Infrared Properties of Ortho and Mixed Crystals of Solid Deuterium at Megabar Pressures and the Question of Metallization in the Hydrogens

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We have studied the infrared absorption spectra of mixed ortho-para and pure ortho deuterium crystals down to liquid helium temperatures and pressures to 194 GPa in search of an insulator-metal transition. Band theory suggests metallization in this range, where densities are increased more than 10 fold. Our energies extend down to 0.37 eV, the lowest yet reported. No clear evidence of metallization is found, according to a Drude analysis. Significant changes in the spectra are observed when mixed ortho-para samples are converted to pure ortho D_2.

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Above pressures of about 150 GPa the solid hydrogens (hydrogen and its isotopes) have transitions to new phases called the hydrogen *A* (H-*A*) and the deuterium *A* (D-*A*) phases [1,2]. Since the D-*A* phase line has recently been shown to be similar to that of hydrogen (see Fig. 1), it is reasonable to assume that the as yet undetermined nature of these phases is the same for the two isotopes [3]. It has been speculated [4], and even claimed [5,6], that the H-*A* phase is the metallic molecular phase, based on optical measurements. An optical method for determination of an insulator-metal (IM) transition is to observe the appearance of a Drude edge in the metallic phase. One of the principal problems in earlier studies was the limited extent of photon energies [5–7]. In this article we extend measurements of infrared absorption down to an energy of 0.37 eV at liquid helium and higher temperatures on both mixed ortho-para (*o*-*p*) and high purity ortho deuterium crystals. Reliable IR measurements in a diamond anvil cell (DAC) in this spectral range are difficult to acquire as the diamond window has an optical absorption length a few thousand times longer than the deuterium sample. We have developed a technique for normalizing out absorption due to the diamond window. In both pure and mixed crystals there is an interesting increase of the absorption with increasing pressure, but we were unable to attribute this to metallization. Significant increases in the low energy absorption of pure o-D_2, compared to mixed crystals, demonstrates an unusual sensitivity of this electronic property to the nuclear spin states. Since the *o*-*p* states determine the molecular orientational states, this may be evidence that the mixed *o*-*p* state leads to electron localization, as has been suggested by Ashcroft [8].

The hydrogens undergo a number of phase transitions, most usefully discussed in terms of their phase diagram shown in Fig. 1. The known phases are those of orientational order. o-H_2 and p-D_2 have orientationally ordered phases at zero pressure and a few degrees kelvin on an fcc lattice. p-H_2 and o-D_2 molecules are essentially in spherically symmetric quantum states at low pressure and form hcp lattices. However, at high pressures the ground quantum state distorts and these species also orientationally order. This phase is called the broken symmetry phase (BSP). For mixed *o*-*p* crystals, phases of orientational order fall between the two extremes of pure ortho and para; since HD does not have metastable *o*-*p* species, it has an unusually shaped phase line for orientational order [9]. The hydrogens are predicted to become metallic in the molecular state by band overlap in the range of 150–300 GPa and to become atomic metals at 300 to 400 GPa [10]. Hemley and Mao [11] first observed a discontinuity in the hydrogen vibron frequency at a single point (150 GPa and 77 K). Lorenzana, Silvera, and Goettel [1] determined the phase line and showed that this signaled a unique new phase that only existed at high pressure; they named this the H-*A* phase. A similar study for deuterium has been carried out by Cui *et al.* [2] to determine the D-*A* phase line. This transition was suspected to be the IM transition for the molecular hydrogens [4,5].

Mao, Hemley, and Hanfland (MHH) studied optical reflection in the IR of hydrogen at room temperature up to 176 GPa [5]. They fit this data to a Drude model [12] and claimed direct evidence that hydrogen becomes metallic above 150 GPa. Eggert *et al.* [7] studied optical absorption and reflection in hydrogen to 230 GPa and

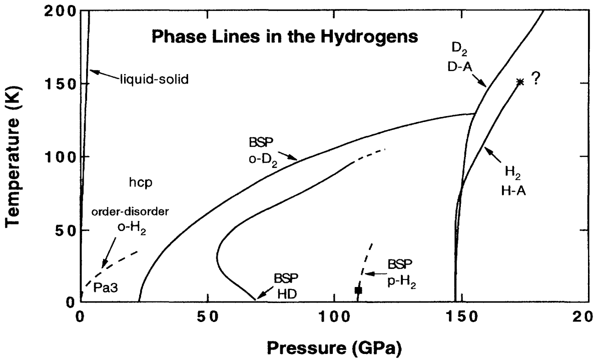

FIG. 1. A phase diagram for the hydrogens. Dotted lines indicate expected behavior.

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found no evidence of a Drude edge and showed that the Drude analysis of MHH was internally inconsistent. Hanfland, Hemley, and Mao (HHM) [6] then presented IR absorption data for hydrogen to 161 GPa, again with a rising edge which required substantial revision of their earlier Drude parameters, still claiming evidence for metallic behavior. Silvera [10] and later Ruoff and Ghandehari [13] pointed out problems with this analysis so that the HHM result seems to be inadequate for a claim of metallization.

A sample of deuterium was pressurized in a DAC; the pear-shaped sample area was about $30 \times 55\ \mu\mathrm{m}^2$ in dimensions. The thickness was less than $2.9 \pm 0.5\ \mu$m at the highest pressure of 194 GPa. This bound was determined from the initial (zero-pressure) volume, the equation of state of deuterium and the sample area at the given pressure. Raman frequencies of the vibrons were used for pressure determination, as discussed in Ref. [2]. At high pressures the sample had a pressure spread of 5–10 GPa. The DAC was in a helium cryostat with a number of windows for *in situ* measurements. Samples could be held at low temperatures indefinitely to convert to essentially pure o-D_2 [14]. At megabar pressures single crystals have never been produced and we assume that our samples are powderlike. Even if the samples are anisotropic, a Drude optical behavior would be observable.

We used a Burleigh tunable color center laser with a useful spectral range from 0.37 to 0.55 eV. The chopped laser beam was split into a reference arm and a sample arm of equal lengths, detected by two independently cooled InSb detectors; the laser beam overfilled the sample. The signal from the reference beam was used to normalize the signal from the sample beam. Such a normalization when properly scaled for beam splitter factors, detector sensitivity, and geometric baffling of the sample yields the absorption of the sample, the diamonds, and the cryostat windows, while compensating for laser fluctuations. Using Beer's law, the intensity at the detector is $I = I_0 \exp(-\Sigma \alpha_i d_i)$, where I_0 is the intensity incident on the cryostat and the optical density (OD) is $\Sigma(\alpha_i d_i)$, the sum of the absorption coefficients times the length of each component in the optical path (we omit interference effects and reflection losses from this discussion). Ignoring the cryostat window effects, the normalization yields for the optical density $[\alpha_s(P,T)d_s + \alpha_D(P,T)d_D]$, where s is the sample at pressure P and temperature T, and D represents the diamonds.

The sample itself has very weak absorption at lower pressures in this region and characteristic transmission spectra are dominated by the absorption from the diamond anvils, as shown in Fig. 2. The strong sample absorption at 194 GPa in the 3150 cm^{-1} region is due to a vibron in the D-A phase; the intensity grows rapidly with increasing pressure [2]. The sharp absorption dip at about 3107 cm^{-1} is due to an impurity in the diamond anvils [15]; the two broad absorption lines at about 3200 and 3700 cm^{-1} are due to intrinsic three-phonon absorption in diamond [16]. Room temperature measurements were made of the unstressed diamond anvils, as well as other representative diamonds to find their characteristic spectra [see Fig. 2(d)]. These were in reasonable agreement with features observed in the stressed, cooled diamonds in the DAC. Figure 2 demonstrates one of the principal difficulties in making accurate measurements of the absorption coefficient of the sample: the diamond windows have a temperature dependent absorption spectrum. Additionally, the absorption signal to noise was limited by two factors: (1) The six cryostat windows yielded complex resolvable interference patterns which could not be normalized out, due to spatial shifts of the laser beam or sample; and (2) the laser beam shifted while it was being swept in frequency, so that the intensity profile of the part of the beam passing through the sample changed, which distorts the measured transmission. To minimize this effect the optics were realigned every 100 cm^{-1}; minor scalings (of order 5%–10%) were necessary in patching

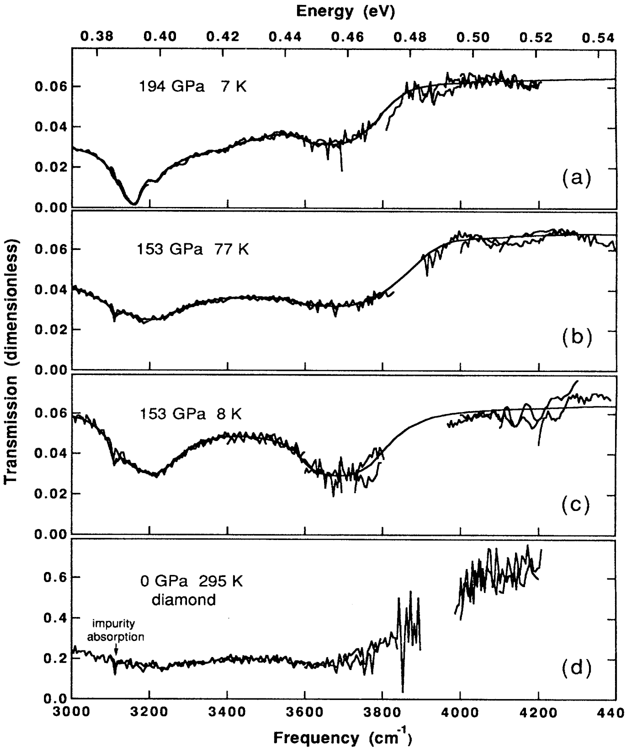

FIG. 2. Absolute transmission spectra. (a)–(c) Deuterium plus diamonds plus cryostat windows. The transmission was reduced by a factor of 15 due to masking by the gasket. Solid lines are guides to the eye. (d) Transmission of diamond corrected to account for absorption by two diamonds, but only two vacuum diamond interfaces, since in the experiment at the diamond-deuterium interface, the indices of refraction are very close and thus there is little reflective loss. Note that the width of the two broad diamond peaks at 3200 and 3700 cm^{-1} are temperature dependent. In the region between 3800 and 4000 cm^{-1} some data were thrown out, due to laser instabilities.

together some of the sections so that the transmission was continuous.

Transmission spectra of samples were measured at constant pressure and temperature. In particular, a spectrum was measured at 153 GPa and 8 K so that the sample was just entering the D-A phase; this was used to normalize most of the spectra presented here. By such a normalization procedure the spectral features of the cryostat and diamonds can in principle be removed, leaving only the differential absorption due to deuterium at the two thermodynamic points. In detail we measure $[\alpha_s(P, 8\text{ K}) - \alpha_s(153, 8\text{ K})d_s + \int[\alpha_D(P, 8\text{ K}) - \alpha_D(153, 8\text{ K})]dd_D$, where the OD of the diamond is an integral since the stress in the diamond varies along d_D, but is mainly concentrated in a region about 50 μm long near the culet. Most of the contribution to the integral cancels out. The contribution from the stressed diamond is small because the stress spreads the phonon dispersion in frequency, yet the total integrated absorption will remain about the same for the three-phonon band, since the total number of states is unchanged.

If the D-A phase is metallic with a Drude edge within our spectral range, then we should observe rising absorption with decreasing frequency. As the pressure is increased, the carrier density will increase due to increased band overlap and the plasma frequency will increase so that the Drude edge will shift to higher frequencies. In Fig. 3 we show absorption spectra for deuterium normalized in the way described. We expect a small normalization problem at 3200 and 3700 cm^{-1} (the peaks of the three-phonon diamond absorption) leading to bumpiness in the background for the 3200–3700 cm^{-1} region. We estimate that the error in optical density at the three-phonon peak is 0.06.

It is most interesting to focus attention on the broad band low frequency behavior (ignoring the vibron absorption line). There are two trends to observe: (1) As the pressure increases, the absorption generally increases, and (2) in comparing the spectra of mixed o-p crystals to those of pure o-D_2 crystals [Fig. 3(b)], the latter absorb more strongly as the frequency decreases.

We give a global view of IR measurements in the hydrogens in Fig. 4 where we have appended the earlier data for hydrogen by Eggert, Goettel, and Silvera [7] and HHM [6] to our deuterium data, as well as the measured vibron peak in hydrogen [17]. The data of Eggert, Goettel, and Silvera, which extend to 230 GPa, show no absorption features., The data of HHM have a rising edge which flattens out in a manner uncharacteristic of a Drude edge. We note that the hydrogen vibron which was measured at 77 K overlaps the region of the rising edge. We speculate as to the possibility that this feature is present at room temperature (temperature of the spectra of HHM) and is thermally broadened so that the "Drude" edge is actually the broadened high frequency side of the vibron line. We expect that their sample was not in the H-A phase at this pressure and temperature, however, the mixed o-p nature of the sample may allow for impurity induced transitions [2].

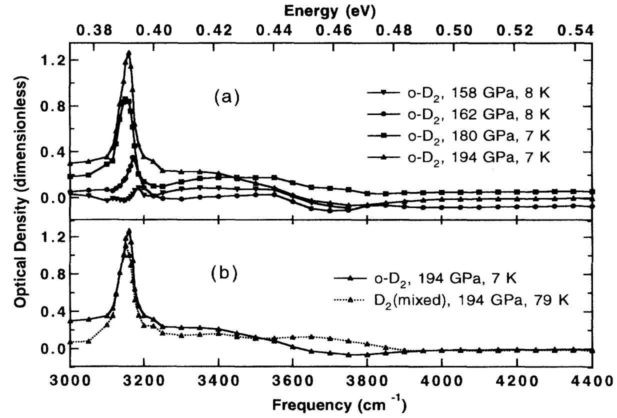

FIG. 3. The differential optical density for deuterium found by normalizing to the absorption for deuterium at 153 GPa and 8 K. (a) shows the progressive development as the pressure is increased at low temperature, while (b) shows the change with o-p concentration. Here, the normalizations are made with corresponding spectra for 7 and 79 K at 153 GPa. In (a) the displacement of the curves in the high frequency range is attributed to small changes in the gasket transmission area for different pressures. We did not correct for this as our microscopic observations of the areal changes were not of sufficient resolution. Shifting of the cure does not affect the conclusions concerning the low frequency trends. Error bars, dominated by systematic errors, represent our estimates of uncertainty due to absorption in the diamond and patching together of spectral ranges.

In addition to the experimental data, we plot some theoretical Drude absorption curves [12]. These Drude curves are not at all meant as fits to our data, but rather to show that there are families of parameters for a metallic state that have slowly rising curves which could be compatible with our data. It is not difficult to find parameters such that the characteristic Drude edge for a metal would not be observed, due to our limited frequency range. In Fig. 4, curves 1 and 4 have sharp edges due to the small value of the scattering rate h/τ; this parameter increases for curves 2 and 5, and becomes very large for 3 and 6. We expect that h/τ might be quite large in the high pressure hydrogens due to strain induced defects and ortho-para impurity scattering. We conclude that all existing data are inadequate to determine if the D-A (H-A) phase is metallic; it will be necessary to extend measurements to still lower energies.

It may be that the A phases are not metallic and new data must be carefully considered. The IR spectrum displays a vibron (Fig. 4) whose intensity grows rapidly with increasing pressure in the A phase which cannot be explained by mechanisms active at low pressure. Orientational disorder of molecules (such as in mixed o-p crystals) may lead to Anderson localization [8]. Localization might occur even for pure crystals such as o-D_2; since the electronic motions are much faster than

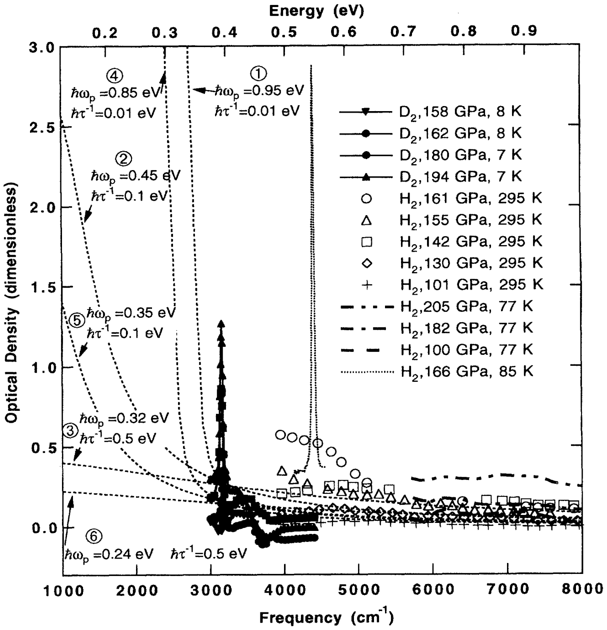

FIG. 4. The differential optical density for deuterium measured in this work (filled symbols) along with the absolute optical density for hydrogen from Ref. [6] (open symbols), [7] (broken lines), and [17] (dotted curve). The dashed curves 4, 5, and 6 are theoretical curves for Drude absorption which possibly could fit to our data.

the nuclear motions, the electrons in a lattice might be sampling a disordered array, which for static observations is perfectly ordered [18].

In summary, we have measured the broad band absorption to the lowest frequencies yet reported for the hydrogens. Deuterium in the D-*A* phase in the 200 GPa pressure region does not exhibit a sharp Drude edge down to 0.37 eV, but shows a tantalizing rising absorption that may be the high frequency wing of a Drude edge. The earlier reported [6] Drude edge in hydrogen was probably misidentified, but measurements similar to those reported here on deuterium should be made. Ortho-para impurities affect the broad band absorption spectra, another fascinating observation, with possible deep implications.

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