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Observation of the $J=4$ Roton Band in Solid Deuterium under Pressure

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Raman scattering in high-pressure solid orthodeuterium has been used to make the first observation of the $J=4$ roton band in o-D_2, not confined to $k=0$. The results are consistent with an almost dispersionless band. A determination of the $J=2$ roton band density of states is in agreement with our computer calculations.

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The rotational energy states in solid parahydrogen and orthodeuterium at low temperature and pressure are roton bands characterized by the even rotational quantum number J. In the ground state the molecules are in the $J=0$ state; detailed spectroscopic studies of the $J=2$ band at the $\mathbf{k}=0$ point in the Brillouin zone have been made earlier,[1] in particular, by Raman scattering of the $J=0\rightarrow 2$ transitions. In general, the $J=4$ and higher bands cannot be excited due to the Raman selection rule of $\Delta J=0,\pm 2$. One method of exciting the $J=4$ band would be to thermally populate the $J=2$ band which would then allow $J=2\rightarrow 4$ transitions; however, at ambient pressures the crystal melts before significant population of the $J=2$ band is achieved. By using pressure to raise the melting temperature of o-D_2 we have been able to populate the $J=2$ state sufficiently to make the first direct observation of the $J=4$ band, not confined to zero wave vector. Because of the very small dispersion of the $J=4$ band, it was possible to experimentally determine the density of states of the $J=2$ band; this compares favorably to our calculated density of states.

At ambient pressure solid H_2 and D_2 melt at $T\approx 14$ and 19 K, respectively. However, the $J=2$ and 4 roton bands remain essentially unpopulated at the melting point. The energy of the center of gravity of the $J=2$ band is about $6B$, where the rotional constant B has a value of 85.4 K for H_2 and 43.0 K for D_2. As a consequence, the Boltzmann thermal factor for the $J=2$ band in deuterium, $\exp(-6B/k_BT)$, is about 10^{-6} at the melting point; the situation is much worse in hydrogen (10^{-16}). Since the melting temperatures of H_2 and D_2 increase rapidly with density, while B remains relatively constant, high pressure can alleviate this problem. We have studied a crystal of o-D_2, which has the hexagonal-close-packed (hcp) structure, at $T=40$ K and a pressure of ~ 4 kbar (molar volume 13.7 cm^3/mole) for which $T_{melt}\approx 75.4$ K. At this temperature the population of the $J=2$ band is about 1.6×10^{-3}; this can provide a measurable Raman intensity in a well designed apparatus. Moreover, the $J=2$ band is still well defined as demonstrated by the characteristic triplet of the $J=0\rightarrow 2$ spectrum shown in Fig. 1.

The energy dispersion of the rotational band states is determined principally by the anisotropic intermolecular pair potential. Since J is an approximately good quantum number in the solid, the single-particle wave functions, which are used to construct the many-body wave functions, are spherical harmonics.[2] The Hamiltonian is

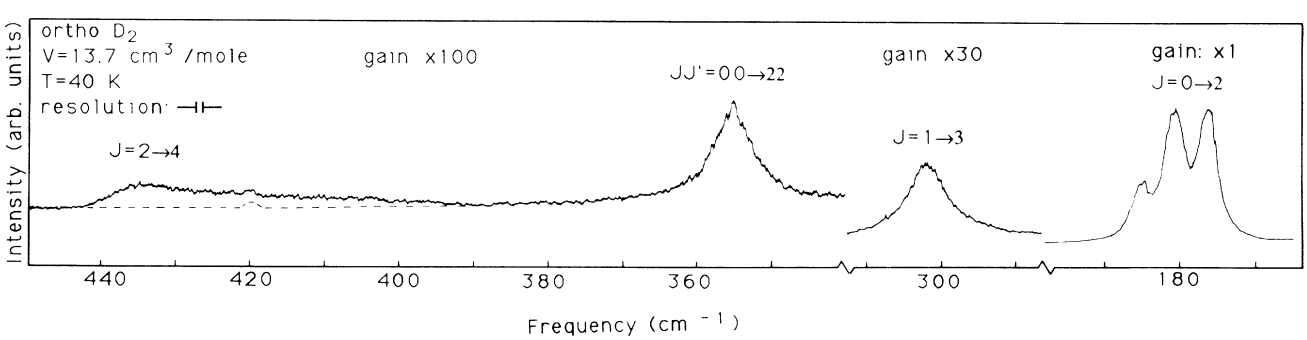

FIG. 1. The Raman spectrum of a pressurized o-D_2 crystal at $T=40$ K, showing the $J=2\rightarrow 4$ band transition. The dashed line shows the $T=4.2$-K background. The other features are discussed in the text.

given by the rotational kinetic energy and a sum over pair potentials,

$$H=\sum_i BJ_i^2+\sum_{i>j} V(\Omega_i,\Omega_j,R_{ij}) , \quad (1)$$

where Ω_i and Ω_j are polar angles of the molecular axes with respect to the vector $\mathbf{R}_{ij}$ between the center of masses of the molecules. It is thus useful to expand the potential in spherical harmonics:[2]

$$V=\sum_{l_1 l_2}\sum_m \varepsilon_{l_1 l_2} C(l_1,l_2,l_1+l_2,m,-m) C_{l_1 m}(\Omega_1) C^*_{l_2 m}(\Omega_2) . \quad (2)$$

Here l_1 and l_2 are even positive integers; the dependence on the molecular separation is contained in $\varepsilon_{l_1 l_2}$. $C(l_1,l_2,l_1+l_2,m,-m)$ is a Clebsch-Gordan coefficient, and $C_{l_1 m}(\Omega_1)$ is a Racah spherical harmonic. If we are only interested in excitations from the $J=0$ level to the $J=2$ band, then it suffices to terminate V at $l_1=l_2=2$. The dominant anisotropic term is due to the permanent electric quadrupole-quadrupole (EQQ) coupling, with $\varepsilon_{22}\equiv(70)^{1/2}Q_2^2/R^5$, where Q_2 is the EQ moment; the matrix elements of higher-order spherical harmonics vanish within these rotational manifolds. When the $J=4$ manifold is considered, the largest anisotropic term which will affect the energy of the $J=4$ roton band is due to the electric hexadecapole-hexadecapole moment, with $\varepsilon_{44}\equiv 3(11\times 130)^{1/2}Q_4^2/R^9$, where Q_4 is the hexadecapole moment. This has been measured at zero pressure in hydrogen[3] and has a value in good agreement with the calculations of Karl, Poll, and Wolniewicz.[4] Evaluating the strength of the EQQ and electric hexadecapole-hexadecapole interactions shows that the latter is about 3 orders of magnitude smaller than the EQQ at the densities of interest in this experiment. As a result, the $J=4$ band will be very narrow and the energy will be essentially independent of the k vector; however, this has never been determined experimentally.

The Raman scattering efficiency is given by

$$S^{\mu\lambda}_{i\to f}=\frac{4\omega_i\omega_f^3}{c^4}\rho P_i\sum_f |\langle f|\alpha_{\lambda\mu}|i\rangle|^2\delta(\hbar\omega_i-\hbar\omega_f-E_{fi}) . \quad (3)$$

Here ω_i and ω_f are the angular frequencies of the initial and final photons, and $|i\rangle$ and $|f\rangle$ are the initial and final states of the crystal, with energy difference E_{fi}. ρ is the molecular number density, P_i is the probability that state $|i\rangle$ is populated, and $\alpha_{\lambda\mu}$ is the $\lambda\mu$ component of the crystal polarizability. As usual, in this formulation a momentum-conserving δ function has been suppressed. For excitations from the ground state this confines the transition probability to $\Delta\mathbf{k}\approx 0$, or $\mathbf{k}_f\approx 0$ since $\mathbf{k}_i=0$.

The center of gravity of the $J=2\to 4$ band transition is expected at about 415 cm^{-1}. For the $J=2$ band all states $\mathbf{k}_i$ can be thermally populated so that transitions with $\mathbf{k}_f\neq 0$, but with the restriction $\mathbf{k}_i-\mathbf{k}_f\approx 0$, are allowed. The sum in Eq. (3) then becomes the product of the polarizability and the convolution of the density of states of the initial and final states. Since the bandwidth of the final state (the $J=4$ band) is expected to be narrow compared to the initial state,[5] the Raman efficiency measures the density of the $J=2$ roton band in the approximation that the polarizability matrix element is mode and energy independent. We shall check this by comparing experiment to theory.

Raman spectra were obtained on a 97.7% o-D_2 sample using the 5145-Å line of an Ar^+ laser. Although a diamond-anvil cell (DAC) allows easy pressurization of deuterium, the small sample size and the diamond windows result in an unfavorably low signal-to-noise ratio for an exploratory experiment of this nature. A low-strain transparent crystal (molar volume 13.7 cm^3/mole) was grown from liquid D_2 in an isochoric high-pressure cell, described elsewhere.[6] The Raman spectra shown in Fig. 1 are for $T=40$ and 5 K (dashed line). The broad, triangular-shaped band in the region $\Delta\nu=390$–440 cm^{-1} is the $J=2\to 4$ band, which disappears at low temperature. The weak bump at 421 cm^{-1}, present at 40 and 5 K, arises from the sapphire cell windows. We also see the strong $J=0\to 2$ roton transition and the $J=1\to 3$ p-D_2 impurity line. The feature at 355 cm^{-1} is due to the $J=0\to 2$ transition of a 0.2% H_2 impurity and the double rotational transition $JJ'=00\to 22$ of o-D_2.[7] In Fig. 2(a) we show the difference of the 40- and 5-K spectra, representing the intensity due to the $J=2\to 4$ transition.

The $J=2$ roton bandwidth was estimated earlier by Van Kranendonk,[5] who used a rectangular band shape to find a bandwidth of $1.05\varepsilon_{22}$. Lagendijk and Silvera[8] have calculated the $J=2$ roton density of states for hcp and fcc hydrogen lattices, as a function of molar volume. We have performed this calculation for hcp deuterium at the experimental molar volume. The energy was calculated for 46650 $\mathbf{k}$ values in the full Brillouin zone and has a width of about $1.19\varepsilon_{22}$. This is compared to the experimentally measured band shape in Fig. 2(b) where we adjust the theoretical curve to $T=40$ K, by multiplying it by the appropriate Boltzmann factor P_i. For comparison, the first moment of the theoretical curve was fixed to the energy of the gas-phase $J=2\to 4$ transition. We expect a shift of the center of gravity of this transition to be no more than 1–2 cm^{-1} in the solid.[9]

In comparing theoretical and experimental results, we note that the triangular shape of the experimental density of states is well portrayed by the theoretical curve. This provides confirmation of the almost dispersionless nature of the $J=4$ band, along with an experimental determination of the density of states of the $J=2$ roton bands, in the approximation that the polarizability-tensor matrix elements are energy independent. We point out that there is a striking disagreement with the density of states of the $J=2$ band recently calculated by Bose and Poll,[10] which we cannot explain. Comparing the theoretical and experimental curves of Fig. 2(b) in

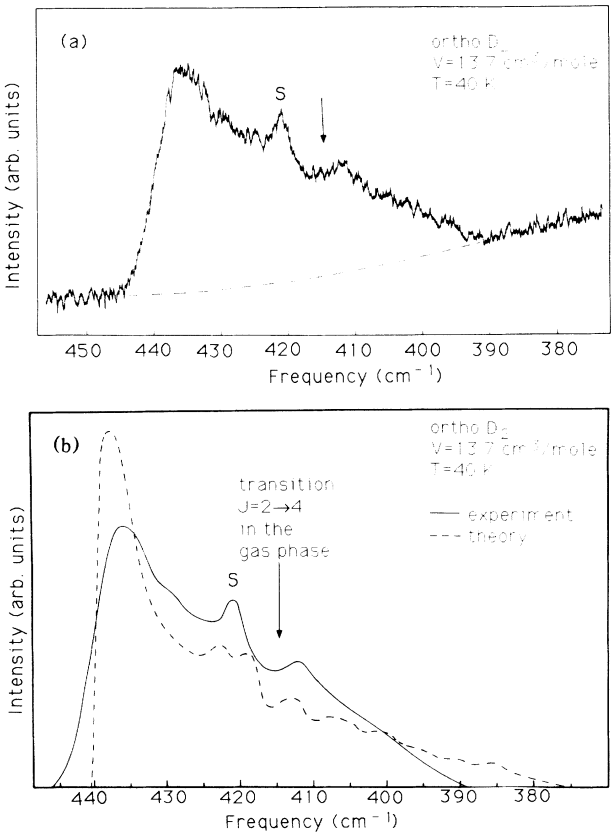

FIG. 2. (a) The Raman spectrum of the $J=2 \rightarrow 4$ band transition. The peak labeled S originates from the sapphire windows of the cell; the arrow indicates the energy of the $J=2 \rightarrow 4$ transition in the gas phase. (b) The $J=2 \rightarrow 4$ band and the calculated density of states. The theoretical curve has been multiplied by a Boltzmann factor corresponding to 40 K. The two curves have approximately the same vertical scale for easy comparison.

more detail, we note differences in the high- and low-frequency sides. A possible explanation for the difference at low frequency is a difficulty in determining the background curve with precision, so the background subtraction gives distortion in flatter regions of the curves (see Fig. 1). On the high-frequency side the experiment is broader and less peaked than theory. This may be a result of other ε_{ij} terms in the Hamiltonian, Eq. (2), which are known to grow with pressure and have been ignored here, or possibly due to anharmonic terms[8] which have also been disregarded in the present calculations.

Now that we have established this technique, it would be very useful to carry out further studies in a DAC to much higher pressures and at elevated temperatures to increase the intensity. In particular, it has been suggested by Lagendijk and Silvera that the broken-symmetry transition to orientational order in o-D_2 at 28 GPa (Ref. 11) and in p-H_2 at 110 GPa (Ref. 12) is due to a softening of a roton mode at the zone edge; Igarashi has suggested that although the mode softens, it does not go to zero energy due to the effects of higher-order interaction terms.[13] Experimental studies of the density of states of the $J=2$ roton band at very high pressures would help to sort out the mechanism of this phase transition.

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