

## Optical absorption measurements of hydrogen at megabar pressures

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Absorption measurements are carried out on solid molecular hydrogen to 172 GPa at 295 K in a diamond-anvil cell from 0.5 to 3.0 eV. Analyses of both absorption and reflectance spectra provide complementary constraints on Drude-model parameters under the assumption that the band gap has closed at the highest pressures. Contributions from interband and vibrational transitions, optical effects associated with preferred orientation of the hydrogen, and stress-induced changes in the diamond refractive index are also examined.

It is now possible to study experimentally solid hydrogen in the megabar range ( $>100$  GPa) in order to examine its theoretically predicted transition to a metallic phase.<sup>1-9</sup> Direct evidence for metallization requires containment of hydrogen at the requisite pressures combined with *in situ* measurements of dielectric properties under these conditions. Although such experiments are becoming feasible with the development of diamond-anvil cell techniques, the measurements are far from routine. Measurements on hydrogen to pressures approaching 300 GPa have demonstrated that significant changes in optical properties at visible wavelengths occur at these very high pressures.<sup>1</sup> These changes were interpreted as indicating significant effects of pressure on the band gap of the solid, giving experimental support for the theoretical prediction that metallization may occur by a band-overlap mechanism. Although it was not possible to ascertain whether the band gap had closed, we pointed out that if the gap is indirect, metallization may occur at lower pressures (e.g., below 200 GPa) with no change in optical properties at visible wavelengths.<sup>1</sup> In this case, the material could transform from a narrow-gap semiconductor to a transparent semimetal with direct interband transitions in the ultraviolet. Alternatively, the measurements were also consistent with the actual point of band-gap closure being above the pressure range of the onset of visible absorption (250–300 GPa).<sup>1</sup>

The possibility of closure of an indirect gap has focused attention on the low-temperature phase transition at 150 GPa (Ref. 2) and the extent to which this is associated with metallization. This transition is characterized by a discontinuous change in the vibron frequency indicative of an abrupt weakening of the molecular bond. In addition to band-overlap metallization, orientational ordering and possible structural transitions are also expected in this pressure range.<sup>2</sup> Measurements carried out on deuterium to test these assignments<sup>3</sup> showed that the heavier isotope undergoes a similar transition, which therefore ruled out assignment of the transition to a simple rotational ordering of the type observed in the low-density

solid.<sup>3</sup> Similar conclusions were reached subsequently by Lorenzana, Silvera, and Goettel<sup>4</sup> on the basis of measurements of the temperature dependence of the transition. Recent measurements of the low-frequency Raman spectrum demonstrate that the transition must proceed with at most a small change in the underlying hexagonal crystal structure.<sup>5</sup> Extended measurements of the temperature dependence of the Raman spectrum from 77 to 295 K also provided evidence for critical behavior of the transition at  $\lesssim 150$  K.<sup>6</sup> These results point toward a fundamental change in electronic properties occurring at 150 GPa.<sup>3,5,6</sup>

Recently, we extended measurements of reflectivity to near-infrared wavelengths and to pressures of 177 GPa.<sup>7</sup> An increase in infrared reflectivity was observed at 150 GPa, which could be fit with a simple Drude-type free-electron model. Eggert, Goettel, and Silvera<sup>8</sup> measured the index of refraction of hydrogen to 73 GPa, and on the basis of extrapolation predicted a high-pressure dielectric catastrophe and closure of an indirect gap at 148–173 GPa. A band-overlap transition in this pressure range is also consistent with recent theoretical predictions for band-gap closure,<sup>9</sup> although these calculations have generally used the local-density approximation, which tends to underestimate band gaps. In this paper, we present measurements of absorption spectra of hydrogen to 172 GPa from 0.5 to 3.0 eV. These complement previous reflectance measurements over the same pressure range<sup>7</sup> and earlier measurements in the visible (1.5–3.0 eV) at higher pressures.<sup>1</sup> In light of the new and previously published data, we examine in further detail the evidence for metallization of solid molecular hydrogen, and point out experiments to test various models.

Absorption spectra from 0.5 to 3.0 eV were measured at 295 K by direct transmission with the previously described optical system used for the reflectance measurements.<sup>7</sup> Pressures were determined by ruby  $R_1$  fluorescence from small grains of ruby, which even at the highest pressures were estimated to occupy less than  $\sim 5\%$  of the sample volume. The Raman-active vibron

was also measured at each pressure to ensure that hydrogen was present in the sample chamber. This is important because it is possible to lose hydrogen at very high pressure (by diffusion into the gasket and diamond), with no change in the visual appearance of the sample. In the present study, no optical spectra are reported for samples in which a strong vibron peak could not be measured. Representative spectra from 100 to 161 GPa are shown in Fig. 1. The high-energy edge shifting with increasing pressure to lower energies arises from the strain-induced absorption in the diamond anvil. The absorption due to hydrogen remains low (below 0.2 absorbance) throughout most of the spectrum (0.7 to 2.5 eV). A similar low absorption was observed in a spectrum measured at 172 GPa. Below 0.7 there is a small increase in absorption, which increases with pressure above 140–150 GPa.

We have shown that the previously reported reflectivity spectra can be fit with a simple Drude model<sup>10</sup> to yield estimates of the plasma frequency  $\omega_p$  and the electron scattering time  $\tau$ .<sup>7</sup> The large values obtained for  $\tau$  indicated the need for a more sophisticated model to explain the results. In the previous study, we used the pressure dependence of the diamond index as modeled by Eggert, Goettel, and Silvera<sup>8</sup> based on measurements of the diamond absorption edge; this result indicates that the effective refractive index of the diamond anvil increases with increasing stress (see Fig. 2). Consistent with the analysis of the reflectivity data, we can fit the new absorption data with a Drude model under the assumption that the solid is metallic. The plasma frequencies obtained from the absorption and reflectivity measurements are consistent. For the spectra measured at 161 GPa, for example, an effective  $\omega_p$  of  $\sim 1.5$  eV is obtained from fits to both spectra. However, the resulting scattering times differ appreciably, with  $\hbar/\tau=0.04$  eV and  $\hbar/\tau=0.8$  eV obtained from fits to absorption and reflectivity, respectively. In other words, quantitatively the

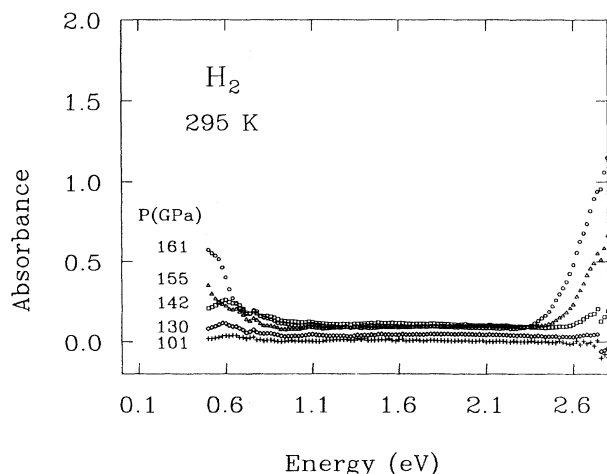


FIG. 1. Absorption spectra of hydrogen as a function of pressure from 100 to 161 GPa.

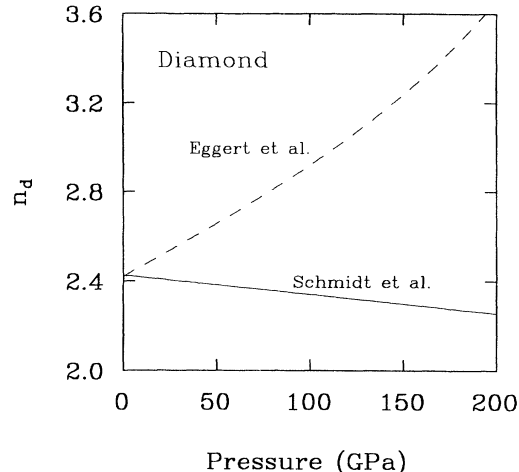


FIG. 2. Proposed load dependences of the refractive index of diamond. Schmidt, Kirk, and Vedam (Ref. 13) (solid line) measured the variation of  $n_d$  under hydrostatic pressure up to 0.7 GPa. Eggert, Goettel, and Silvera (Ref. 8) (dashed line) estimated  $n_d$  from measurements of the diamond absorption edge up to 40 GPa.

intensity of infrared absorption is lower than that predicted by Drude-model fits to the reflectivity with the previously assumed optical constants.<sup>7,8</sup>

Quantitative differences in Drude-model fits to high-pressure data have been observed previously for other materials. Optical measurements for xenon in its reported semimetallic state, for instance, show qualitative agreement;<sup>11</sup> however, the reflectivity predicted from the absorption measurements are inconsistent with the proposed Drude model (e.g., the measured reflectivity at 0.75 eV is 60% higher than that predicted by the fit to the absorption).<sup>11</sup> The difference indicates the need for a more extended treatment of the optical response. We now discuss several ways in which the differences in hydrogen can be reconciled, and propose experimental tests for these models. Specifically, we consider effects associated with the diamond refractive index, the role of interband and vibrational transitions, and anisotropy in the optical response of hydrogen.

We have shown that the plasma frequencies obtained from Drude-model fits to the reflectivity are dependent on the value of the index of refraction used for both diamond and hydrogen at high pressure.<sup>12</sup> The refractive index of hydrogen  $n_H$  is partially constrained by the number and position of measured interference fringes,<sup>8,12</sup> providing that the thickness of the sample is known. On the other hand, the refractive index of diamond,  $n_d$ , at the high-stress condition of the diamond-hydrogen interface is not independently determined. In fact, even the sign of the stress effect on  $n_d$  is uncertain. Proposed load dependences of  $n_d$  ranging from rapidly increasing<sup>8</sup> to slightly decreasing with pressure<sup>13</sup> are shown in Fig. 2. The absolute value of difference in refractive indices  $|\Delta n|=|n_d - n_H|$  is constrained by measurements of the

intensity of Fabry-Pérot interference fringes. These measurements indicate that  $|\Delta n|$  is close to zero at  $\sim 130$  GPa,<sup>7,12</sup> and increases at higher pressures but its sign remains undetermined. In the previous analysis, it was assumed that  $n_d < n_H$  above 130 GPa. However, if we assume that  $n_H$  remains below  $n_d$  at higher pressures, a quantitative fit of the Drude model to both sets of spectra can be obtained with the same parameters.

Simulated reflectance and absorption spectra calculated for  $n_d < n_H$  and  $n_d > n_H$  are shown in Fig. 3. In both cases the expected reflectivities are very similar, while the absorption obtained for  $n_d > n_H$  is much lower compared to the absorption obtained under the assumption that  $n_d < n_H$  above 130 GPa. By assuming  $n_d > n_H$  one finds that the reflectivity measurements carried out above 0.5 eV effectively determine  $\omega_p$ , whereas the absorption provides a constraint on  $\hbar/\tau$ , the low absorption in the near infrared and visible giving an upper bound on the latter parameter. Least-squares fits to the spectra give  $\hbar/\tau < 0.15$  eV, which is reasonable for a metal,<sup>10</sup> and  $\omega_p \leq 0.7$  eV over the present pressure range. A linear fit of  $\omega_p^{4/3}$  as a function of density or volume gives the pressure of the onset of infrared reflectivity in agreement with that reported previously.<sup>7</sup> The value of the hydrogen refractive index predicted by such an analysis is lower than previous estimates<sup>7,8</sup> but is in accord with the results of quantum Monte Carlo simulations, which find that  $n_H$  reaches a constant value of  $\sim 2.7$  above 50 GPa.<sup>14</sup> This result, however, requires there to be an appreciable increase in the effective refractive index of diamond (the appropriate dielectric tensor components of the anisotropically strained crystal) above 100 GPa. Experimental determination of  $n_d$  under the strain conditions of the anvil can uniquely resolve the two alternative assignments.<sup>15</sup>

Since typically only a rise in reflectivity and absorption is observed with decreasing energy below 0.7 eV, it is not yet possible to rule out that the feature is actually the high-frequency tail of a peak (or peaks) instead of a Drude edge. We consider the possibility that the peak is due to an interband transition modeled by a single oscillator with  $\omega_0 \sim 0.5$  eV added to the Drude model. A close fit for both absorption and reflectivity spectra is obtained, with comparable bandwidths, but again the results are dependent on the sign of  $|\Delta n|$ . With this assignment the increase in intensity of the band can be used to determine the onset of band overlap, since the integrated intensity of the peak would be proportional to the number of free carriers. Such a calculation for the reflectivity at 0.5 eV gives an onset of  $\sim 155$  GPa; this is close to the onset calculated assuming the simple Drude model [ $149(\pm 10)$  GPa].<sup>7</sup> This assignment implies that the actual Drude component may remain below the 0.5 eV cutoff of our measurements and  $\hbar/\tau < 0.01$  eV. Notably, low-energy interband transitions are observed in anisotropic semimetals graphite, antimony, and bismuth.<sup>16,17</sup>

The molecular vibron frequency (initially at 0.515 eV) occurs in the energy range in which the infrared absorption and reflectivity are observed above 150 GPa. The

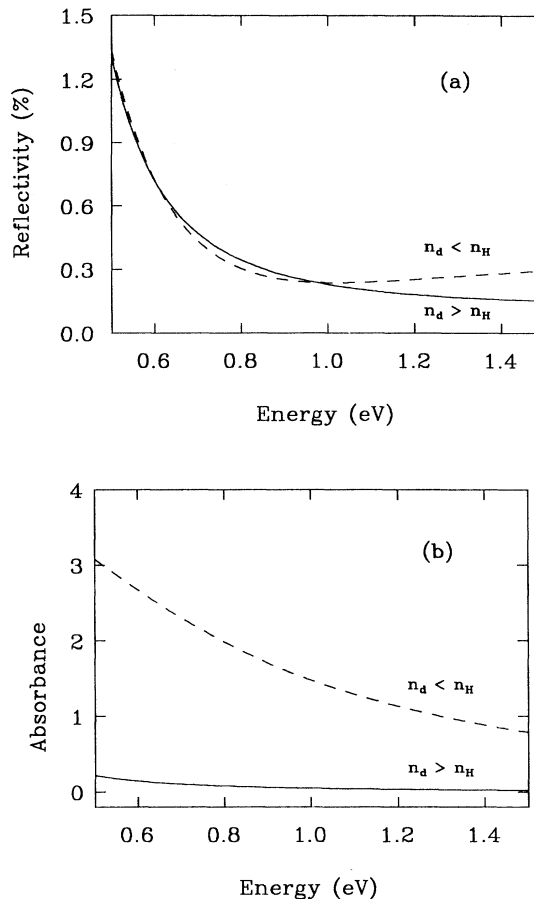


FIG. 3. Simulated reflectance (a) and absorption (b) spectra of solid hydrogen using the parameters  $\omega_p=1.21$  eV,  $\hbar/\tau=0.72$  eV,  $n_H=2.77$  and  $\omega_p=0.62$  eV,  $\hbar/\tau=0.05$  eV,  $n_H=2.26$  for  $n_d < n_H$  and  $n_d > n_H$ , respectively. In both cases we assumed  $d_{\text{sample}}=2.5 \mu\text{m}$  and  $n_d=2.42$ .

mode is ir inactive in the free molecules but is weakly active in the hcp structure in the solid [ $Q_1(1)$  band].<sup>18</sup> The pressure dependence of the vibron has been measured by infrared absorption in the diamond-anvil cell to 54 GPa (295 K).<sup>19</sup> The present spectra can be fit assuming the single oscillator is a vibrational transition peaking near the fundamental vibron frequency ( $\sim 0.5$  eV), analogous to the case of an interband transition. If the feature arises from a vibrational transition, the increase in intensity documented previously between 150 and 177 GPa may be associated with the continuous passage<sup>6</sup> into the high-pressure phase, which may involve changes in ir absorption intensities for the vibron (see Ref. 18). Extension of these measurements to lower energies would clarify whether the rise in reflectivity and absorption at 0.5 eV is associated with an edge or a peak (e.g., interband or vibron transition).

X-ray-diffraction studies to 36 GPa show that crystal structure of hydrogen becomes increasingly anisotropic at high pressure,<sup>20</sup> and vibrational spectra indicate that this anisotropy persists over the range of the present

measurements.<sup>5,12</sup> An accurate model of the optical response therefore requires the determination of the complete dielectric tensor (e.g., for a hexagonal system).<sup>21</sup> The evidence for a decreasing  $c/a$  ratio with pressure and the observed single-crystal orientation in x-ray studies suggests that there may be preferred orientation of hexagonal hydrogen at very high pressures, with the  $c$  axis tending to become parallel with the load axis of the diamond-anvil cell as in graphite.<sup>22</sup> Should strongly preferred orientation extend to the vicinity of the 150 GPa transition, there could be a significant effect on the measured optical response of the sample in the high-pressure cell (i.e., the measured absorption and reflectivity would also depend on the texture of the polycrystalline  $H_2$  sample). It is useful to point out that considerable anisotropy in the optical response is documented for low-carrier metals such as graphite.<sup>16</sup> Extension of the capability of x-ray diffraction of hydrogen to and beyond 100 GPa would provide a quantitative measurement of the preferred orientation and the degree of anisotropy.

In conclusion, the low absorption measured in hydrogen at 0.5–3.0 eV to 172 GPa places important constraints on the dielectric properties of the dense solid over this pressure range. Similar low values for optical absorption, but over a more limited spectral range (above 0.7 eV), have also been reported by other investigators.<sup>23</sup> The new optical data presented here are consistent with, but alone do not necessarily require metallization. If the

material becomes metallic below 172 GPa, then the data indicate that the plasma frequency is small, and/or optical masses large, as expected for the initial band-overlap (semimetallic) state.<sup>21</sup> It is highly significant that the dielectric properties of dense hydrogen obtained from the measured spectra are strongly dependent on assumptions concerning the refractive index of both hydrogen and diamond. A significant increase in the effective  $n_d$  above 100 GPa cannot be ruled out in view of the fact that significant elastic deformation and stress-induced fluorescence of the diamond anvils begin in this pressure range.<sup>1,24</sup> Although no direct measurements are available, it should be pointed out that metallization by band-gap closure is predicted for diamond strained along [100], which suggests an increase in  $n_d$  under these conditions.<sup>25</sup> In order to test each of the possibilities examined here, it will be necessary to extend the measurements of the absorption and reflectivity to lower energies (below 0.5 eV), to determine the refractive index of diamond under anvil stress conditions, and to study the texture and anisotropy of hydrogen by x-ray diffraction.

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