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are related by  $P_x(2\omega) = \epsilon_0 d_{14}^0 E_y(\omega) E_z(\omega)$ , where  $\epsilon_0$  is the vacuum permittivity. This relation defines  $d_{14}^0$ . Conversion relations are  $r(\text{cgs}) = 3 \times 10^4 r(\text{mks})$  and  $d(\text{cgs}) = (3 \times 10^4/4) d(\text{mks})$ .

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## Raman-Active Optical Phonons in the Hexagonal Phases of Solid $\text{H}_2$ , $\text{D}_2$ , and HD

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Raman scattering from the transverse optic phonon in the hcp phase of single crystals of the five modifications of solid hydrogen has been observed. Frequencies have been measured to a precision of  $0.05\text{ cm}^{-1}$  and are compared with results of recent quantum-crystal theories of lattice dynamics. Reasonable agreement with theory is found, although frequency differences between ortho and para modifications of the same isotope are much larger than predicted. Absolute measurements of the phonon scattering efficiencies are made by comparing to the intensities of the  $J=1 \rightarrow 3$  or  $0 \rightarrow 2$  rotational Raman lines. The results are in good agreement with Werthamer's recent theory for light scattering in van der Waals-type crystals. A broad continuous feature observed at shifts of  $40\text{--}200\text{ cm}^{-1}$  is tentatively identified as a two-phonon band. Predictions are made for the phonon intensities expected in solid hcp helium.

### I. INTRODUCTION

In the past several years there have been increasing theoretical advances in the understanding of the dynamical properties of the so-called quantum solids (notably solid He,  $\text{H}_2$ , and their isotopes). In these solids the kinetic energy of a particle as-

sociated with a lattice site is comparable to its potential energy, even at 0 K, and as a consequence the zero-point motion is substantial. This large zero-point motion and the attendant anharmonicity render the standard methods of lattice dynamics invalid and new methods have been developed.<sup>1</sup> The

basic approach of these theories is to average the bare intermolecular potential over the zero-point motion and so obtain an effective potential that allows the standard methods of dynamics to be applied. Since the bonding in the quantum solids is of the van der Waals-type and the gas-phase interatomic potentials are fairly well known, comprehensive checks on the theories can be made.

The solid hydrogens ( $H_2$ , HD, and  $D_2$ ) represent a particularly interesting system of quantum crystals to study because of the large range of particle mass with only minor variations in intermolecular potentials, and because the effects of the anisotropic intermolecular interactions can be studied by varying the ortho-para concentrations. Furthermore, preparation of the solid samples is relatively simple compared to that for solid helium which exists only at elevated pressures. Techniques of crystal growth have been developed in which single crystals of all of the isotopic modifications of solid hydrogen can be grown.<sup>2,3</sup>

The three classic methods for obtaining the phonon-dispersion relations in solids are inelastic neutron scattering, infrared absorption, and Raman scattering. The first technique provides the greatest amount of information, yielding the dispersion relations throughout the Brillouin zone, whereas the information from the latter two techniques is generally confined to the zone center. On the other hand, the neutron technique is very time consuming and cannot be used to study nonequilibrium ortho-para mixtures if the measurement time is large compared to the characteristic ortho-para conversion time. Furthermore, good energy resolution is difficult to obtain for the quantum solids since neutron cross sections are quite small resulting in poor counting statistics and high relative background.

The technique of infrared absorption has been used previously to study the optical phonons in  $H_2$  and  $D_2$  in the ordered state.<sup>4</sup> In the hcp phase the phonons are no longer infrared active, but one of the optical branches is Raman active and can be studied by light scattering. An unusual feature of the hydrogens is that the phonon intensities can be measured absolutely by comparing to the intensities of the  $J=0 \rightarrow 2$  or  $1 \rightarrow 3$  rotational Raman lines.<sup>2,5</sup> These measurements can then be used to check the theory and make predictions of the intensities for solid hcp helium.

In this paper, we present a detailed and more precise investigation of the earlier reported<sup>2</sup> optical phonons observed by Raman scattering in the solid hydrogens in the hcp phase. We proceed with a brief description of the experiment and results, and finally a comparison of the observed scattering cross sections with the recent theory of Werthamer.<sup>6</sup>

## II. PROPERTIES OF SOLID HYDROGEN

Molecular hydrogen, hydrogen deuteride, and deuterium crystallize in the bulk to form hcp lattices with freezing points in the range 14–20 K. A feature in the hydrogens, not present in the quantum-solid helium, is the presence of the orientational degrees of freedom. A peculiarity of the solid hydrogens, distinguishing them from all other molecular solids, is that the rotational quantum number  $J$  of the free molecule remains a good quantum number in the solid state since the anisotropic interactions, which mix the  $J$  states, are small ( $\sim 10$ – $20$  K) compared to a separation of several hundred degrees between the lowest rotational levels. Transitions between odd and even states are strongly forbidden,<sup>7</sup> and thus nonequilibrium mixtures of the odd and even  $J$  species are metastable, converting towards equilibrium at the rate  $\sim 1.9\%/h$  for solid  $H_2$  and  $\sim 0.11\%/h$  for solid  $D_2$ . At low temperatures only the  $J=0$  (para-hydrogen or ortho-deuterium) and the  $J=1$  (ortho-hydrogen or para-deuterium) levels are populated. The HD molecule does not possess a center of inversion symmetry so that the odd to even  $J$  transitions are allowed, and at low temperatures essentially all of the molecules are in the  $J=0$  state.

The crystal structure of pure  $p$ - $H_2$  or  $o$ - $D_2$  remains hcp to 0 K. For high enough concentrations of the  $J=1$  species,<sup>8</sup> the anisotropic intermolecular interactions, due mainly to the molecular electric-quadrupole moment, are responsible for a transition into an orientationally ordered state.<sup>9</sup> Accompanying the ordering is a crystal structure change, and in the low-temperature state (space group  $P\alpha 3$ ) the molecular centers form an fcc Bravais lattice. For decreasing temperature the transition occurs at 2.8 K for pure  $o$ - $H_2$  and 3.8 K for pure  $p$ - $D_2$ . The critical temperature decreases linearly with increasing concentration of  $J=0$  species, reaching 0 K for a concentration of about 60%  $J=1$  species.<sup>8</sup>

## III. DYNAMICS

The dynamical properties, i. e., the dispersion relations and polarization properties of the phonon modes in an hcp crystal, have been treated for both classical<sup>10</sup> and quantum crystals.<sup>11</sup> The hcp lattice has two molecules per unit cell and thus six phonon modes in all, three acoustic and three optical. Selection rules restrict the Raman observations to the optical phonons in the vicinity of the Brillouin-zone center for the first-order processes.<sup>6</sup> The LO mode, polarized along the  $c$  axis, is Raman inactive, while the two degenerate TO modes are polarized within the hexagonal planes and are Raman active. The scattering intensities of these modes are proportional to  $\sin^2\theta_i \sin^2\theta_s$ , where  $\theta_i$  and  $\theta_s$  are the angles formed between the incident and

scattered electric fields and the  $c$  axis of the crystal.<sup>6</sup> In addition, two-phonon Raman scattering is allowed in the hcp structure.<sup>12</sup>

In the quantum crystals, because of the large zero-point motion and hard repulsive atomic or molecular core potentials, short-range correlation plays an important role. To take account of these correlations, Nosanow<sup>13</sup> introduced the Jastrow factor

$$f(R) = e^{-cv(R)/2}, \quad (1)$$

where  $v(R)$  is the gas-phase Lennard-Jones (LJ) intermolecular potential and  $c$  is a constant. Using a trial wave function of the form

$$\psi(r_1, \dots, r_N) = \sum_{i=1}^N \phi(\vec{r}_i - \vec{R}_i) \prod_{i < j} f(\vec{r}_i - \vec{r}_j), \quad (2)$$

where  $\phi(\vec{r}_i - \vec{R}_i)$  is a single-particle wave function localized on lattice site  $\vec{R}_i$ , variational techniques were used with one result being that the particles behaved as if they interacted via the effective potential

$$W(R) = f^2(R) [v(R) - \frac{1}{2}(\hbar^2/M)\nabla^2 \ln f(R)]. \quad (3)$$

Phonon frequencies and polarizations have been calculated for hcp helium<sup>11</sup> with the result that one obtains the classical eigenvalue equation with the bare LJ potential replaced by a ground-state lattice average of the effective potential. These results have been compared with experiment<sup>14</sup> and the resultant picture that emerges is that for low values of  $\vec{k}$ ,<sup>15</sup> the quantum crystals do not exhibit behavior qualitatively different from that of ordinary crystals which can be treated by the standard methods of lattice dynamics in the harmonic approximation,<sup>16</sup> even though in the classical harmonic approximation the quantum crystals are unstable. More recently Klein and Koehler (KK)<sup>17</sup> and Biem and Mertens (BM)<sup>18</sup> have calculated the phonon-dispersion relations for solid H<sub>2</sub> and D<sub>2</sub> using self-consistent phonon theory. Resulting phonon frequencies are in good agreement with experiment, and in particular, have been obtained experimentally throughout  $\vec{k}$  space in the neutron work of Nielsen and Møller<sup>19</sup> in solid ortho-deuterium.

#### IV. EXPERIMENTAL

##### A. Apparatus

The basic features of the Raman scattering cell have been described elsewhere,<sup>2</sup> the major improvements being the use of a first-surface dielectric reflector on the bottom of the cell and a more pointed cold finger for initiating crystal growth.<sup>3</sup> Samples of  $o$ -H<sub>2</sub> and  $p$ -D<sub>2</sub> were prepared from normal gas using an adsorption column of the type described by Depatie and Mills.<sup>20</sup> The  $p$ -H<sub>2</sub> and  $o$ -D<sub>2</sub> were prepared by passing normal gas through an Fe(OH)<sub>3</sub> gel catalyst maintained at 20.4 K. Initial

ortho-para concentrations were measured in the gas with a thermal conductivity bridge<sup>21</sup>; in the solid, they were determined by the temperature of transition into the ordered state or by the intensity ratios of the  $J=1 \rightarrow 3$  and  $J=0 \rightarrow 2$  rotational Raman lines. The high-purity HD was obtained by double distillation at 20.4 K of chemically prepared HD.

The exciting source for the Raman spectrometer was the 5145-Å line of an argon-ion laser, the right-angle scattered light being observed with a Spex model No. 1400 double monochromator and a cooled I. T. T. FW-130 photomultiplier whose output was detected with a picoammeter. Frequency shifts could be determined to within 0.05 cm<sup>-1</sup> using a frequency calibrator based on the spectral comb generated by a Fabry-Perot etalon illuminated with white light.<sup>22</sup> This increase in accuracy over that obtainable with the dial calibration of the monochromator ( $\sim 1$  cm<sup>-1</sup>) was important in view of the fact that the spread in optical-phonon frequencies of the five species of hydrogen is less than 3 cm<sup>-1</sup>.

Single crystals were grown of all species by techniques described elsewhere.<sup>2,3</sup> Growth takes place in the birefringent hcp phase with the  $c$  axis generally oriented along the axis of the tube, i.e., in the direction of the main thermal gradient. Observation of the crystals between crossed polarizers clearly showed the presence of grain boundaries in non-single-crystal samples. Single crystals of  $p$ -H<sub>2</sub>,  $o$ -D<sub>2</sub>, and HD were easiest to prepare, while the  $o$ -H<sub>2</sub> and  $p$ -D<sub>2</sub> were considerably more difficult and depended delicately on the thermal gradients in the cold helium gas and on other parameters.

##### B. Results

The Raman spectra of all species of hydrogen showed a single sharp, but weak, line in the hcp phase, which can be identified as a zone-center optical phonon by its frequency, intensity, and polarization properties which were measured on what were apparently single crystals. In addition, the abrupt disappearance of the line in the  $J=1$  species when the temperature was lowered through the orientational transition temperature was further support for its identification. The intensity data for the  $J=1$  species used here was always taken before the sample was cycled below and above the transition temperature since repetitive cycling progressively destroys the hexagonal phase.<sup>8</sup> Typical spectra are shown in Fig. 1 for deuterium; similar results were obtained for hydrogen. HD spectra exhibited no other structure between the phonon and the laser line, as in H<sub>2</sub> and D<sub>2</sub>, since the  $J=1$  level is not metastably occupied. In Table I the measured frequencies are listed along with the theoretical results of KK<sup>17</sup> and BM.<sup>18</sup>

An interesting aspect of this study is the linewidth of the phonon lines. Unfortunately most of the data

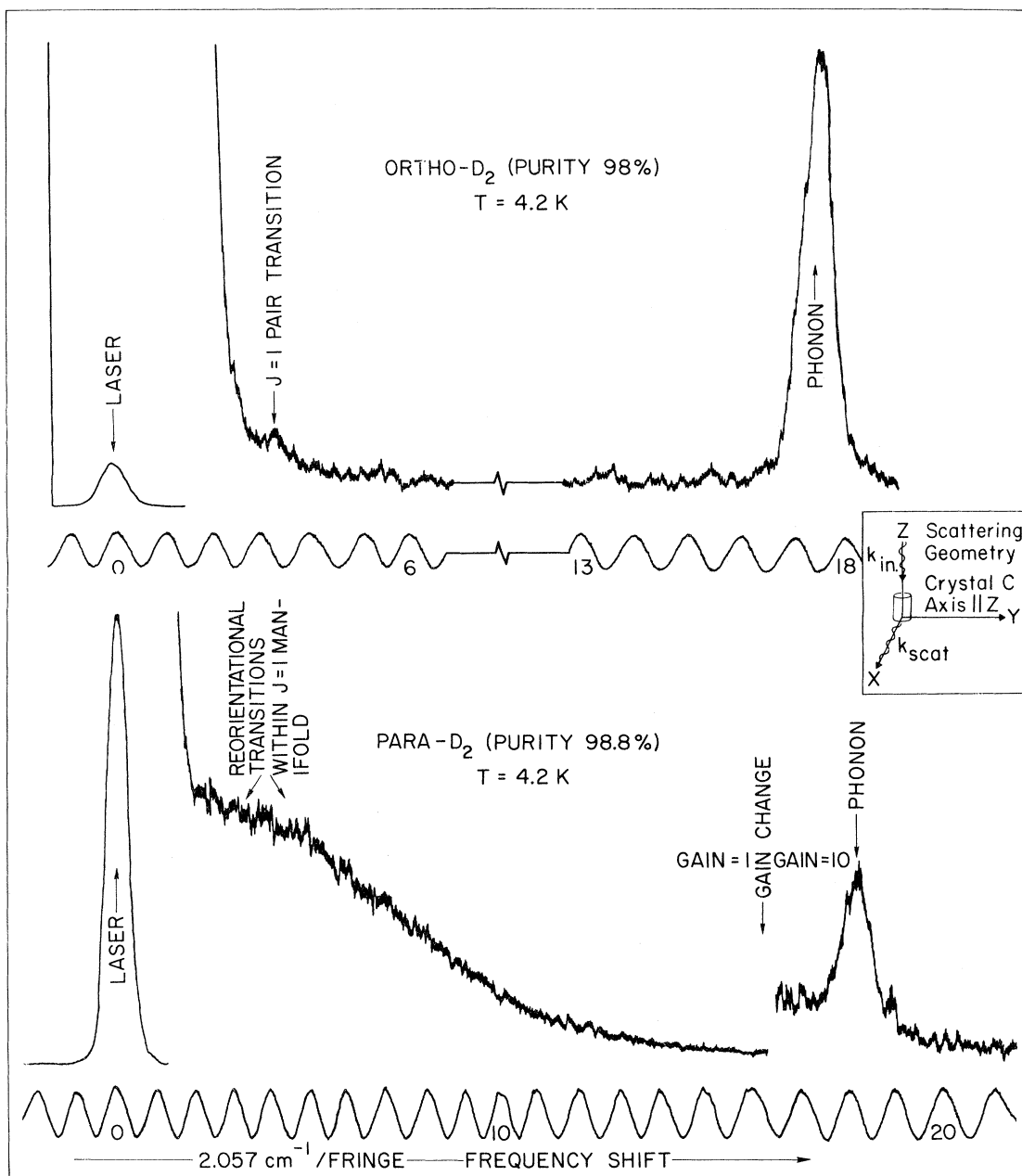


FIG. 1. Raman spectra in para- and ortho-deuterium at 4.2 K showing the phonon lines and other structure arising from transitions within the  $J=1$  molecular rotational states. The scattering geometry is shown in the inset. Polarization is  $XY+XZ$ , where the first letter denotes the polarization of the incident field and the second that of the scattered field. The frequency of any features can be measured by multiplying the number of fringes between the feature and the laser line by the calibration constant  $2.057 \text{ cm}^{-1}/\text{fringe}$ . A linear frequency axis is not given because of inherent nonlinearities in the spectrometer drive. The gains of the upper and lower traces are not related.

for the phonons were taken at lower resolution (and higher signal-to-noise) to optimize the accuracy of the line position measurements. Nevertheless, crude attempts to unfold the instrumental slit function from the observed line shape to obtain the true linewidths indicate full widths at half-maximum of  $1.3$  and  $1.1 \text{ cm}^{-1}$  for  $p\text{-D}_2$  and  $o\text{-H}_2$ , respectively,

and  $0.6$  and  $1.1 \text{ cm}^{-1}$  for  $o\text{-D}_2$  and  $p\text{-H}_2$ , respectively, with error limits of order  $0.5 \text{ cm}^{-1}$ . In the  $o\text{-H}_2$  there were indications that the line broadened after the sample was thermally cycled through the orientationally ordered phase and back (corresponding spectra were not obtained in  $\text{D}_2$ ). This is not surprising since cycling transforms the crystal into a

mixture of fcc and hcp regions.<sup>8</sup>

No changes of the frequency or intensity were noted in the hcp phase in the temperature range 1.1–4.2 K. In a *p*-D<sub>2</sub> sample at 14.2 K (triple point ≈ 18.8 K) the phonon line was observed to broaden and shift down a few cm<sup>-1</sup> in frequency to 35.48 ± 0.2 cm<sup>-1</sup>.

In addition to the single one-phonon line observed in all the samples, close examination of the higher-frequency regions (40–200 cm<sup>-1</sup>) of a spectrum of HD revealed a broad continuous feature (Fig. 2). Corresponding spectral regions were not studied in H<sub>2</sub> or D<sub>2</sub>. The feature is partially obscured by the low-frequency tail of the intense *J*=0 → 2 transition, centered at ~ 268 cm<sup>-1</sup>. The frequency distribution is consistent with that expected by analogy with solid helium<sup>12</sup> for two-phonon scattering, as is the integrated intensity (~ 5 times that of the one-phonon line). However, definitive assignment must await theoretical calculations of the lattice dynamics and scattering cross sections of HD.<sup>23</sup>

### C. Discussion

The theoretical predictions for the phonon frequencies at the Brillouin-zone center are in fair agreement with the experimentally observed frequencies, and are somewhat better for D<sub>2</sub> than H<sub>2</sub>, probably because the quantum effects are smaller due to the larger mass of the former. For the TO modes the calculations of KK<sup>17</sup> are from 3 to 10% high, while those of BM<sup>18</sup> are ~ 30% high. However, BM agree better with the LO mode, being ~ 25% high compared to KK which is ~ 35% high. Both calculations are based on self-consistent phonon theory with effective potentials of the form given in Eq. (3), and both use an LJ intermolecular potential *v*(*R*), but with slightly different parameters. The KK calculations follow the collective picture,

whereas BM use the single-particle random-phase approximation.<sup>1</sup> Unfortunately, the two approaches for the phonon calculations cannot be directly compared since KK used a single-parameter Jastrow function *f*(*R*) [see Eq. (1)], while BM employed a less restrictive two-parameter Jastrow function. Lattice sums well beyond first neighbors were employed in both calculations.

A comparison of the calculated shapes of the dispersion curves to those obtained from neutron measurements<sup>19</sup> show good agreement, except for a scale factor. Nielsen and Møller apparently have compared their results to KK's dispersion relations for the self-consistent frequencies ω<sub>*k*</sub>, rather than the poles of the displacement-displacement correlation function Ω<sub>*k*</sub>, which is used to identify the phonon frequencies in the collective picture. The agreement with ω<sub>*k*</sub> is better than that for Ω<sub>*k*</sub>, but this is presumably fortuitous.

One of the most dramatic aspects of the quantum crystals is the near absence of the isotopic-mass effect of classical lattice dynamics, which predicts the phonon frequencies to vary inversely as the ratio of the square root of the masses. This would predict a frequency increase of √2 = 1.414 in going from D<sub>2</sub> to H<sub>2</sub>, whereas for the TO modes the observed increase is only 1.03 for both the *J*=1 and the *J*=0 species, in fairly good agreement with theoretical values of ~ 1.06. Although the gas-phase intermolecular potentials are almost identical for H<sub>2</sub> and D<sub>2</sub>, the effective intermolecular potentials for the solid given by Eq. (3) (and the lattice parameters) differ significantly in a manner such that the effective-force constants are softened for the lighter mass.

A further observation, which does not agree with theory in magnitude, is the frequency differences between the *J*=1 and *J*=0 species: +1.76 cm<sup>-1</sup> for

TABLE I. Experimental observations and theoretical predictions for the phonon frequencies in the various species of hydrogen.

Species	Ground state <i>J</i>	Temperature (K)	Mode	Observed phonon frequencies (cm <sup>-1</sup> )		Theoretical phonon frequencies (cm <sup>-1</sup> )	
				Raman <sup>a</sup>	Neutron	KK	MB
<i>o</i> -H <sub>2</sub>	1	4.2	TO	38.55 ± 0.05	...	40.8	...
			LO	...	...	119.2	...
<i>p</i> -H <sub>2</sub>	0	4.2	TO	36.79 ± 0.05	...	40.5	48.4
		4.3	LO	...	87.9 (Ref. 37)	118.3	110.4
HD	0	4.2	TO	36.16 ± 0.05	...	...	...
			LO	...	...	...	...
<i>p</i> -D <sub>2</sub>	1	4.2	TO	37.27 ± 0.05	...	38.3	...
			LO	...	...	108.9	...
			TO	35.48 ± 0.2	...	...	...
<i>o</i> -D <sub>2</sub>	0	14.2	TO	35.83 ± 0.05	37.0 ± 0.8 (Ref. 19)	38.2	45.2
		4.2 <sup>b</sup>	LO	...	79.8 ± 2.4 (Ref. 19)	108.6	97.8

<sup>a</sup>This work.

<sup>b</sup>Neutron measurements made at 5 K.

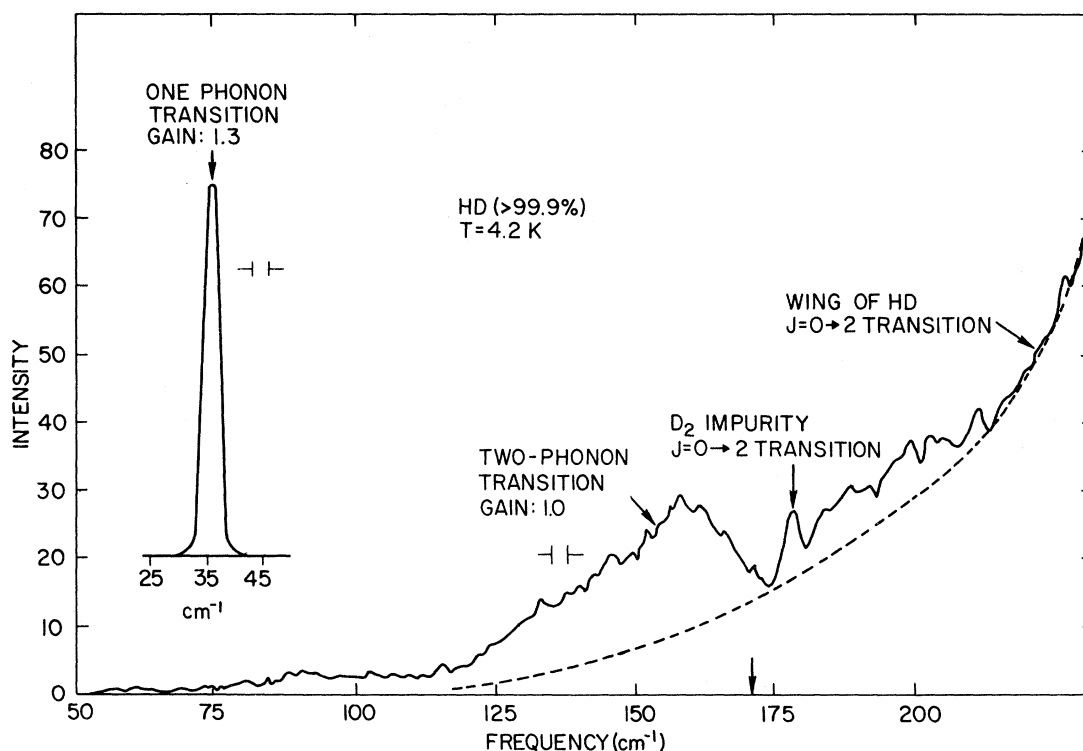


FIG. 2. Spectrum showing light scattering feature in the region where two-phonon scattering is expected. The two-phonon density of states for HD extends in frequency from zero to the estimated position indicated by the arrow on the frequency axis. The one-phonon line is shown in the inset for comparison. Interfering features are identified including that due to a trace of  $D_2$  impurity. The data shown is computer smoothed by taking a running average of five adjacent points separated by  $\sim 0.3 \text{ cm}^{-1}$ .

$H_2$  and  $+1.44 \text{ cm}^{-1}$  for  $D_2$ , compared to predictions by KK of  $+0.3 \text{ cm}^{-1}$  for  $H_2$  and  $+0.1 \text{ cm}^{-1}$  for  $D_2$ . The latter estimates are calculated from the small differences between the gas-phase intermolecular potentials of the ortho and para species. Due to the attractive electric-quadrupole-quadrupole (EQQ) anisotropic intermolecular interaction, in the orientationally ordered phase there is a coherent effect and the phonon frequencies should be shifted of order  $3 \text{ cm}^{-1}$ <sup>24</sup> from the value they would have if the interaction were zero. However, in the orientationally disordered phase, if the molecules are randomly oriented there should be no shift of the phonon frequencies because the mean energy shift due to the EQQ interaction is zero. The most plausible source for the large observed shift is the short-range orientational order that must exist when  $kT$  is of order or less than the pair-interaction energies. A careful study of the temperature dependence of the phonon frequencies in the  $J=0$  and 1 species should provide an answer, if this effect can be separated from frequency shifts due to ordinary thermal expansion.

For completely random molecular orientations the main effect of the EQQ interaction should be to broaden the phonon lines. In fact, crude estimates

of the linewidths appear to support this conjecture (see Sec. IV B) in the case of  $D_2$  with the  $J=1$  species having broader lines than the  $J=0$  species. For  $H_2$ , the linewidths were roughly equal in the two species. However, the width in the  $J=0$  species was measured in only one sample, and strains could possibly account for its width being equal to that of the  $J=1$  species. Further work is required in this area to make other than speculative statements.

## V. CROSS SECTIONS

The integrated intensity of the Raman lines provides information that can be compared to Werthamer's<sup>6</sup> recent theory for light scattering efficiencies in van der Waals-type crystals. This theory assumes a model in which each atom (or molecule) is regarded as a neutral but polarizable point mass interacting via induced dipole-dipole interactions. Short-range overlap interactions are ignored, but this should be a good approximation for solid hydrogen at low pressures.<sup>25</sup> The neglect of the local field in hydrogen ( $\epsilon = 1.3$ ) is not as good an approximation as for helium ( $\epsilon = 1.05$ ), but is still a relatively small effect and tends to cancel when comparing the optical-phonon intensities with

the rotational intensities. The Raman scattering efficiency for the excitation of a single optical phonon, i. e., the fraction of incident light scattered per units frequency solid angle, and length of the crystal is given by<sup>6</sup>

$$S_{10} = \rho \left( \frac{\omega_i}{c} \right)^4 (n_f + 1) \frac{\pi \hbar}{M \omega_{ph}} \alpha_{av}^4 w^2 \sin^2 \theta_i \sin^2 \theta_s \times \delta(\omega_{if} - \omega_{ph}), \quad (4)$$

where  $\rho$  is the number density,  $\omega_i$  the incident frequency,  $\omega_{if}$  the frequency shift,  $\omega_{ph}$  the phonon frequency,  $M$  the molecular mass,  $\alpha_{av}$  the average polarizability, and  $n_f$  the phonon occupation number. The angles  $\theta_i$  and  $\theta_s$  were defined in Sec. III. The factor  $w$  is proportional to the Raman matrix element and is estimated by Werthamer to have the value  $w^2 \sim 6.5/a^8$  for the hcp structure with nearest-neighbor distance  $a$ . In the solid hydrogens a reasonably accurate experimental measure of  $S_{10}$  can be obtained by comparing it to the scattering efficiency of the rotational transitions  $S(J \rightarrow J+2)$  for  $J=0$  or  $J=1$ , which can be calculated in terms of known constants. Since these measurements can be made on the same sample under identical conditions, less reliably known factors such as efficiency of the light-collection system, efficiency of the detection system, etc., can be eliminated by taking ratios.

To calculate  $S(J \rightarrow J+2)$  in the orientationally disordered hcp phase with large  $J=1$  concentration, we assume a model in which the molecules are treated as noninteracting free rotors fixed to the crystal sites. The scattering efficiency appropriate to compare with Eq. (4) is given by<sup>26</sup>

$$S^{ij}(J \rightarrow J') = 4\rho \left( \frac{\omega_f}{c} \right)^4 (n_J) |\langle J' M_{J'} | \alpha_{ij} | J M_J \rangle|^2 \times \delta(\omega_{if} - \omega_{\Delta J}), \quad (5)$$

where  $\omega_f$  is the frequency of the scattered light,<sup>27</sup>  $\omega_{\Delta J}$  is the frequency of the rotational transition,  $\alpha_{ij}$  is the  $ij$ th component of the traceless part of the molecular-polarizability tensor in the laboratory scattering frame (see inset, Fig. 1), and  $n_J$  is the Boltzmann thermal-population factor for the state  $\langle J M_J |$ . The Cartesian components  $\alpha_{ij}$  can be written as linear combinations of second-order spherical harmonics<sup>28</sup>  $Y_{2m}(\Omega_i)$ , where  $\Omega_i$  denotes the direction of the molecular axis with respect to the laboratory fixed frame. The wave functions  $\psi_{J, M_J}$  for the state  $|J, M_J\rangle$  are simply the spherical harmonics  $Y_{J, M_J}(\Omega_i)$  and thus Eq. (5) can be easily evaluated. The usual selection rules  $\Delta J=0, \pm 2$ ,  $\Delta M_J=0, \pm 1, \pm 2$  are found. In evaluating (5) we average over the initial states and sum over the final states. We note that because of the initial assumption that the molecules are in free-rotor states, the results are independent of crystal orien-

tation. For high concentrations of  $J=1$  species where there is short-range orientational order near the transition temperature this assumption may introduce errors in the intensities. For high concentration of  $J=0$  species, the roton wave functions<sup>29</sup> must be used in evaluating Eq. (5) along with the respective form of  $\alpha_{ij}$ .<sup>5</sup> To compare to the phonon scattering efficiency, Eq. (4) must be evaluated for the appropriate orientation of the crystal  $c$  axis with respect to  $E_{in}$  and  $E_{scat}$ . All of the samples evaluated for the relative intensities had the  $c$  axis within  $10^\circ$  of the  $Z$  axis as shown in the inset of Fig. 1 which also shows the scattering coordinate system. The theoretical efficiencies for both the  $J=0 \rightarrow 2$  and  $J=1 \rightarrow 3$  transitions are given in Table II and comparison with experiment is in Table III. The notation for polarization such as  $XY$  means the incident electric field is polarized along the  $X$  direction and the scattered field along the  $Y$  direction.

The scattering efficiencies given in Table II are identical to the results one would obtain for a powdered sample. This is an example of the principle of spectroscopic stability<sup>30</sup> which is effective here since the intensities are summed over a complete set of final states. Because of this, the integrated rotational intensities should be insensitive to any error in the identification of the sample orientation. On the other hand, the phonon intensities do depend on the sample orientation, and any misorientation of the  $c$  axis from the  $Z$  direction will decrease the measured strength, although the effect should be small for small error angles. (An error of  $10^\circ$ , of the incident or scattered light from the assumed geometry should decrease the intensity by  $\sim 3\%$ .) Another interesting result in Table II is that the calculated intensities are identical for the  $J=0 \rightarrow 2$  transitions whether calculated for the free-rotor model or the roton model, in which the motions of the molecules are highly correlated. A detailed analysis shows that, due to the correlation, the

TABLE II. Theoretical values of the scattering efficiencies for the  $J=0 \rightarrow 2$  and  $1 \rightarrow 3$  rotational transitions given in terms of  $A = (\omega/c)^4 \rho (\alpha_{11} - \alpha_{\perp})^2$ . The intensities for  $J=1 \rightarrow 3$  were calculated on the basis of free-rotor states, whereas the results for  $J=0 \rightarrow 2$  are equally valid for free-rotor or roton states. For the 5145-Å laser line,  $J=0 \rightarrow 2$  transition,  $A$  has the value  $5.9 \times 10^{-7}$  for  $H_2$  and  $6.6 \times 10^{-7}$  for  $D_2$ , in units of  $\text{cm}^{-1} \text{sr}^{-1}$ .

Polarization	$J=0 \rightarrow 2$	$J=1 \rightarrow 3$
	rotors or free-rotor model	free-rotor model
XY	$\frac{12}{45} A$	$\frac{12}{75} A$
XZ	$\frac{12}{45} A$	$\frac{12}{75} A$
YY	$\frac{16}{45} A$	$\frac{16}{75} A$
YZ	$\frac{12}{45} A$	$\frac{12}{75} A$

TABLE III. Experimental ratios of rotational to phonon intensities, with a comparison to theory. Experimental accuracies are estimated to be 10%. The experimental ratios are corrected to 100% concentration of the rotational ground state indicated.

Species	Rot. transition		Intensity ratio $S(J \rightarrow J+2)/S_{10}$	
	$J \rightarrow J+2$	Polarization	Obs.	Theoret.
<i>o</i> -H <sub>2</sub>	1 → 3	XY + XZ	267	311
<i>p</i> -D <sub>2</sub>	1 → 3	XY + XZ	304	412
<i>p</i> -H <sub>2</sub>	0 → 2	YY + YZ	429	577
HD	0 → 2	YY + YZ	532	721
<i>o</i> -D <sub>2</sub>	0 → 2	XY + XZ	458	661

strength of a single-roton transition is twice that of an uncorrelated free-rotor transition. However, half of the roton modes are Raman inactive,<sup>29</sup> and the net effect is that the integrated intensities are equal for both models since the total number of final states is equal, i.e., the degeneracy  $2J+1$  times the number of molecules  $N$ .

The values used for the polarizability anisotropy  $\gamma_{JJ'} = (\alpha_{\parallel} - \alpha_{\perp})_{JJ'}$ , and the average polarizability  $\alpha_{JJ'} = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})_{JJ'}$ , are the static ones calculated by Kolos and Wolniewicz<sup>31</sup> and are given in Table IV. They have only calculated the off-diagonal terms (i.e.,  $J \neq J'$ ) for hydrogen; in the case of HD and D<sub>2</sub> we have used  $\alpha_{JJ'} = \frac{1}{2}(\alpha_{JJ} + \alpha_{J'J'})$ , etc. The justification for using the static values rather than the dynamic polarizabilities is as follows: Victor and Dalgarno<sup>32</sup> and also Kelly<sup>33</sup> have calculated  $\alpha$  and  $\gamma$  for optical frequencies finding an increase in value of order 5% in going from infinite wavelength to  $\sim 5000$  Å. Using the static values which enter in the second and fourth powers might give rise to sizable errors. However, we note that the ratio used in the relative intensities,  $\gamma^2/\alpha^2$ , changes by less than 3% in the same wavelength span. We assume the same is true for the off-diagonal polarizabilities, and then use the static values.

The results are in good order of agreement with Werthamer's theory, the observed intensity ratios being  $\sim 25\%$  lower than the respective theoretical values. The main source of error for the phonon intensities is probably in the squared matrix element  $w^2 \approx 6.5/a^8$ , for phonon scattering. In the estimate by Werthamer,  $w$  has not been averaged over the zero-point motion of the lattice which could substantially reduce its value through the dependence on the lattice parameter.<sup>34</sup>

It is interesting to compare the phonon scattering intensity in hydrogen to that expected for solid helium. Minkiewicz *et al.*<sup>14</sup> have experimentally determined the dispersion relations of solid hcp He by neutron scattering at a molar volume of 21.1 cm<sup>3</sup>, roughly that of unpressurized solid H<sub>2</sub>. Using

$\alpha \approx 1.35$  a.u., about four times smaller than that of H<sub>2</sub>,  $\omega_{\text{ph}} = 7.4$  cm<sup>-1</sup> from Ref. (14), and  $M_{\text{He}} = 2M_{\text{H}_2}$ , we find that the intensity in He of the TO phonon should be about 10<sup>-2</sup> that of H<sub>2</sub>, which indicates that the measurement will be difficult, but still feasible. Decreasing the molar volume will increase the matrix element  $w^2$ ; however, this will be compensated by the increase in  $\omega_{\text{ph}}$  which Reese *et al.*<sup>35</sup> have observed to depend exponentially on molar volume  $V_m$ , i.e.,  $\Delta\omega_{\text{ph}} = e^{-b\Delta V_m}$ , with  $b = 0.1262$  cm<sup>-3</sup>. In fact, halving the molar volume of 21.1 cm<sup>3</sup> will only increase the intensity by  $\sim 1.3$  if quantum crystal effects are ignored. The estimate may be somewhat low, however, since the quantum-crystal effects, which tend to reduce  $w^2$ , will be less pronounced at the lower molar volumes.<sup>36</sup>

## VI. CONCLUSION

Our study of the Raman-active TO phonon in the hcp phase of all five modifications of hydrogen yields the following information:

To the extent that the polarizability approximation holds for the rotational Raman intensities, absolute measurements of the phonon intensities have been made. They agree quite well with Werthamer's theory and give increased confidence in the intensity predictions for solid helium.

The zone-center frequencies have been measured to high accuracy ( $< 0.05$  cm<sup>-1</sup>) using a Fabry-Perot generated spectral comb. In the one instance where inelastic neutron data is presently available (*o*-D<sub>2</sub>) the agreement of measured frequencies is only fair. Because of the much higher accuracy, the Raman results will always be a valuable supplement to neutron data; in the case of ortho-hydrogen, the fast conversion rate probably precludes neutron scattering on pure crystals.

A rather large difference between the phonon frequencies for the ortho and para modifications of the same species has been noted. The difference is well outside that predicted by the slight difference in the isotropic part of the gas-phase potentials. We suggest that short-range orientational order

TABLE IV. Static polarizability parameters used in evaluating the scattering efficiencies. The values are given in atomic units,  $a_0 = 0.5292 \times 10^{-8}$  cm. See the text for a discussion concerning their use at optical frequencies.

Species	Transition $J \rightarrow J'$	$\alpha = \alpha_{\parallel} - \alpha_{\perp}$ ( $a_0^3$ )		Nearest-neighbor distance (Å)
		$\alpha = \alpha_{\parallel} - \alpha_{\perp}$ ( $a_0^3$ )	$\alpha = \frac{1}{3}(\alpha_{\parallel} + 2\alpha_{\perp})$ ( $a_0^3$ )	
H <sub>2</sub>	0 → 2	2.0338	5.4255	3.755
	1 → 3	2.0488	5.4429	
D <sub>2</sub>	0 → 2	1.9642	5.3524	3.59
	1 → 3	1.9718	5.3619	
HD	0 → 2	2.0053	5.3932	3.68
	1 → 3	2.0141	5.4075	



(that must exist when  $kT$  is less than or comparable to the average pair interaction) is responsible for the effect. The downward shift in frequency observed at high temperature in  $p$ -D<sub>2</sub> probably confirms this view, although further measurements would be required to determine how much of the shift is due to normal thermal expansion. A care-

ful study of the temperature dependence for both ortho and para modifications would be of interest.

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<sup>1</sup> See, for example, the review by N. R. Werthamer, *Am. J. Phys.* **37**, 763 (1969), and references therein.

<sup>2</sup> I. F. Silvera, W. N. Hardy, and J. P. McTague, *Discussions Faraday Soc.* **48**, 54 (1969); J. P. McTague, I. F. Silvera, and W. N. Hardy, *Bull. Am. Phys. Soc.* **15**, 296 (1970).

<sup>3</sup> W. N. Hardy, I. F. Silvera, and J. P. McTague, *Phys. Rev. Letters* **26**, 127 (1971).

<sup>4</sup> W. N. Hardy, I. F. Silvera, K. N. Klump, and O. Schnepf, *Phys. Rev. Letters* **21**, 291 (1968).

<sup>5</sup> J. P. McTague, I. F. Silvera, and W. N. Hardy, in *Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1971).

<sup>6</sup> N. R. Werthamer, *Phys. Rev.* **185**, 348 (1969).

<sup>7</sup> See, for example, K. Motizuki, *J. Phys. Soc. Japan* **17**, 1192 (1962).

<sup>8</sup> A. F. Schuch, R. L. Mills, and D. A. Depatie, *Phys. Rev.* **165**, 1032 (1968).

<sup>9</sup> See, for example, H. M. James, *Phys. Rev. B* **2**, 2213 (1970), and references therein.

<sup>10</sup> R. E. DeWames, T. Wolfram, and G. W. Lehman, *Phys. Rev.* **138**, A717 (1964).

<sup>11</sup> N. S. Gillis, R. T. Koehler, and N. R. Werthamer, *Phys. Rev.* **175**, 1110 (1968).

<sup>12</sup> N. R. Werthamer, R. L. Gray, and T. R. Koehler, *Phys. Rev. B* **4**, 1324 (1971).

<sup>13</sup> L. H. Nosanow, *Phys. Rev.* **146**, 120 (1966).

<sup>14</sup> V. J. Minkiewicz, T. A. Kitchens, F. P. Lipschultz, R. Nathans, and G. Shirane, *Phys. Rev.* **174**, 267 (1968); R. A. Reese, S. K. Sinha, T. O. Brun, and C. R. Tilford, *Phys. Rev. A* **3**, 1688 (1971).

<sup>15</sup> Recent neutron scattering experiments in solid H<sub>2</sub> indicate that there are regions in the Brillouin zone for  $k \neq 0$  in which phonons exhibit considerable damping [M. Nielsen (private communication)].

<sup>16</sup> M. Born and K. Huang, *Dynamical Theory of Lattice Vibrations* (Oxford U. P., Oxford, England, 1956).

<sup>17</sup> M. L. Klein and T. R. Koehler, *J. Phys. C* **3**, L102 (1970); *Phys. Letters* **33A**, 253 (1970).

<sup>18</sup> W. Biem and F. G. Mertens (private communication); F. G. Mertens, *Institute für Festkörperforschung, Jülich, Bundesrepublik Deutschland Report No. Jul-734-F* (unpublished).

<sup>19</sup> M. Nielsen and H. B. Møller, *Phys. Rev. B* **3**, 4383 (1971).

<sup>20</sup> D. A. Depatie and R. L. Mills, *Rev. Sci. Instr.* **39**, 105 (1968).

<sup>21</sup> E. R. Grilly, *Rev. Sci. Instr.* **24**, 72 (1953).

<sup>22</sup> I. F. Silvera, W. N. Hardy, and J. P. McTague, *Rev. Sci. Instr.* (to be published).

<sup>23</sup> In HD, due to the separation of the molecular center of mass and center of charge, the usual selection rules in the solid hydrogen can breakdown. Another possible assignment of the feature is to a  $J=0 \rightarrow 1$  transition plus a phonon which would satisfy the peak frequency shift ( $90 \pm 70 \text{ cm}^{-1}$ ). In this case, the intensity at frequencies lower than  $90 \text{ cm}^{-1}$  would have to be assigned to the wing of the  $J=0 \rightarrow 2$  transition.

<sup>24</sup> Mertens, Ref. 18, has calculated the frequencies for  $J=1$  H<sub>2</sub> and D<sub>2</sub> in the fcc  $Pa\bar{3}$  ordered phase and for the hypothetical  $J=0$  fcc lattice with resulting effect of  $\sim 3 \text{ cm}^{-1}$  in the phonon frequencies.

<sup>25</sup> Absolute intensity measurements of collision induced light scattering in gaseous hydrogen at room temperature [P. Lallemand, *Phys. Rev. Letters* **25**, 1079 (1970)] suggest that the dipole-dipole approximation is approximately 25% in error at high temperatures. In the solid at low temperatures and pressures the approximation should improve considerably since here the short-range overlap interactions are less important.

<sup>26</sup> E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955), p. 48.

<sup>27</sup> That  $\omega_1^4$  appears in Eq. (5) and  $\omega_2^4$  in Eq. (4) seems to be a difference between the semiclassical (Ref. 26) and quantum-mechanical treatments of light scattering [see Ref. 6 and also R. Loudon, *Advan. Phys.* **13**, 423 (1964)]. For our purposes, the difference can be neglected.

<sup>28</sup> W. N. Hardy, I. F. Silvera, and J. P. McTague (unpublished).

<sup>29</sup> J. van Kranendonk, *Physica* **25**, 1080 (1960); *Can. J. Phys.* **38**, 240 (1960).

<sup>30</sup> See, for example, J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford U. P., Oxford, England, 1932).

<sup>31</sup> W. Kolos and L. Wolniewicz, *J. Chem. Phys.* **46**, 1426 (1967).

<sup>32</sup> G. A. Victor and A. Dalgarno, *J. Chem. Phys.* **50**, 2535 (1969).

<sup>33</sup> H. P. Kelly, *Phys. Rev. A* **1**, 274 (1970).

<sup>34</sup> A. B. Harris, *Phys. Rev. B* **1**, 1881 (1970).

<sup>35</sup> Reese *et al.*, Ref. 14, have measured the dispersion relations in He at a molar volume of  $16 \text{ cm}^3$ .

<sup>36</sup> Recent computer calculations of the scattering intensities in solid hcp helium (Ref. 12) do not change the order of magnitude of the estimates here. Averaging of the matrix elements over the lattice zero-point motion reduces them by a factor of  $\sim 2$  or  $s_{10}$  by roughly 4. Results predict an increase of intensity by  $\sim 1.7$  in reducing the molar volume to  $16$  from  $20 \text{ cm}^3$ .

<sup>37</sup> W. Schott, *Z. Physik* **231**, 243 (1970).