Ultrahigh Pressures: Optical Observations and Raman Measurements of Hydrogen and Deuterium to 1.47 Mbar

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Hydrogen and deuterium have been pressurized under static conditions to 1.47 Mbar, which is higher by a factor of 2 than previously reported static data. Measurements of the vibron indicate an initial increase and then a sharp decrease in frequency at pressures above 0.5 Mbar. At 1.14 Mbar the vibron frequency decreased to the zero-pressure value, and at 1.47 Mbar the frequency of the vibron in hydrogen is 90 cm^{-1} below the value of the vibrational mode of the isolated molecule. This pronounced softening of the vibron suggests strengthened intermolecular interaction.

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Experimental data on the high-pressure behavior of crystalline hydrogen and deuterium solids are of fundamental interest for the characterizing of intermolecular interactions in a prototype quantum solid.[1] In regard to solid hydrogen itself at very high compressions and at relatively high temperatures (i.e., ambient room temperature), the behavior of the molecular vibron in response to increasing pressures above 300 kbar has aroused considerable interest.[2] Details of solid hydrogen's molecular behavior at pressures in excess of 1 Mbar are speculative, awaiting experimental observation. The results of the present study, which was conducted with this range of pressure, may have bearing on the processes in hydrogen that eventually lead to formation of a metallic superconducting state. Prior studies had no success in raising the pressure of hydrogen above 0.7 Mbar. An important part of the study, therefore, was development of techniques and calibration to perform the experiments under the required extreme pressure conditions.

Optical observations of hydrogen and deuterium have been particularly valuable. The change in bonding can be determined by vibrational Raman and infrared spectroscopy. One of the striking features of the vibrational spectra measured to date in these systems is the behavior of the intramolecular stretching mode (vibron) on compression. The frequency of the mode (zone center, $\mathbf{k}=0$) of solid normal hydrogen increases with increasing pressure to 0.36 Mbar, but then decreases with the further application of pressure. This turnover in frequency was first noted in room-temperature Raman-scattering measurements on n-H_2 to a pressure of 0.63 Mbar.[3] Similar phenomena were observed in room-temperature Raman spectra[4] of n-D_2 and infrared spectra[5] of n-H_2 to 0.54 Mbar. The turnover was also observed in p-H_2 and o-D_2 at low temperatures in subsequent studies by Silvera and coworkers.[6]

The negative pressure shift in vibron frequency has been variously interpreted as a possible precursor effect of the eventual dissociation of the molecular bond thereby leading to an atomic (metallic) phase. It has also been predicted that the solid will transform gradually over a range in pressure before undergoing a first-order transition to an atomically bonded phase at higher pressure.[7,8] The maximum pressures attained in the present study are within or close to the region of the predicted transitions in the molecular phase.[2]

In this Letter, observations and measurements of the frequency shift of the vibron of n-H_2 and n-D_2 to 1.47 and 1.26 Mbar, respectively, are reported. The maximum pressures reached in the present study, which are higher by a factor of 2 than those of previous studies of hydrogen,[3] were achieved by means of new experimental designs.[9] Recently, experiments significantly exceeding 2 Mbar have been conducted in this laboratory on samples of corundum (ruby) and stainless steel[9] and on samples of gold plus ruby to provide a reliable pressure-calibration scale.[10] In this development work the shift with pressure of the ruby R-luminescence spectral line was calibrated against the equation of state of gold determined by *in situ* measurements of unit-cell volume. Shock-wave data on gold for the relationship of volume and pressure were used for reference.[11] Thus, the pressure was determined in the present experiments by measurement of the frequency of luminescence of ruby crystals included in the sample chamber of the high-pressure apparatus with hydrogen or deuterium. Four experimental runs, each reaching pressures exceeding 1 Mbar, were performed: three on hydrogen plus ruby, and one on deuterium plus ruby.

In the present experiments the sample chamber of the high-pressure apparatus was filled with hydrogen or deuterium as fluids prepressurized to 2 kbar at room temperature. The technique used is similar to the design of Mills *et al.*[12] In addition to its role as an internal calibrant for measurement of the pressure, ruby was used as a strong filler material to vary the sample volume in the experimental runs. The volume ratios are indicated in Table I. Raman spectra of the samples as well as luminescent spectra of the included

TABLE I. Experimental parameters.

Run	Diamond shape[a]						Gasket hole	Initial	Maximum	
	Cylinder side			Piston side						
No.	A (mm)	B (mm)	θ (deg)	A (mm)	B (mm)	θ (deg)	diameter (mm)	V_{H_2}/V_{tot}[b]	P (Mbar)	Sample
1	0.317	0.052	5	0.310	0.057	5	0.053	0.8	0.9	H_2
2	0.310	0.116	10	0.309	0.102	7	0.050	0.5	1.5	H_2
3	0.285	0.110	10	0.290	0.110	7	0.050	0.2	1.3	H_2
4	0.301	0.104	5	0.313	0.099	5	0.050	0.5	1.3	D_2

[a] A and B refer to the bevel and sample areas, respectively, and θ, to the bevel angle (see Ref. 9).

[b] Relative volume of H_2 in the sample at the time of loading, which was carried out at 2 kbar pressure of H_2.

ruby grains were measured with a specially designed micro-optical system coupled to a triple monochromator (Spex Industries Model 1877) that was equipped with an optical scanning multichannel analyzer (OSMA, Princeton Instruments Co.). The optical system was interfaced with a pentaprism simultaneous viewing of the sample, diaphragms, and back-lighted entrance slits while the sample was under pressure. The beam of an Ar^+-ion laser (Spectra Physics Co. Model 165; 488.0 nm) entered the high-pressure cell at an angle of 45° with respect to the load axis (135° scattering configuration). The beam was focused to a diameter of 10 μm on the sample, and an adjustable diaphragm in the system reduced the area sampled by the spectrometer to a diameter of approximately 5 μm. This geometrical arrangement had a number of advantages. The effects of pressure gradients within the hydrogen and deuterium samples were minimized. The diaphragm also reduced interference effects from the diamond emission, which increased significantly at pressures above 1 Mbar.

Another detectable signal resulted from first-order Raman scattering of diamond itself. The shift of this band, excited at the face of the diamond (culet), provided an indication of the pressure[13,14] that was consistent with the calibrated ruby scale, as did the increase in diamond fluorescence with pressure. Relatively low-power conditions of the exciting laser (20 mW) were employed in the measurements; no heating effects were detected when the laser power was varied by a factor of 5.

Both hydrogen and deuterium remained transparent to the highest pressures reached (1.47 and 1.26 Mbar, respectively, for the two solids). As shown in Fig. 1, the molecular vibron is clearly evident in the Raman spectra of these samples at ultrahigh pressure. At lower pressures the observed bands are assigned as $Q_1(1)$ ($\Delta v=1$; $\Delta J=0$, $J=1$) in hydrogen and $Q_1(2)$ ($\Delta v=1$; $\Delta J=0$, $J=2$) in deuterium. It should be noted, however, that these bands represent an envelope of bands in the Q branch of each solid. No clear resolution of possible contributions from ortho versus para isomers can be made.

The percentage frequency shift of the Raman bands of hydrogen and deuterium measured in this study is plotted as a function of pressure in Fig. 2. Also plotted are polynomial curves that had been fitted to earlier data.[3,4] The new data follow a similar trend to decreasing frequencies. The frequency of the vibron of solid hydrogen crosses the zero-pressure value and the shift becomes negative on further compression. At 1.47 Mbar the band in hydrogen is 90 cm^{-1} below the initial value. At low pressures the percentage shift in deuterium is similar to that in hydrogen. The ratio of frequencies of the corresponding bands in hydrogen and deuterium appears to be linear in pressure, as was observed in the earlier results at lower pressures.[4]

In both sets of spectra the decrease in frequency with pressure occurs with a corresponding increase in bandwidth. As discussed previously,[3,4] the room-temperature bandwidth decreases markedly at the solidification pressure. The drop is most notable for hydrogen (15 to 6 cm^{-1} vs 8 to 5 cm^{-1} in deuterium), and the decrease continues initially in the solid phase. A minimum value for the bandwidth occurred at 0.18 Mbar for both solids (4.5 and 3 cm^{-1} for hydrogen and deuterium, respectively). On further compression the bands broaden again, the bandwidth reaching 20 cm^{-1} in deuterium and 41 cm^{-1} in hydrogen at 1.26 Mbar. At the highest pressures of these experiments (1.47 Mbar) the bandwidth of hydrogen is ~ 80 cm^{-1}, although there is some uncertainty in the measurement because the apparent intensity of the band has dropped and the interference from the emission of the diamonds has increased.

The vibron evidently is the strongest band in the Raman spectra of hydrogen at high pressures, but it is also probable that other bands, such as those due to lattice phonons, could be observed if interference effects (i.e., from the diamond) were reduced still further.[5,16] Although the shift of the vibron to lower frequencies suggests that the intramolecular bond is continuing to weaken at a pressure of 1.47 Mbar, the solids must be considered predominantly molecular at

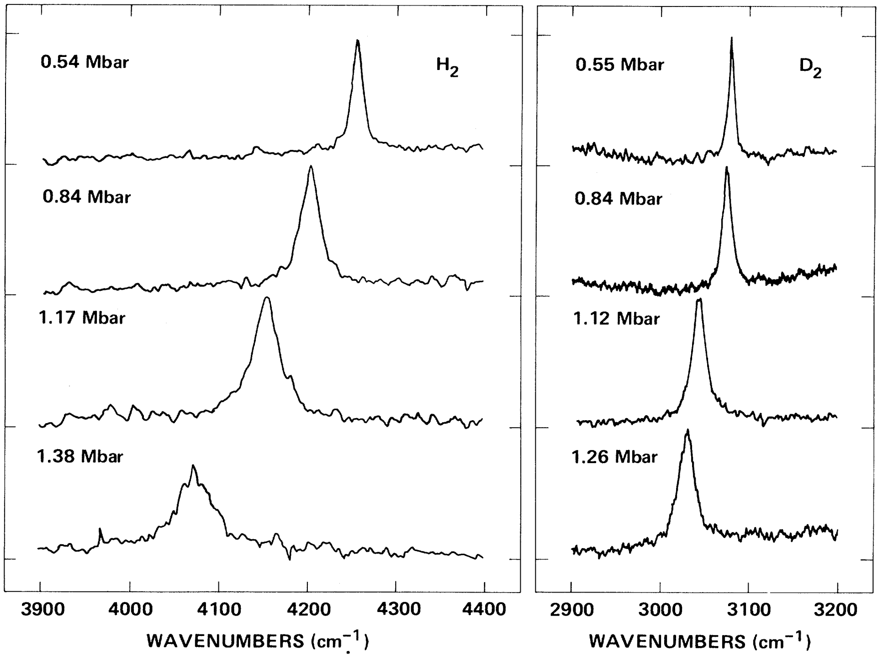

FIG. 1. Room-temperature high-pressure Raman spectra in the region of the vibron fundamental of solid normal hydrogen (instrumental resolution, 10 cm^{-1}) and solid normal deuterium (instrumental resolution, 3 cm^{-1}).

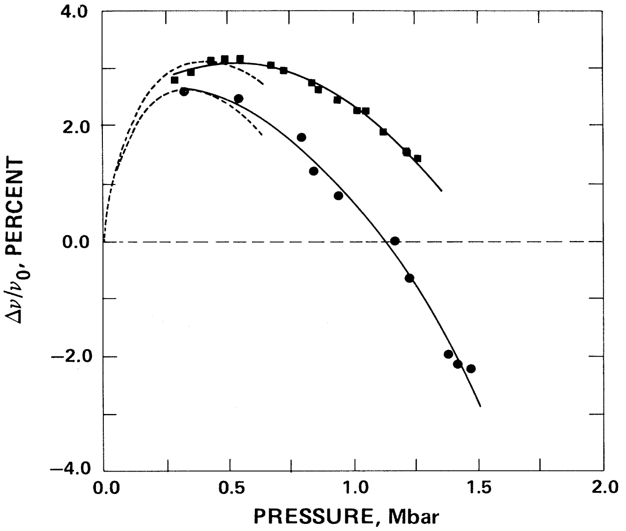

FIG. 2. Pressure shift of the molecular vibron of normal hydrogen (solid circles) and deuterium (solid squares) at room temperature. The zero-pressure frequency (horizontal line; $\Delta\nu = 0$ cm^{-1}) is 4155.2 cm^{-1} for hydrogen and 2987.2 cm^{-1} for deuterium (Ref. 15). The solid curves are quadratic least-squares fits to the data with the function $\Delta\nu$ (cm^{-1}) $= 105.78 + 55.66P - 135.35P^2$ (hydrogen) and $\Delta\nu$ (cm^{-1}) $= 65.72 + 100.77P - 95.70P^2$ (deuterium). The dashed curves in the lower-pressure region are fits to the previous data for the liquid (to 0.055 Mbar) and the solid (0.055–0.630 Mbar, hydrogen; 0.055–0.54 Mbar, deuterium).

the highest pressures on the basis of the character of the measured spectra. The difference between the pressure shifts of the vibron in hydrogen and deuterium is striking. Reference equations of state calculated for the two isotopes do not indicate large differences in compressibility,[17] and thus the larger shift in the frequency of the hydrogen band may imply that dissociation is more advanced than is the case for deuterium under equivalent pressures.

Neither the reversal in pressure shift of the vibron nor the difference in shift between hydrogen and deuterium has yet been explained theoretically.[6,18] Friedli and Ashcroft[8] have predicted a continuous insulator-metal transition in the molecular solid, with band crossing at a volume of 2.4 cm^3/mole, corresponding to a pressure of 2.1 Mbar.[17] It is interesting to note, however, that Hartree-Fock calculations on solid molecular hydrogen by Ramaker, Kumar, and Harris[7] do indicate a gradual increase in the intramolecular bond length with compression at high pressure. The increase in bond length would result in a softening of the observed vibron. Concomitantly these calculations show a continuous transition from the insulator to a metallic state in the molecular phase. According to their results such a transition would have begun at a volume of 3.5 cm^3/mole. Although the corresponding pressure was not given for this static-lattice calculation, from estimates of the equation of state[17] this volume appears to be equivalent to approximately 0.7

Mbar. The calculated dissociation of the molecular bond is consistent with the measured Raman spectra.

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