Synchrotron Infrared Spectroscopy to 0.15 eV of H_2 and D_2 at Megabar Pressures

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New synchrotron infrared absorption and reflectivity techniques have been developed to test predicted band overlap metallization in H_2 and D_2 above 150 GPa at various temperatures. Measurements on both isotopes to maximum pressures of 216 GPa show no evidence for Drude excitations in the midinfrared to near-infrared spectrum. The most definitive are measurements on D_2, which remains transparent down to 0.15 eV at 170 GPa and 83 K. The results put new bounds on the optical conductivity and possible band-gap closure at the 150-GPa transition. In addition to strong vibrational transitions, new infrared absorption features are observed.

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The possibility that solid molecular hydrogen will transform to a metallic state prior to pressure-induced dissociation at megabar pressures (>100 GPa) has been the focus of experimental and theoretical study since the predictions of Ramaker, Kumar, and Harris [1] and Friedli and Ashcroft [2] of band-overlap metallization. With systematic improvements in diamond-cell techniques, Mao, Bell, and Hemley [3] pressurized hydrogen to 147 GPa and room temperature but found no evidence for metallization. In 1988, Hemley and Mao [4] discovered a phase transition in the molecular solid at 150 GPa and 77 K, and theoretical calculations by Barbee *et al.* [5] suggested that the new phase could be metallic. A large number of subsequent calculations predicted significant changes in electronic properties at these pressures, and one of the major theoretical problems was how to preserve the band gap to these pressures [6–8]. The spectroscopic features indicated that the transition involved orientational and structural changes. In addition, the sample remained transparent in the high-pressure phase to at least 250 GPa [9]; at higher pressures there was evidence for absorption at visible wavelengths, results that provided the first experimental support for the theoretically predicted decrease in the band gap with pressure and the band-overlap mechanism of metallization.

Optical experiments were subsequently designed and conducted specifically to test the theoretical prediction of metallization and to determine the transition pressure. Eggert, Goettel, and Silvera [10] measured the index of refraction to 70 GPa and on the basis of an extrapolation of a single-oscillator model for the index predicted band-overlap metallization at 148 GPa from an apparent dielectric catastrophe. Direct measurements of the index of refraction at these pressures revealed no dielectric catastrophe [11] but instead showed there is a decrease in energy of electronic transitions associated with the direct gap, consistent with earlier observations to ~300 GPa [9]. However, closure of the indirect gap was still possible. In fact, a large number of theoretical calculations predicted closure below 200 GPa (e.g., [2,5,7,8]).

Searching for a Drude feature as direct evidence of metallization by closure of the indirect gap started in 1990 [12]. Because hydrogen remained transparent in the visible region to at least 250 GPa [9], it was necessary to extend the measurements into the infrared region. The constraints of possible Drude parameters have since depended most upon the experimental progress of measurement capabilities to lower energy at high pressures. Mao, Hemley, and Hanfland [12] measured IR reflectivity of hydrogen at 177 GPa down to 0.5 eV and showed a systematic and reproducible increase at the low energy range of the spectrum. They demonstrated that the increase could be modeled as a Drude edge with a plasma frequency ω_p as high as 2.42 eV, suggesting metallization.

However, when both absorption and reflectance over a limited energy range (>0.8 eV) were measured later [13], the low absorbance contradicted the Drude model of high ω_p. Eggert *et al.* [13] concluded that either the hydrogen above 150 GPa might not be metallic or it was metallic with a small ω_p which could be tested at lower photon energy (further into the infrared). Their absorption measurements did not reach the energy range (0.8–0.5 eV) in which the reflectivity increase was observed [9]. Hanfland, Hemley, and Mao [14] presented absorption measurements down to 0.5 eV, and showed a systematic rise with increasing pressure; but the strength of the absorption was weaker than that predicted by the reflectivity with a large ω_p. It was pointed out that if sample texture due to the anisotropy of the material, thin film effects, and diffraction were significant, the reflectance (measurement of an interface property) and the absorption (which measures a bulk property) might be uncoupled [14]. Alternative hypotheses [14] proposed to explain the observations included Drude absorption with a small ω_p, vibron excitation, and electronic interband transitions. Meanwhile, motivated by considerations of Ashcroft [6], theoretical calculations by Kaxiras, Broughton, and Hemley [15] revealed a new class of structures that are both more stable than those previously considered and preserved the band gap to considerably higher pressures than the 150-GPa transition.

The problem has been the focus of several more recent studies. Theoretical calculations have been carried out which go beyond the local density approximation and/or treat lower energy structures [16–18]. Although these calculations generally find evidence for band overlap above 200 GPa, the question has not been resolved because the crystal structure of phase III is not known; in addition, most calculations do not include important dynamical effects. In a recent experimental study, Cui, Chen, and Silvera [19] presented absorption data down to 0.37 eV, showing a "tantalizing rising absorption" that they interpreted as supporting the possibility that phase III is metallic. They showed that Drude models with ω_p as high as 0.95 eV in phase III (D_2 at 194 GPa) were still consistent with the data. Due to the limited frequency range, however, they concluded that all existing data were inadequate to determine whether the phase III is metallic; it would be necessary to extend measurements to still lower energy.

To test the hypotheses of a Drude feature with a small ω_p or interband transitions requires measurement capabilities to unprecedented low energy and high resolution. Since 1992, the high-pressure synchrotron infrared technique has been successfully developed and used for vibrational spectroscopy of dense hydrogen to 0.5 eV [20–22]. We report here extended synchrotron infrared absorption and reflectivity spectra to significantly lower energies. The measurements extend the energy range of previous measurements [14,19] by over a factor of 2 and place new bounds on possible carrier density to 216 GPa.

A number of improvements in synchrotron technique were required for the present studies. This included the design and implementation of Cassegrain-type mirror objectives with large working distance and sufficiently large-angle aperture (0.25) for simultaneous absorption and reflectivity measurements over a broad range with 10–15 μm sample dimensions [23]. In addition, the study required careful analyses of data, which are complicated by several factors. First, unambiguous determination of a broad absorption component requires accurate measurement of the baseline. This is not a problem for the vibron features because they are narrow, but is important for broader electronic (or vibrational) excitations. A second (and related) problem is the determination of pressure- (and temperature-) induced changes in the diamond anvils. Examples of such effects in the visible spectrum for natural diamonds at pressures above 150 GPa have been documented [24]. These features could include both narrow or broad bands. Information on these effects can be obtained by varying the type of diamond anvils (e.g., type I or II) as well as by numerous control experiments with a variety of samples. Third, diffraction effects can attenuate the transmitted light as the wavelength approaches the dimensions of the sample. This contribution was determined by using samples of varying size and shape.
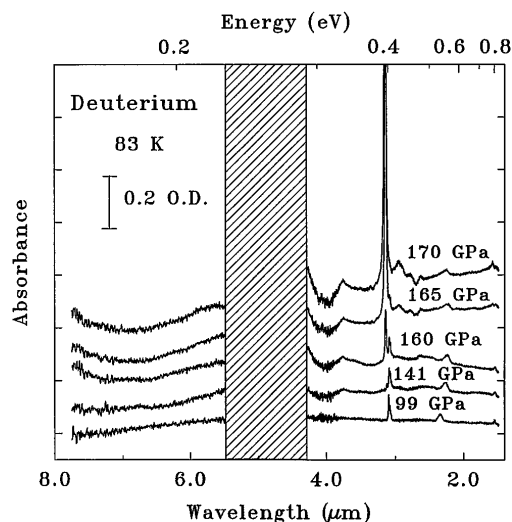

FIG. 1. Infrared spectra of deuterium as a function of pressure at 83 K. The sharp band near 0.4 eV is the vibron fundamental, and the higher frequency peaks are vibron combinations and overtone bands. The frequency range of the high two-phonon absorption of the diamond windows is hatched. Derivativelike structure near 0.4 eV arises from the pressure-induced change in diamond three-phonon absorption.

Representative low-temperature spectra as a function of pressure are shown in Fig. 1. The transition to phase III is easily observed by the onset of the strong vibron absorption near 3.1 μm (0.4 eV). With type II diamonds and KBr optics, we are able to measure the spectrum down to 8.3 μm (0.15 eV or 1200 cm^{-1}). With the extended range, we are able to access an important new window of the spectrum below the two-phonon diamond anvil absorption. We find no evidence for Drude absorption in this region. The small increase at the longest wavelengths is suggestive; however, such changes can be modeled as arising from diffraction effects due to decreasing sample size as the wavelength approaches the sample dimensions. Figure 2 compares the measurements at the highest pressure with Drude model curves taken from the recent study of Cui, Chen, and Silvera [19], which were consistent with the laser measurements reported in that study. We find that the Drude behavior from models 4 and 5 is consistent with the present direct measurements, but that of models 1, 2, and 3 is not. The transmission observed to 0.15 eV puts a strong bound on possible carrier density; specifically, if the phase is metallic at this pressure, the plasma frequency ω_p is less than 0.3 eV. However, we emphasize that the data are equally well fit with $\omega_p = 0$ (i.e., no Drude feature).

A large number of experiments were performed to test the reproducibility of the measurements. In addition, it is important to examine the temperature dependence of the spectra to test for the possibility of thermal excitations across the band gap, and to compare with the earlier room temperature measurements, which were carried out with conventional methods [13,14]. Figure 3 shows
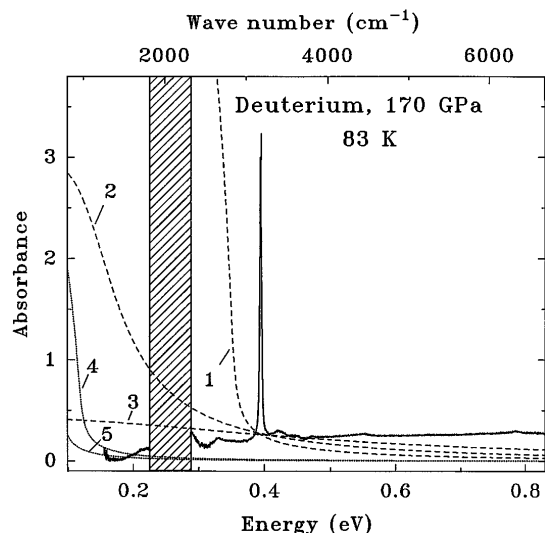
FIG. 2. Synchrotron infrared absorption spectrum for deuterium in phase III compared with calculated Drude model curves. Curves 1–3 are those calculated by Cui, Chen, and Silvera [19], which fit their data but are inconsistent with the present direct measurements to lower energies (1: $\hbar\omega_p = 0.55$ eV, $\hbar/\tau = 0.01$ eV; 2: $\hbar\omega_p = 0.45$ eV, $\hbar/\tau = 0.1$ eV; 3: $\hbar\omega_p = 0.32$ eV, $\hbar/\tau = 0.5$ eV). Curves 4 and 5 represent a family of models consistent with the new data and provide upper bounds on possible carrier density (4: $\hbar\omega_p = 0.32$ eV, $\hbar/\tau = 0.01$ eV; 5: $\hbar\omega_p = 0.24$ eV, $\hbar/\tau = 0.01$ eV). The baseline offset between the measurement and models is associated with the mismatch in refractive index between diamond and sample, and changes in multiphonon absorption in diamond.

representative spectra for H_2 between 167 and 212 GPa, and variable temperature from different experiments. With the orders of magnitude improvement of resolution and sensitivity made possible by the synchrotron technique, the absorption features associated with the vibron, rotons, and phonon can be distinguished. The temperature dependence of the vibron intensity at 167 GPa shows that the phase I-III boundary [25] was crossed with no measurable broad band absorption at low energy (to 0.18 eV). The spectra show some isotope-independent structure in the 0.3–0.5 eV range (Figs. 1 and 3), which is attributed to the pressure and temperature dependence of third-order diamond absorption from the anvils. The measurements show that the previously observed structure in the absorption at 0.5–0.8 eV [14] arises from the vibrational transitions (as discussed in Ref. [14]).

Reflectivity spectra were also measured with the new synchrotron technique. Figure 4 shows the reflectivity and absorption measured in the vicinity of the vibron for hydrogen. Reflectivity spectra show a dip shifted to higher energies with respect to the absorption peak. This structure is superimposed on interference fringes from 0.4 to 1.1 eV (not shown), which also indicates no measurable broad band absorption. The spectrum is modeled with dielectric function for hydrogen of the form
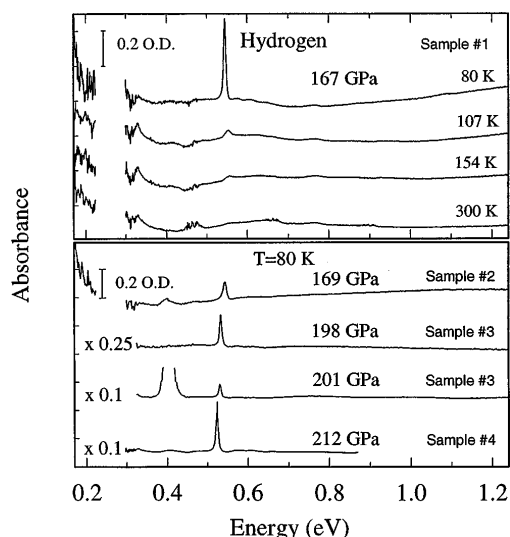

FIG. 3. Absorption spectra of hydrogen above 150 GPa over a broad spectral range from different experiments. The temperature dependence of the absorption is shown. The transition from phase I to phase III occurs between 107 and 80 K. The absorption spectra shown in the lower panel correspond to samples with different thicknesses. There is a dramatic rise in absorption near 0.41 eV for sample 3 at 201 GPa (absorbance >2 OD, which is not measurable).

$\varepsilon(\omega) = \varepsilon + f\omega_0^2/(\omega_0^2 - \omega^2 - i\omega\gamma_0)$, where f is the oscillator strength, ω_0 and γ_0 are the vibron frequency and damping, and $\varepsilon = n^2$ is the high-frequency dielectric constant. The model accurately reproduces the data and gives $f = 0.013$ for the strong infrared vibron, consistent with previous work [22]. The fact that the dip in reflectivity is shifted to higher frequencies indicates that the refractive index of hydrogen is larger than that of stressed diamond, a result that could not be determined from previous measurements [14].

The above results are thus consistent with the theoretical calculations predicting preservation of a band gap up to at least 200 GPa [15–17,26,27]. Many of these calculations now predict band overlap in the vicinity of 250–400 GPa. It has also been proposed that, within a band picture, overlap should occur, but the transition is precluded by the existence of intermediate insulating states that are not treated in typical electronic structure calculations. These include the formation of an excitonic insulator [28], states in which the electrons are localized by the presence of disorder [28], and an intermediate ionic phase [27,29]. It is therefore of interest also to look for spectroscopic signatures of such states. A number of anomalous optical features have been observed that may be relevant to this issue. Experiments on H_2, D_2, and HD show the appearance of an intense band system near 0.4 eV with a variable onset pressure. An example from a H_2 experiment is shown in Fig. 3, where the intensity of the band increases abruptly near 200 GPa. The temperature dependence of the band was studied closely in experiments on
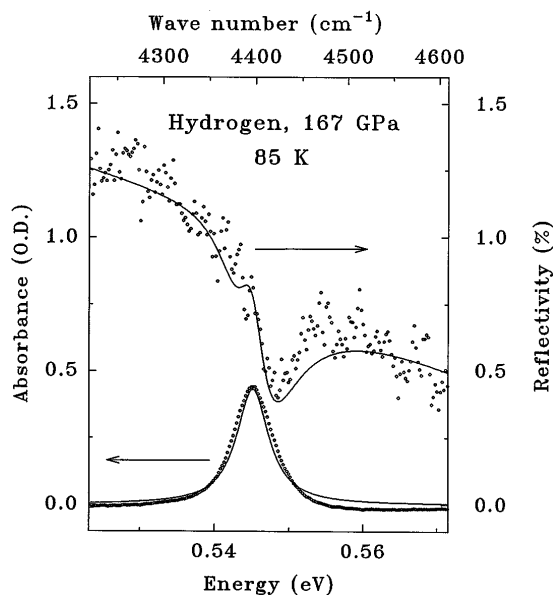
FIG. 4. Absorption and reflectivity in the vicinity of the strong vibron of hydrogen in phase III. The points are the experimental data; the lines correspond to the dielectric model calculated with the following parameters (see text): $f = 0.0134$, $\omega/2\pi = 4396$ cm^{-1}, $\gamma_0 = 42$ cm^{-1}; diamond refractive index, $n_d = 2.4$; hydrogen refractive index, $n_{H=2.7}$; and sample thickness, $d = 0.72$ μm.

D_2 and found to disappear at a T_c of 200 K. This behavior is close to previously observed anomalous low-frequency Raman bands (240−280 cm^{-1}) [30]; both sets of features appear in the same pressure range and exhibit the same critical temperature behavior. The lack of an isotope effect on the frequency demonstrates that the excitation does not involve hydrogen or deuterium vibrations; although the infrared band is close to the diamond three-phonon absorption, its intensity is significantly higher. This leads to the hypothesis that these features are associated with unusual behavior of the diamond-sample interface or the bulk sample, perhaps a nonvibrational (i.e., electronic) excitation. Understanding these phenomena, as well as testing the theoretical predictions of band overlap above 200 GPa, requires continued measurements at higher pressures over a wide energy range.

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