega_p) , \qquad (2.3)$$

where d is the internuclear distance and we note that

$$Y_1^\nu(\Omega_1) = - Y_1^\nu(\Omega_2) , \qquad (2.4)$$

then we find that

$$\mathcal{H}_{ss}^{(1)} = A\gamma_{ss}(d/R_0) \sum_{\substack{m,n\\ \mu,\nu}} \sum_{\delta} C(112;\ m,n)$$

$$\times C(213;\ m+n,\ \mu) C(314;\ m+n+\mu,\ \nu)(U_\delta^\mu/R_0)$$

$$\times Y_1^\nu(\Omega)(i_1^m - i_2^m) I_\delta^n Y_4^{m+n+\mu+\nu}(\Omega_\delta)^* , \qquad (2.5)$$

where

$$A = 560\pi \left(\frac{2}{105}\right)^{1/2} , \qquad (2.6a)$$

$$\gamma_{ss} = \mu_p^2 / R_0^3 , \qquad (2.6b)$$

$$\vec{I}_\delta = \vec{i}_{\delta,1} + \vec{i}_{\delta,2} , \qquad (2.6c)$$

and R_0 is the equilibrium distance between nearest-neighbor molecules. The difference of nuclear spins in Eq. (2.5) results from using Eq. (2.4) to perform the sum over p in Eq. (2.2), and we have written Ω_1 simply as Ω, which measures the orientation of the internuclear axis of the central molecule.

The ortho-para conversion rate is given by

$$r = \frac{2\pi\alpha}{\hbar} \sum_{i,f} P_i \,|\, \langle f | \mathcal{H}_{ss}^{(1)} | i \rangle \,|^2 \delta(E_i - E_f) , \qquad (2.7)$$

where α is as described above Eq. (2.1). The initial state $|i\rangle$ is one in which the central molecule has total nuclear spin $I = 1$ and we sum over $m_I = 0$, ± 1. Its rotational state is ($J = 1$, $m_J = 0$, ± 1), since we are assuming that the solid is in its rotationally disordered phase. The neighbors are assumed to have total nuclear spin one with the z component of their nuclear spin given by $m_\delta = 0$, ± 1. The final state of the central molecule is ($I = J = 0$). The total nuclear spin of the neighbors is unchanged with the z component being written as m_δ'. Since the tem-

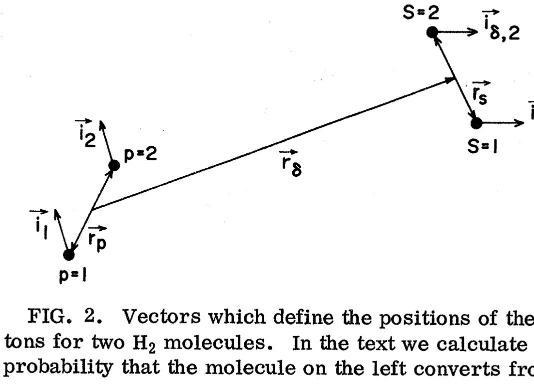

FIG. 2. Vectors which define the positions of the protons for two H_2 molecules. In the text we calculate the probability that the molecule on the left converts from ortho to para due to its interactions with its twelve nearest neighbors which are located at $\vec{r}_\delta$, $\delta = 1, \ldots 12$.

perature is much less than the Debye temperature, we can take the initial state of the lattice to be a zero-phonon state and the final state to be a one-phonon state. P_i is the probability that the system is in a particular initial state $|i\rangle$. We assume that both the nuclear spin and rotational systems are completely disordered and take $P_i = \frac{1}{27}$. Then the matrix elements necessary to evaluate Eq. (2.7) are

$$\langle I'=0,\, m_I'=0 | i_1^m - i_2^m | I=1, m_I\rangle = \delta_{m,-m_I}\,, \tag{2.8a}$$

$$\langle m_\delta' | I_\delta^n | m_\delta\rangle = \sqrt{2}\, C(111; m_\delta, m_\delta' - m_\delta)\,\delta_{n, m_\delta' - m_\delta}\,, \tag{2.8b}$$

$$\langle J'=0, m_J'=0 | Y_1^\nu(\Omega) | J=1, m_J\rangle = \frac{1}{(4\pi)^{1/2}}(-1)^{m_J}\delta_{\nu,-m_J}\,. \tag{2.8c}$$

The matrix elements of the displacement operator $\vec{U}_\delta$ may be combined with the δ function in Eq. (2.7) to form a one-phonon spectral function. If we ignore all of the energy differences except for the rotational energy E_{10} which is lost in ortho-para conversion and the energy $\epsilon_{\vec{k},\tau}$ which is carried away by the phonon of wave vector $\vec{k}$ and polarization τ, then r depends on

$$\langle U_\delta^\mu U_\delta^{\nu *}\rangle_{E_{10}} = \sum_{\vec{k},\tau} \langle 0 | U_\delta^\mu | \vec{k}\tau\rangle\langle\vec{k}\tau | U_\delta^{\nu}{}^* | 0\rangle\,\delta(E_{10} - \epsilon_{\vec{k}\tau})\,. \tag{2.9}$$

Equations (2.5)–(2.9) allow us to write r as

$$r = \frac{\alpha\gamma_{ss}^2}{27\hbar} A (d/R_0)^2 \sum_{\substack{k, m_J\\ \mu,\nu}} C(213; k, \mu) \times C(213; k, \nu) C(314; k+\mu, -m_J) C(314; k+\nu, -m_J) \times \sum_\delta \langle U_\delta^\mu U_\delta^{\nu *}\rangle_{E_{10}} R_0^{-2} Y_4^{k+\mu-m_J}(\Omega_\delta)^* Y_4^{k+\nu-m_J}(\Omega_\delta)\,. \tag{2.10}$$

We may write the product of two Y_4's as a sum of spherical harmonics,

$$Y_4^{k+\mu-m_J}(\Omega_\delta)^* Y_4^{k+\nu-m_J}(\Omega_\delta) = 9(-1)^{k+\mu-m_J}\sum_l [4\pi(2l+1)]^{-1/2} C(44l; 00) \times C(44l; m_J - \mu - k, k+\nu - m_J) Y_l^{\nu-\mu}(\Omega_\delta)\,. \tag{2.11}$$

In Eq. (2.11) l may take on even values as high as 8. However when Eq. (2.11) is inserted into Eq. (2.10) and the sums over k and m_J are performed we obtain

$$r = -21\alpha(\gamma_{ss}^2/h) A^2 (d/R_0)^2 \sum_l [4\pi(2l+1)]^{-1/2} \times C(44l; 00) W(31l443) W(12l331) \times \sum_{\mu\nu}(-1)^\mu C(11l; \mu, -\nu) \times \sum_\delta Y_l^{\nu-\mu}(\Omega_\delta)\langle U_\delta^\mu U_\delta^{\nu *}\rangle_{E_{10}} R_0^{-2}\,, \tag{2.12}$$

where $W(abcdef)$ is a Racah coefficient.[6] Because of the Clebsch-Gordan coefficient $C(11l; \mu, -\nu)$ and the restriction to even values, l can only be equal to 0 or 2. Thus we can write

$$r = r_0 + r_2\,, \tag{2.13}$$

and if we insert the values of the Racah coefficients and of A we find

$$r_0 = (17\,920\pi\alpha/9)(\gamma_{ss}^2/\hbar)(d/R_0)^2 \times \sum_\mu \langle U_\delta^\mu U_\delta^{\nu *}\rangle_{E_{10}} R_0^{-2}\,, \tag{2.14a}$$

$$r_2 = (2560\pi^2\alpha/9)(5/24\pi)^{1/2}(\gamma_{ss}^2/\hbar) \times (d/R_0)^2 \sum_{N,\delta} Y_2^N(\Omega_\delta)^* T_2^N(\delta; E_{10})\,, \tag{2.14b}$$

where

$$T_2^N(\delta; E_{10}) \equiv \sum_M (-1)^{M-N} C(112; M, N-M) \times \langle U_\delta^M U_\delta^{M-N *}\rangle_{E_{10}} R_0^{-2}\,. \tag{2.15}$$

The density dependence of the total rate r may be thought of as arising from two sources. First there is a $(\rho/\rho_0)^{10/3}$ dependence which comes from the square of the second derivative of the dipole-dipole interaction. Second there is a very complicated density dependence implicit in the spectral function $\langle U_\delta^\mu U_\delta^{\nu *}\rangle_{E_{10}}$. There is no simple way to evaluate this spectral function for the densities which are relevant to this problem. If the conversion energy E_{10} were much smaller than the Debye energy, then we could use the Debye approximation, and the solution would be straightforward. However, in order to interpret the data of Ref. 4 we focus on the density range $1.0 \leq \rho/\rho_0 \leq 1.7$ where the density dependence of E_D is such that $E_D/2 \lesssim E_{10} \lesssim E_D$, and thus the Debye approximation is inapplicable to a calculation of the rate due to one-phonon processes.

The simplest approximation which might be expected to give a reasonable description of the phonons for our problem is one which the lattice vibrational modes result from central forces between nearest-neighboring molecules. The advantage of this approximation is that, like the Debye model, it assumes only one parameter, the nearest-neighbor force constant which sets the energy scale. The disadvantage of this approach is that it requires a computer calculation, although fortunately the calculation need not be very sophisticated.

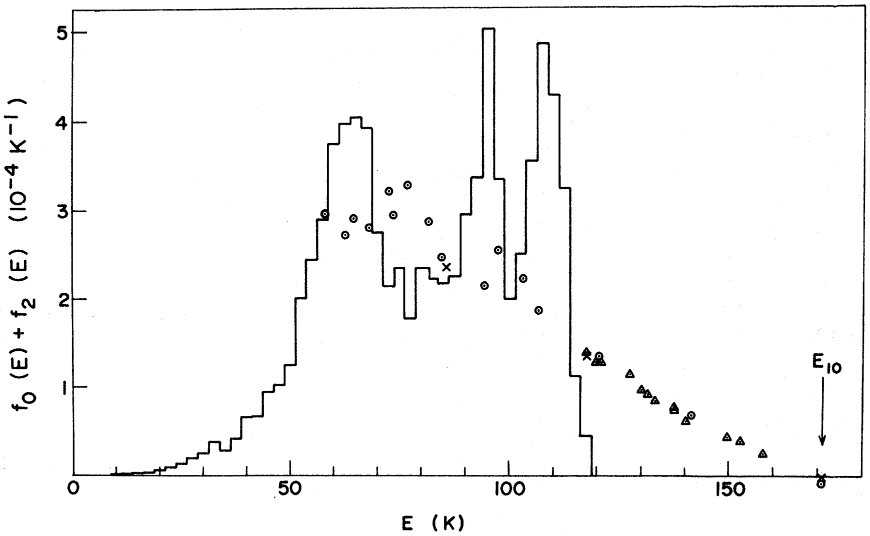

FIG. 3. One-phonon spectral function $f_0(E) + f_2(E)$ for zero pressure. The functions f_0 and f_2 are defined in Eq. (2.16). The histogram is the result of a harmonic single force constant calculation for 1306 values of $\vec{k}$ in an irreducible section of the Brillouin zone, with the force constant chosen to fit the ($\vec{K} = 0$) optical-phonon energy reported in Ref. 6. The X's, circles, and triangles are based on the data of Refs. 3, 4, and 5, respectively, as discussed in the text.

To calculate the phonon spectral functions we diagonalized the dynamical matrix for the single force constant model at 1306 points in an irreducible section of the hexagonal-close-packed Brillouin zone. The resulting eigenvalues and eigenvectors were used to construct histograms which approximate the sums of δ functions in Eq. (2.9). In Fig. 3 the histogram represents the sum of the two functions

$$f_0(E) = \left(\frac{1}{36}\right) \sum_{\mu,\delta} \langle U_\delta^\mu U_\delta^{\mu *} \rangle_E R_0^{-2} , \qquad (2.16a)$$

$$f_2(E) = \frac{5}{504} \left(\frac{24\pi}{5}\right)^{1/2} \sum_{N,\delta} Y_2^N(\Omega_\delta)^* T_2^N(\delta ; E) . \qquad (2.16b)$$

We should note that $|f_2|$ is about a tenth of f_0, and that the main effect of f_2 is to shift some spectral weight from the first peak near 60 K up into the two high-energy peaks. The energy scale for zero pressure has been set by fitting the highest-energy optical phonon to Nielsen's[7] coherent-neutron-scattering data. In terms of these spectral functions the zero-pressure one-phonon conversion rate is given by

$$r = (17\,920\pi\alpha/3)(\gamma_{ss}^2/\hbar)(d/R_0)^2 [f_0(E_{10}) + f_2(E_{10})] . \qquad (2.17)$$

This rate is zero in the harmonic approximation since the spectral functions are zero at $E_{10} = 171$ K. For nonzero pressure the force constant which scales the phonon spectrum should increase as some power of the density. On the other hand the rotational energy E_{10}, released in ortho-para conversion is relatively insensitive to the pressure. Thus as the pressure increases, the width of the phonon spectrum increases like a power of ρ while its amplitude contracts (for two reasons, because the total number of modes is conserved and because the amplitude of vibration for the stiffer system is a decreasing fraction of R_0). The ortho-para conversion energy E_{10} acts as a fixed point on the energy axis (the arrow in Fig. 3), at which the broadened spectral function is evaluated to compute the conversion rate.

More formally we parametrize the problem for non-zero pressure as follows: At some density ρ the phonons responsible for conversion are those whose zero pressure energy is E. Then we may use a Grüneisen-type formula to relate ρ and E

$$\left(\frac{E_{10}}{E}\right) = \left(\frac{\rho}{\rho_0}\right)^\gamma , \qquad (2.18)$$

where we take $\gamma = 2.1$ as deduced by Jarvis *et al.*[8] from $(\partial P/\partial T)_V$ measurements and in agreement with the specific-heat data of Ahlers,[9] and ρ_0 is the zero pressure density. The phonon spectral functions scales as the inverse square of the phonon energy $\hbar\omega_p$ [since $U_\delta \sim (\hbar\omega_p)^{-1/2}$ and $\delta(\hbar\omega_p - E) \sim (\hbar\omega_p)^{-1}$]. Thus the spectral function at high density ρ and energy E_{10} is equal to the zero-pressure function evaluated at energy E, as defined by Eq. (2.18), multiplied by $(E/E_{10})^2 (\rho/\rho_0)^{2/3}$, where the ρ dependence results from the R_0^{-2} in the defining Eq. (2.16). Additional density dependence results from the factors γ_{ss}^2 and $(d/R_0)^2$. Thus we may write the density dependent conversion rate as

$$r(\rho/\rho_0) = (17\,920\pi\alpha/3)\{(\gamma_{ss}^2/\hbar)(d/R_0)^2\}_{\rho=\rho_0}$$

$$\times \eta [f_0(E) + f_2(E)] , \qquad (2.19)$$

where $\eta = (\rho/\rho_0)^{10/3-2r}$ and the quantity in curly brackets in Eq. (2.19) is evaluated at zero pressure. Then taking $\gamma_{ss} = 2.73 \times 10^{-8}$ K, $R_0 = 3.75$ Å and $d = 0.74$ Å, we have

$$r(\rho/\rho_0) = 26\,400\eta[f_0(E)+f_2(E)]\%/\text{h} \qquad (2.20)$$

if f_0 and f_2 have units of K^{-1}. Equations (2.18)–(2.20) may be used to infer values of the spectral function $f_0(E)+f_2(E)$ from the data of Refs. 3–5 if the two-phonon contribution (the dotted line in Fig. 1) is subtracted from the experimental rates. The result is shown by the X's, circles and triangles (from Refs. 3, 4, and 5, respectively) in Fig. 3. Comparing these points to the histogram which was calculated in the harmonic approximation, we see that our theory leads to quantitatively reasonable values for the conversion rate and that the effect of anharmonicity is to "wash out" the high-energy features of the phonon spectrum into a high-energy tail which extends at least up to E_{10}. Of course the exact value which we assign to the spectral function at E_{10} depends on the value which we calculate for the two-phonon conversion rate at zero pressure. Since this value is in fact slightly higher than that measured, a reasonable conclusion is that two-phonon processes are responsible for most of the conversion and that the one-phonon spectral function is small above E_{10}. The fact that the optical-phonon peaks are completely smeared out in the one-phonon spectrum is in agreement with the neutron scattering work of Schott,[10] Stein *et al.*,[11] and of Nielsen[7] and is consistent with previous experimental and theoretical work on solid ^{4}He.[12,13]

An interesting feature of the comparison in Fig. 3 is the behavior which it implies for the conversion rate at still higher densities. From Eq. (2.18) we find that $\rho/\rho_0 > 1.7$ corresponds to the region $E < 60$ K of the zero-pressure phonon spectrum. Here the phonons are of the long-wavelength acoustic type and are relatively lightly damped. Both neutron-scattering results[10,11] and sophisticated numerical calculations[14] which take into account the quantum nature of the solid, are in qualitative agreement with our simple harmonic theory which predicts that the spectrum decreases sharply for $E < 60$ K. Since the density factor η in Eq. (2.20) also decreases with increasing density one expects the conversion rate to decrease sharply for $\rho/\rho_0 > 1.7$.

Pedroni *et al.*[4] have proposed that the conversion rate as a function of density be measured by means of Raman scattering by comparing the intensities of the $J=1\rightarrow 3$ and $J=0\rightarrow 2$ rotational transitions as a function of time. It would also be interesting if simultaneous measurements were made of the frequency of the optical phonon, thus providing a direct comparison of the phonon frequencies and the ortho-para conversion rate.

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