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

Luc Lassche,<sup>(1)</sup> Isaac F. Silvera,<sup>(2),(3)</sup> and Ad Lagendijk<sup>(1),(4)</sup>

<sup>(1)</sup>*Natuurkundig Laboratorium, Universiteit van Amsterdam, Amsterdam, The Netherlands*

<sup>(2)</sup>*Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138*

<sup>(3)</sup>*Laboratoire de Spectroscopie Hertzienne de l'École Normale Supérieure, 24 Rue Lhomond, 75005 Paris, France*

<sup>(4)</sup>*Foundation for Fundamental Research on Matter (FOM)- Institute for Atomic and Molecular Physics, Amsterdam, The Netherlands*

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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<sub>2</sub>, 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,<sup>1</sup> 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<sub>2</sub> 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<sub>2</sub> and D<sub>2</sub> 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 rotational constant  $B$  has a value of 85.4 K for H<sub>2</sub> and 43.0 K for D<sub>2</sub>. As a consequence, the Boltzmann thermal factor for the  $J=2$  band in deuterium,  $\exp(-6B/k_B T)$ , is about  $10^{-6}$  at the melting point; the situation is much worse in hydrogen ( $10^{-16}$ ). Since the melting temperatures of H<sub>2</sub> and D<sub>2</sub> increase rapidly with density, while  $B$  remains relatively constant, high pressure can alleviate this problem. We have studied a crystal of  $o$ -D<sub>2</sub>, which has the hexagonal-close-packed (hcp) structure, at  $T=40$  K and a pressure of  $\sim 4$  kbar (molar volume 13.7 cm<sup>3</sup>/mole) for which  $T_{\text{melt}} \approx 75.4$  K. At this temperature the population of the  $J=2$  band is about  $1.6 \times 10^{-3}$ ; 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.<sup>2</sup> The Hamiltonian is

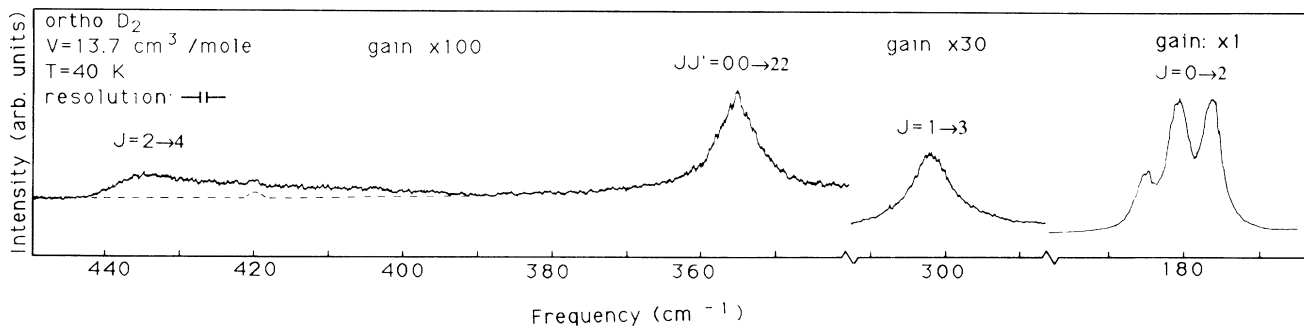


FIG. 1. The Raman spectrum of a pressurized  $o$ -D<sub>2</sub> crystal at  $T=40$  K, showing the  $J=2 \rightarrow 4$  band transition. The dashed line shows the  $T=4.2$ -K background. The other features are discussed in the text.

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

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

where  $\Omega_i$  and  $\Omega_j$  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:<sup>2</sup>

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

Here  $l_1$  and  $l_2$  are even positive integers; the dependence on the molecular separation is contained in  $\epsilon_{l_1 l_2}$ .  $C(l_1, l_2, l_1 + l_2, m, -m)$  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  $\epsilon_{22} \equiv (70)^{1/2} Q_2^2 / R^5$ , 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  $\epsilon_{44} \equiv 3(11 \times 130)^{1/2} Q_4^2 / R^9$ , where  $Q_4$  is the hexadecapole moment. This has been measured at zero pressure in hydrogen<sup>3</sup> and has a value in good agreement with the calculations of Karl, Poll, and Wolniewicz.<sup>4</sup> 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

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

Here  $\omega_i$  and  $\omega_f$  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  $E_{fi}$ .  $\rho$  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  $\delta$  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  $J=2 \rightarrow 4$  band transition is expected at about  $415 \text{ cm}^{-1}$ . 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,<sup>5</sup> 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<sub>2</sub> sample using the 5145-Å line of an Ar<sup>+</sup> 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  $13.7 \text{ cm}^3/\text{mole}$ ) was grown from liquid D<sub>2</sub> in an isochoric high-pressure cell, described elsewhere.<sup>6</sup> The Raman spectra shown in Fig. 1 are for  $T=40$  and 5 K (dashed line). The broad, triangular-shaped band in the region  $\Delta\nu=390\text{--}440 \text{ cm}^{-1}$  is the  $J=2 \rightarrow 4$  band, which disappears at low temperature. The weak bump at  $421 \text{ cm}^{-1}$ , present at 40 and 5 K, arises from the sapphire cell windows. We also see the strong  $J=0 \rightarrow 2$  roton transition and the  $J=1 \rightarrow 3$  *p*-D<sub>2</sub> impurity line. The feature at  $355 \text{ cm}^{-1}$  is due to the  $J=0 \rightarrow 2$  transition of a 0.2% H<sub>2</sub> impurity and the double rotational transition  $JJ'=00 \rightarrow 22$  of *o*-D<sub>2</sub>.<sup>7</sup> In Fig. 2(a) we show the difference of the 40- and 5-K spectra, representing the intensity due to the  $J=2 \rightarrow 4$  transition.

The  $J=2$  roton bandwidth was estimated earlier by Van Kranendonk,<sup>5</sup> who used a rectangular band shape to find a bandwidth of  $1.05\epsilon_{22}$ . Lagendijk and Silvera<sup>8</sup> 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 46 650  $\mathbf{k}$  values in the full Brillouin zone and has a width of about  $1.19\epsilon_{22}$ . 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  $J=2 \rightarrow 4$  transition. We expect a shift of the center of gravity of this transition to be no more than  $1\text{--}2 \text{ cm}^{-1}$  in the solid.<sup>9</sup>

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,<sup>10</sup> which we cannot explain. Comparing the theoretical and experimental curves of Fig. 2(b) in

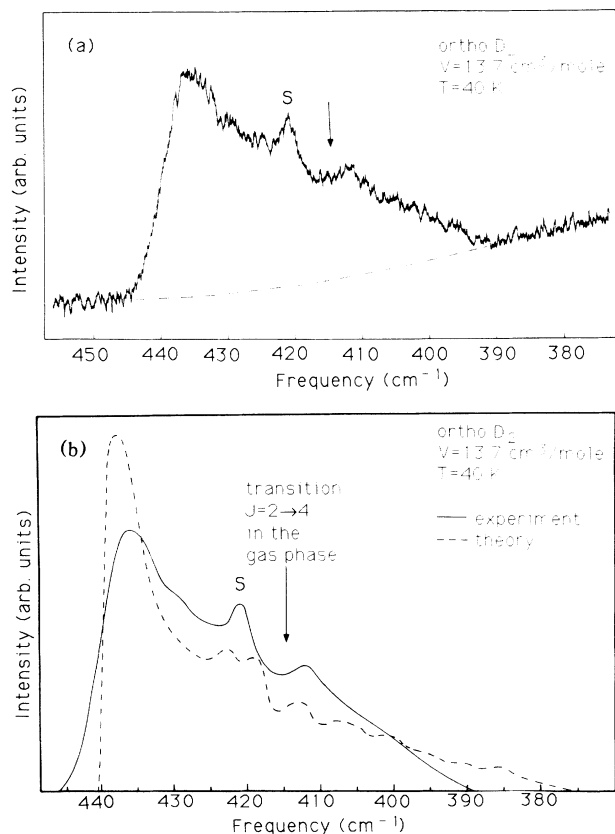


FIG. 2. (a) The Raman spectrum of the  $J=2 \rightarrow 4$  band transition. The peak labeled *S* originates from the sapphire windows of the cell; the arrow indicates the energy of the  $J=2 \rightarrow 4$  transition in the gas phase. (b) The  $J=2 \rightarrow 4$  band and the calculated density of 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  $\epsilon_{ij}$  terms in the Hamiltonian, Eq. (2), which are known to grow with pressure and have been ignored here, or possibly due to anharmonic terms<sup>8</sup> which have also been disregarded in the present calcula-

tions.

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 Legendijk and Silvera that the broken-symmetry transition to orientational order in *o*-D<sub>2</sub> at 28 GPa (Ref. 11) and in *p*-H<sub>2</sub> 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.<sup>13</sup> 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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<sup>1</sup>S. S. Bhatnagar, E. J. Allin, and H. L. Welsh, *Can. J. Phys.* **40**, 9 (1962).

<sup>2</sup>J. Van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983).

<sup>3</sup>T. K. Balasubramanian, C-H. Lien, K. N. Rao, and J. R. Gaines, *Phys. Rev. Lett.* **47**, 1277 (1981).

<sup>4</sup>G. Karl, J. D. Poll, and L. Wolniewicz, *Can. J. Phys.* **53**, 1781 (1975).

<sup>5</sup>J. Van Kranendonk, *Physica (Utrecht)* **25**, 1080 (1959).

<sup>6</sup>P. J. Berkhout, Ph.D. thesis, Universiteit van Amsterdam, 1977 (unpublished).

<sup>7</sup>P. J. Berkhout and I. F. Silvera, *Commun. Phys.* **2**, 109 (1977).

<sup>8</sup>A. Legendijk and I. F. Silvera, *Phys. Lett.* **84A**, 28 (1981).

<sup>9</sup>J. Van Kranendonk and G. Karl, *Rev. Mod. Phys.* **40**, 531 (1968), consider a self-energy term, found to be of order  $1 \text{ cm}^{-1}$ ; other terms giving shifts under pressure are due to the change of the molecular bond length, or *B*, which is also of the same order of magnitude.

<sup>10</sup>S. K. Bose and J. D. Poll, *Can. J. Phys.* **68**, 159 (1990).

<sup>11</sup>I. F. Silvera and R. J. Wijngaarden, *Phys. Rev. Lett.* **47**, 39 (1981).

<sup>12</sup>H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, *Phys. Rev. Lett.* **64**, 1939 (1990).

<sup>13</sup>J. Igarashi, *J. Phys. Soc. Jpn.* **53**, 2629 (1984).