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New Low-Temperature Phase of Molecular Deuterium at Ultrahigh Pressure

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We have studied ortho- D_2 and para- H_2 at pressures up to 540 kbar (54 GPa) and 1.1 K $< T < 300$ K by means of Raman scattering in a diamond anvil cell. A phase transition in which the molecules which are spherically symmetric at low pressure go into an orientationally ordered state has been observed in o - D_2 at 278 ± 5 kbar. Line broadening of the roton bands for $p \approx 200$ kbar is interpreted as a precursor of this transition.

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At zero pressure and $T=0$ K the molecules of solid parahydrogen (p - H_2) and orthodeuterium (o - D_2) are in spherically symmetric states. At a sufficiently high density it is predicted that the anisotropic interactions deform the molecular density distributions so that the molecules spontaneously enter an orientationally ordered state at $T=0$ K. We have observed this broken (rotational) symmetry phase (BSP) transition in o - D_2 at 5 K for pressures $p \geq 278 \pm 5$ kbar in a diamond anvil cell (DAC) by means of Raman scattering. In p - H_2 no phase transition has yet taken place down to $T=6$ K and up to $p=540$ kbar. In o - D_2 for $p \approx 200$ to 278 kbar the $J=2$ rotational band undergoes a remarkable broadening. This may be a precursor of the BSP or of a second phase transition with a critical temperature lower than our lowest accessible temperature (1.1 K). In this Letter we present high-pressure data on D_2 and H_2 including a proposed new phase diagram.

At low pressure and down to $T=0$ K, p - H_2 and o - D_2 form hcp lattices.¹ Because of the weakness of the anisotropic intermolecular interaction which is mainly due to the electric-quadrupole-quadrupole (EQQ) interaction, J is a good quantum number and the molecules are in $J=0$ rotational and $v=0$ vibrational states, and thus are in one-particle quantum mechanical spherically symmetric molecular states. The low-lying excitations are phonons, the $J=2, 4, \dots$ roton bands [with energies $BJ(J+1)$ of a few hundred cm^{-1} and higher] which are split by the weak anisotropic interactions and the $J=0$, $v=0 \rightarrow v=1$ or $Q_1(0)$ vibron bands with energies of a few thousand inverse centimeters. Early mean-field calculations by Raich and co-workers² and by Felsteiner and Friedman³ predicted that at a critical density, corresponding to pressures of 70 and 30 kbar, respectively, higher rotational states would spontaneously mix into the $J=0$ ground state so that the order parameter, $\eta = (4\pi/5)^{1/2} N^{-1} \langle \sum_i Y_{20}(\Omega_i) \rangle$,

becomes nonzero. Here, $Y_{20}(\Omega_i)$ is a spherical harmonic of argument $\Omega_i = (\theta_i, \varphi_i)$ which describes the molecular state of orientation and N is the number of molecules. An fcc lattice was assumed and the ground state of the ordered phase was assumed to be the $Pa3$ crystal structure, that of zero-pressure o - H_2 and p - D_2 . In contrast with the mean-field theories, Raman measurements of Berkhout and Silvera⁴ have clearly shown that even at $p=0$ there is a weak admixture of rotational states that rapidly increases with density. Recently, Lagendijk and Silvera⁵ have studied the density dependence of the $J=2$ rotons. This theory incorporates the admixture of rotational states in the low-density symmetric phase (SP) and demonstrates that the BSP arises from the softening of a Brillouin-zone-boundary $J=2$ roton. With use of a pure EQQ interreaction a phase transition was predicted for D_2 at about 110 kbar on an fcc lattice and 120 kbar for the hcp lattice. In the former, the $Pa3$ structure was found. The critical parameter which determines the rotational mixing is $\langle V_{\text{anis}} \rangle / B$, where $\langle V_{\text{anis}} \rangle$ is the mean intermolecular anisotropic interaction and B is the rotational constant. Since B of D_2 is half that of H_2 (due to the mass differences) and since $\langle V_{\text{anis}} \rangle$ is roughly the same at a given density, the BSP should be observed at a much lower pressure in D_2 .

Raman scattering should be a very useful probe of the state of the solid for the following reasons. In the low-pressure symmetric phase (SP) there are three distinct sharp $J=0 \rightarrow J=2$ Raman transitions; in the BSP $Pa3$ structure the excitations are librations and one expects to observe eight distinct transitions.⁶ Above the critical temperature of the BSP the expected spectrum is a broad featureless rotational band (paralibrations). In the hcp structure the E_{2g} phonon is Raman active; in fcc there are no Raman-active phonons; the $Q_1(0)$ vibron is an allowed transition in both fcc and hcp.

High pressures were achieved by means of a DAC mounted in a cryostat with an optical tail having a temperature range of 1.1 to 300 K. The DAC can be completely submerged in liquid helium for good thermal contact. Samples of 97.5% *o*-D₂ and 99% *p*-H₂ were studied. Diamonds were selected as described elsewhere⁷ to minimize bothersome diamond luminescence. Pressures as high as 540 kbar on samples of volume $\sim 10^{-4}$ mm³ were determined from the luminescence spectrum due to a few grains of ruby enclosed with the sample.⁸ A backscattering geometry was used for the Raman measurements. An argon ion laser with power up to 500 mW in the 5145-Å line was employed.

Next we shall describe our data. Figure 1 shows the frequency of the rotational, phonon (*P*), and vibron (*V*) transitions as a function of pressure and density. Although the equation of state (EOS) of H₂ and D₂ are unknown at high density, we use the theoretical EOS of Silvera and Goldman⁹ to provide a reasonable scale. The pressure, according to the ruby scale,⁸ is also

shown. In these figures each transition has a width; the center of the transition is the peak frequency indicated by the data points and the shaded area represents the full width at half maximum of the line. To obtain the sharpest lines (those shown) the samples were thermally annealed. In the low-pressure region we see the three $J=0 \rightarrow J=2$ roton lines as well as the hcp phonon. Its crossing and hybridization with the rotors has been described elsewhere.¹⁰ The general behavior is similar for H₂ and D₂. However, in D₂ at about 150 kbar, the rotors begin to broaden and turn down in frequency. From 200 to 278 kbar there is but one discernible, broad rotational band. In this range the temperature was varied from 1.1–20 K, but no change in the spectrum was observed. In H₂ no such behavior is observed. However above the phonon crossing, the roton E_{2g} mode splits into a doublet, possibly due to strain. Finally, in D₂, above 278 kbar and below a critical temperature T_c , the rotational band splits with a reduction in intensity and the vibron shifts sharply in frequency. We consider this to

FIG. 1. Raman frequency shift of excitations as a function of density for *para*-D₂ and *ortho*-H₂ at $T=5$ K. *V* is the vibron, *P* the phonon, and *S* is a spurious strain-induced transition discussed elsewhere. The remaining transitions are rotational. The zero-pressure results of McTague, Silvera, and Hardy (Ref. 11), as well as the results of Lassche, Zandveld, and Silvera (Ref. 12), and Bhatnagar, Allin, and Welsh (Ref. 13) are also shown. The density proportional to the inverse of the molar volume is scaled to the zero-pressure volume $V_{0H_2}=23.16$ cm³/mole of *p*-H₂ for both D₂ and H₂ so that density scales are the same for ease of comparison. The shaded areas indicate the linewidth (full width at half maximum) of the transitions. Broken lines indicate weak intensity.

FIG. 2. T_c and vibron frequency shift as a function of pressure. Note the left- and right-hand scales. The inset shows the vibron frequency as a function of temperature. T_c is determined as T where the shift of $\Delta\nu$ is $\frac{1}{2}$. The asterisk on $(\Delta\nu_{50K} - \Delta\nu_{5K})^*$ means that unimportant temperature dependences of $\Delta\nu$ have been subtracted.

be the manifestation of the phase transition. This shift cannot be resolved on the scale used in Fig. 1, but is shown in Fig. 2. Here we also plot T_c , determined by the temperature at which the vibron shifts, as a function of pressure. Above T_c the rotational band is unstructured and broad, just as the bands observed for pressures lower than 278 kbar.

We shall now interpret our observations. The sharp shift of the vibron frequency, the weakening and splitting of the rotational spectrum for $p \geq 278$ kbar, and the absence of this phenomenon in H_2 at equal or lower densities, seems to be clear evidence that orientational ordering or the BSP transition has taken place below T_c . The fact that the vibron band has a shift that is rather insensitive to pressure indicates that this is not a driving force, but rather it is responding to a change in the crystal structure. The continuous approach of this shift to zero as $p \rightarrow p_c$ is an indication that the centers of mass of the molecules do not abruptly shift such as in an hcp-fcc transition, which should give rise to a jump. No strong characteristic of a first-order transition has been observed. We have not yet been able to identify the structure from the spectrum. It was not possible to follow the hcp phonon to higher pressures than shown because of its weakness, broadening, and interfering background luminescence. Thus it is not possible to state on firm experimental grounds that an hcp-to-fcc structural change has not taken

place, analogous to the case of zero-pressure o - H_2 and p - D_2 .

In the range $p \approx 200$ –278 kbar at temperatures $T \geq 1.1$ K the roton spectrum severely broadens into one band. The most probable explanation for this is lifetime broadening of the rotons. At low pressure there are no single- ($\vec{k}=0$) or double-excitation ($\vec{k} \neq 0$) final states to conserve momentum and energy for roton decay. Lagendijk and Silvera⁵ have recently shown that the BSP transition arises from the softening of a zone-boundary roton mode, ρ . Above a certain pressure, states exist with energy $E_\rho(\vec{k})$, such that two of these rotons with $\vec{k}$ and $-\vec{k}$ have the energy required to relax the zone-center ($\vec{k}=0$) Raman-active roton.¹⁴ This could possibly account for the severe line broadening above $p \approx 200$ kbar, although detailed calculations have not yet been performed. A second possible explanation is that a second phase exists in a narrow sliver in the p - T phase diagram, with T_c lower than our lowest temperatures. The broad band would then be interpreted as being characteristic of a disorder phase. A tentative phase diagram is shown in Fig. 3.

With regard to p - H_2 , from Fig. 1 we see that for $p > 500$ kbar it appears to be entering the region where phase transitions will occur but somewhat higher densities are still required. The BSP transition will most likely occur before the insulator-metal transition.

As a last point we mention that slowly cycling

FIG. 3. p - T phase diagram of o - D_2 . Above 200 kbar severe roton broadening is observed in the shaded region. Lowest accessible temperatures were 1.1 K. The melting line is due to a theory of Young and Ross (Ref. 15) to 50 kbar. Above 50 kbar we show a hypothetical melting line.

the pressure in the region 230–370 kbar gave reasonably reversible behavior. At the conclusion of a run on D_2 we rapidly reduced the pressure to 150 kbar and then to 30 kbar. A rotational spectrum quite similar to, but much more intense than, the $T < T_c$ BSP spectrum was observed for both pressures and could not be thermally annealed out (up to 300 K).

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