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Raman excitations and orientational ordering in deuterium at high pressure

Alexander F. Goncharov, Jon H. Eggert,* I. I. Mazin, Russell J. Hemley, and Ho-kwang Mao
Geophysical Laboratory and Center for High-Pressure Research, Carnegie Institution of Washington,
5251 Broad Branch Road N.W., Washington, DC 20005-1305

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High-resolution Raman spectra of ortho/para mixed crystals of deuterium to 4 K and pressures to 40 GPa reveal a number of phenomena. We find for para-containing samples a large enhancement of high-frequency vibron sidebands, a total of 11 vibron peaks, and significant changes in the low-frequency rotational excitations upon passage into the low-temperature phase. Analysis of the spectra reveals that the phase is orientational ordered and may form a superstructure derived from the high-temperature hcp lattice. The results also suggest that orientational frustration accompanies the transition in ortho/para mixed crystals. [S0163-1829(96)50346-2]

Vibrational spectroscopy has been instrumental in elucidating the crystal structures, bonding properties, and orientational state in the solid hydrogens since the earliest investigations of these materials. The Raman excitations of these solids consist of vibrons, rotons, and phonons; they contain a great deal of information because of selection rules derived from weak interactions between molecules in the solid, the persistence of J as a good quantum number to moderate pressures, coupling of nuclear spin and angular momentum, and translational lattice symmetry. Measurements of these excitations have been useful for structural studies as a function of temperature, pressure, and ortho-para state.[1] At low densities, the Raman vibrons form a multiplet associated with splitting of the $Q_1(J)$ bands ($\Delta\nu=1$; $\Delta J=0$),[1,2] the rotons [$S_0(J)$, $\Delta J=2$] are split into a triplet, and a single phonon [$Q_1(J)$; $\Delta\nu=1$, $\Delta J=0$)] are characteristic of the hexagonal-close-packed (hcp) structure. This was found to be stable for the $J=0$ solids and for ortho/para mixtures at high temperatures (e.g., near the melting line). In contrast, the crystal structure of the low-temperature ordered state for $J=1$ enriched solids at low densities is ordered fcc (space group $Pa3$), which is the lowest energy structure for electric quadrupoles.

The crystal structures and ordering schemes of the low-temperature phases at higher density, however, are unknown. At low pressures, H_2 and D_2 crystallize in the orientationally-disordered hcp structure (phase I).[3] Above about 20 GPa for D_2, 60 GPa for HD, and 100 GPa for H_2 a phase transition is observed by both Raman scattering and infrared absorption (phase II).[4–9] At pressures higher than 150 GPa, a transition to another phase (phase III) takes place in all three isotopes.[3,10,11] In contrast to the transition to phase III, the I-II transition pressure is expected to be dependent on the ortho/para state of the samples.[3] In o-D_2 (even J) the transition to phase II is reported to occur at 28 GPa in the low-temperature limit.[4] The Raman-active phonon has been observed in phase II of D_2 near 80 K.[7] Up to four infrared vibron bands have been observed for phase II of D_2 at these temperatures.[10] Both of these observations, as well as a recent low-temperature IR study,[12] rule out the $Pa3$ structure originally discussed for phase II.[4] Measurements are needed to characterize the phase and to test proposed structures over a wider P-T range; for example, the structure of phase II may depend on the ortho/para concentration, and further structural changes as a function of pressure and temperature may occur.

As for the low-density solid, spectroscopic techniques can be used to test structural models, including the states of orientational order-disorder, in these phases. The multiplet structure of the Raman vibron spectrum [$Q_1(J)$ bands] characteristic of the low-density solid evolves under pressure so that the spectrum is dominated by a single strong band over a wide pressure range.[13] With the continued development of spectroscopic techniques (see, Ref. 3), additional features have been observed in Raman spectra of dense hydrogens.[8,13,14] Here we present detailed measurements down to 4 K for deuterium that unexpectedly reveal up to eleven vibron bands as the solid passes into the low-temperature phase II. Moreover, we find a previously unobserved multiplet structure in the low-frequency roton spectrum. We suggest that this rich spectral activity can be understood as arising from band folding associated with molecular ordering in a structure derived from hcp. The measurements also reveal an intermediate region between phases I and II possibly associated with orientational glasslike behavior.

High-purity n-D_2 was loaded at room temperature in modified Mao-Bell diamond-anvil cells. Pressure was measured by the ruby gauge, using the quasihydrostatic pressure scale.[15] A helium cryostat was used in a continuous-flow regime for Raman measurements from 4 to 80 K. Spectra were collected (each usually within one minute) during temperature scans lasting 2 to 4 h; between scans the temperature was kept at 80 K to insure an equilibrium ortho/para concentration of close to 2:1.[1] The conversion rate is very small (0.06%/h) at low pressures; studies on both isotopes indicate that the rate increases with pressure but still remains low enough to consider the ortho/para ratio constant during the present measurements.[16] Several temperature runs were performed at different pressures, during which the pressure was found to be approximately constant (within 0.1 GPa). Ortho-rich D_2 was produced by keeping samples at l-He temperatures within phase I for several days. During this period, Raman roton spectra were monitored, and the intensity of the $J=0\rightarrow2$ roton transition was found to increase

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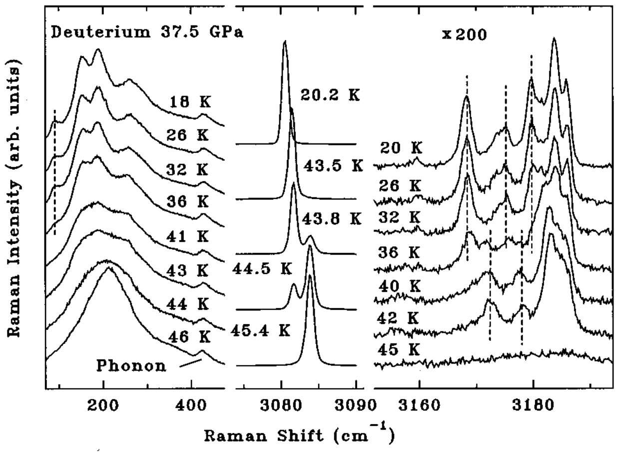

FIG. 1. Raman spectra of deuterium as a function of temperature at 37.5 GPa. The spectra are normalized for background intensity and corrected for the Bose factor at low frequencies. The dashed vertical lines identify the changes between 37 and 38 K.

relative to that of $J=1\rightarrow3$, indicating conversion. Raman spectra were excited with an argon-ion laser (488.0 and 514.5 nm) and recorded with both a 1.33 meter single-grating spectrograph (for higher resolution vibron spectra at 3100–3200 cm^{-1}) and triple spectrographs (for rotons and phonons at 50–1000 cm^{-1}). All systems were equipped with CCD detectors and the spectral resolution was 1 and 5 cm^{-1}, respectively.

The evolution of the Raman spectrum of D_2 with temperature at 37.5 GPa is shown in Fig. 1, and the corresponding frequency shifts are given in Fig. 2. The sample was an ortho/para mixture close to that of n-D_2.[17] Significant changes are observed in all three frequency ranges at 44 K. The main vibron at 3082 cm^{-1} shows a shift to lower frequency of about 2 cm^{-1}. Peaks corresponding to each phase are clearly resolved in the transition-temperature region (2 K), indicating that the frequency shift is discontinuous [Fig. 2(b)]. We also observed a dramatic intensity increase and narrowing of the high-frequency vibron sidebands in the transition temperature region (right panel of Fig. 1); these are very weak and broad in the high-temperature phase and approximately 200 times weaker than the principal vibron in the low-temperature phase. In previous work, two sidebands were evident;[8] with the increase in sensitivity and resolution, we now observe a total of 11 vibrons in the low-temperature phase. The low-frequency roton band, which is continuous with the ambient pressure $J=0\rightarrow2$ transition (left panel), splits at the transition and develops into a triplet, and a weak feature appears at lower frequency. The phonon persists at all temperatures and pressures, indicating that the structure is not $Pa3$; this is also observed in the ortho-rich samples. Reference 4 reported a splitting of the roton band (into a doublet) but no measurements of the phonon. All changes observed here are reversible, and no hysteresis was observed at the transition within the precision of the temperature determination (~0.5 K). We also observed no time evolution of the low-temperature phase spectrum in a control experiment in which the sample was held overnight at 6 K, thus showing there are no effects of ortho-para conversion.

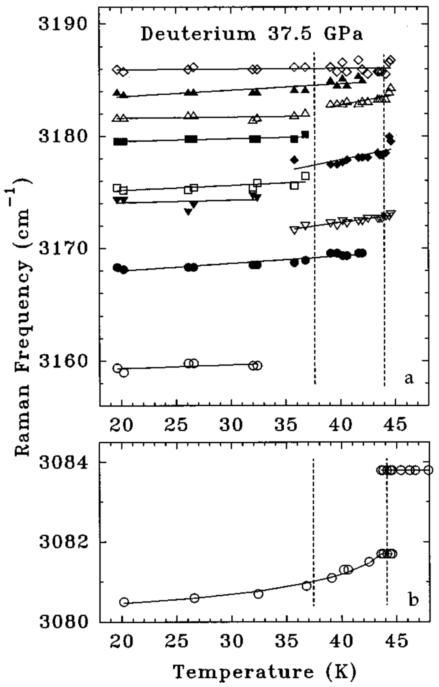

FIG. 2. (a) Temperature dependence of the Raman frequencies at 37.5 GPa in the vicinity of the phase transitions (dashed vertical lines). (b) Temperature dependence of the principal vibron. The value of $d\nu/dT$ decreases from about 0.2 cm^{-1}/K below the discontinuity to 0.04 cm^{-1}/K at low temperature where its frequency asymptotically approaches 3080.3 cm^{-1} at this pressure.

A second change in the spectra occurs between 37 and 38 K in the above samples. Although the main vibron is continuous, there are clear changes in the high-frequency vibron sideband region. Three of the lower sidebands show a discontinuity in frequency [Fig. 2(a)], and new, weak lines appear between the main vibron and the higher frequency sidebands (see below). Also, a new low-frequency line appears at 100 cm^{-1} and each component of the broad triplet narrows and becomes more distinct. We tentatively designate the intermediate (or transitional) region as II′, with the field of the lower temperature phase labeled as II (Fig. 3). The temperature difference between the first and second change in the spectra decreases with increasing pressure such that the two lines would merge near 45 GPa and 50 K, although the existence of two separate phase transitions remains to be determined. We point out, however, that the lower temperature boundary (II-II′) is close to the I-II line measured for ortho-rich deuterium. The I-II′ boundary was not observed in measurements on the ortho-rich D_2 samples. The lower temperature line (I-II) agrees with that determined by Silvera and Wijngaarden[4] for o-D_2. The I-II′ boundary is close to the phase line reported by Cui *et al.*[12] who studied a sample loaded as n-D_2.

The new vibron spectrum is thus remarkably rich, with at least eleven vibron bands observed in phase II of the para-containing sample. These bands could be associated with local modes due to the mixed crystal character of the sample. However, this is unlikely because (a) the bands appear abruptly at the phase transition; (b) they are weak, but sharp, unlike typical disorder-induced features; and (c) their pressure dependence follows that of the vibron fundamental.

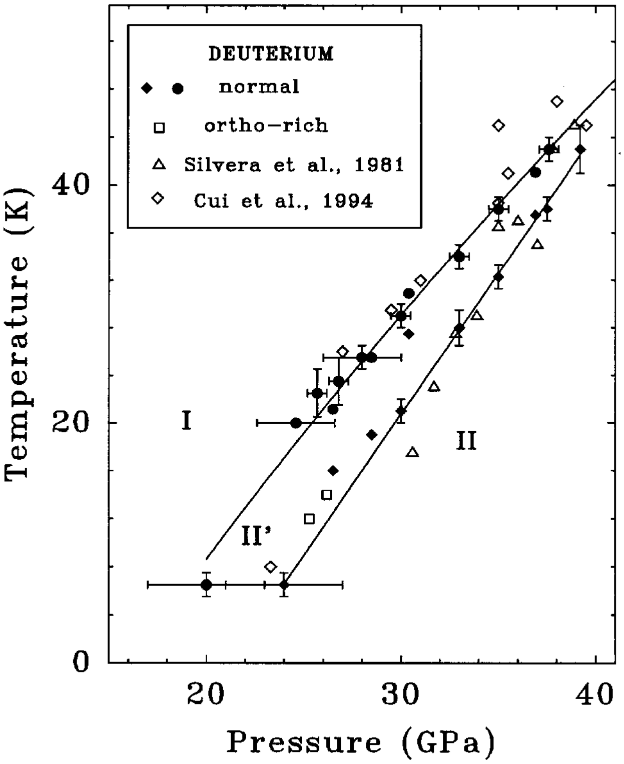

FIG. 3. Phase diagram of deuterium at low temperatures. The pressures reported in Ref. 4 have been corrected using the more recent quasihydrostatic pressure calibration (Ref. 15).

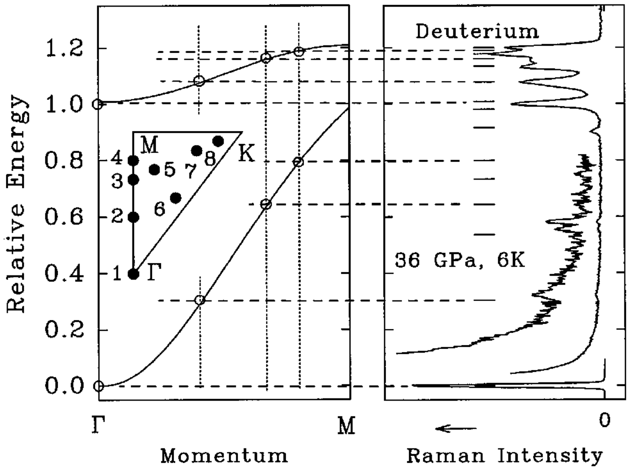

FIG. 4. Left panel: Calculated vibron band structure for hcp-structured hydrogen. The open points on the dispersion curves correspond to the zone center for a zone-folded structure. The irreducible zone is shown in the insert. Right panel: Detail of the vibron sidebands at 36.1 GPa and 6 K. The horizontal lines denote calculated frequencies for 3×5 zone folding as shown in the insert. The dashed lines show the frequencies corresponding to high-symmetry points obtained from the zone folding (i.e., along Γ-M). Improved agreement can be obtained by the introduction of additional effects (and parameters) such as anisotropy in the force constants and changes in the c/a ratio.

Alternatively, the origin of the new bands lies in a crystallographic change. The lack of hysteresis rules out a reconstructive transformation, and the phonon persists into the low-temperature phase; these observations indicate that the structure is derived from hcp.

Further insight can be gained from the band structure of the vibron. Infrared spectra of pure solids and Raman spectra of isotopic alloys reveal the width of the vibron band for the hcp solid (see Ref. 3), and one can calculate the vibron dispersion. We used the tight-binding model of van Kranendonk[1] and, as in Ref. 14, we neglected the effect of $J=1$ molecules and assume an R^{-6} dependence for the hopping amplitudes. The scale for the overall intermolecular hopping was set to match the bandwidth at the appropriate density. We included 400 nearest neighbors and used the ideal c/a ratio. Orientational ordering lowers crystal symmetry and allows modes that had been Raman inactive to be seen. Which specific modes may acquire Raman activity in this way depends on what superstructure the ordered phase forms with respect to the orientationally disordered hcp phase. We have tested all superstructures up to 6×6×6.

The results are shown in Fig. 4 for a representative spectrum at 36 GPa and 6 K. We find quite good agreement between the vibron frequencies and the calculations for a 3×5×1 superstructure. Most of the vibron sidebands (including the weak features at 3100–3150 cm^{-1}) can be explained as arising from this symmetry lowering and expansion of the unit cell, with vibrons having zero Raman activity in the hcp structure acquiring intensity by Brillouin zone folding and loss of inversion symmetry (Fig. 4). Unlike phase I,[18] similar bands appear in both the Raman and infrared spectra, indicating that phase II lacks inversion symmetry. Moreover, the pressure dependence of the frequency of the Raman vibron sideband at 3165.4 cm^{-1} coincides well with the infrared mode in phase I (Ref. 12). Infrared absorption spectra of D_2 in phase II (Refs. 10 and 12) show sidebands of similar shape and width to the Raman sidebands in Fig. 4 and are likely of the same origin. The present results suggest that the structures of such ortho-para mixed crystals of D_2 in phase II are quite complex (e.g., lower symmetry than those considered in Ref. 12 for o-D_2). Notably, Raman spectra of ortho-rich D_2 have a smaller number of vibron and roton bands,[19] indicative of a simpler ordering scheme.

Finally, we comment on the close proximity of the II-II′ boundary to the I-II phase line of o-D_2. Increasing concentration of para ($J=1$) molecules shifts the main ordering transition to higher temperature. We suggest that in the intermediate region the ordering is incomplete, and the process is finished with further cooling as the transition temperature for pure o-D_2 is approached. We further speculate that in the intermediate region the material exhibits glassy behavior arising from orientational frustration, perhaps analogous to the orientational glass found for ortho-para mixtures in a narrow temperature interval at ambient pressure.[20] The zone-folding calculation discussed above may be viewed as an illustration of how the vibron sidebands develop during the transition to the high-pressure ordered state. Further understanding of these phenomena will require detailed measurements as a function of ortho/para content and additional theoretical study. Direct structural information on the low-temperature phases of this material should be possible with the recent development of third-generation synchrotron x-ray techniques.

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*Present address: Department of Physics, Colorado School of Mines, Golden, CO 80401.

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[17] The equilibrium ortho/para concentration for D_2 is only weakly dependent on temperature above liquid nitrogen temperature (Ref. 1). At room temperature (i.e., n-D_2) it is 66–33% and changes to 70–30% at 77 K, where the sample was equilibrated in the present experiments.

[18] The broad infrared band in phase I is due to local breaking of the inversion symmetry by disorder associated with ortho/para impurities and rotational motion. The structure that appears in the Raman spectra in phase II is much richer and the peaks are much sharper. Comparison with phase I clearly shows that local symmetry breaking cannot produce this structure, unless there is a substantial change in the impurity distribution at the phase transition. That would imply diffusive motion which is inconsistent with the observed lack of hysteresis at the transition.

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