PHYSICAL REVIEW B VOLUME 37, NUMBER 11 15 APRIL 1988-I

Pressure dependence of the optical-absorption edge of solid hydrogen in a diamond-anvil cell

Joop van Straaten and Isaac F. Silvera
Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 13 July 1987; revised manuscript received 16 November 1987)

We have used a diamond-anvil cell loaded with solid H_2 as a Fabry-Perot étalon. From the interference patterns of transmitted light in the visible region the dispersion of the index of refraction is determined. This is related by a dielectric model to the optical-absorption threshold energy which is found to decrease with pressure.

For a number of decades, since the early work of Wigner and Huntington,[1] physicists have been fascinated by the possibility of metallizing molecular hydrogen by submitting it to pressure. The critical pressure is now believed to be in the 3–5 Mbar range.[2] It is also believed that, with increasing pressure, H_2 will first become a conducting molecular solid, then an atomic metallic solid.[3] Diamond-anvil cells (DAC's) have been used to achieve pressures of order 1.5 Mbar on H_2,[4] however no direct evidence of an approach to metallization has been observed. An important method in the investigation of such transitions is to study the pressure dependence of the optical-absorption threshold energy (ATE) in the insulating phase.[5] The ATE is the lowest energy at which optical absorption due to electronic transitions occur. If there are no optically active excitons below the (valence-conduction) band gap, the ATE corresponds to the lowest optical band gap. Optical-absorption measurements for H_2 under high pressure in a DAC can only be done if the ATE of H_2 is lower than the ATE of the diamond windows, which is expected at extremely high pressures. Since the dielectic function of a solid has a very broad frequency dependence, shifts of the ATE in the uv will effect the real part of the dielectric response in the visible, as is well known from the Kramers-Kronig relations. Thus in principle it is possible to study the uv ATE in the visible.

In this paper we present a simple new technique to measure the dispersion of the index of refraction in a DAC, and a connection to the ATE is made via the dielectric theory of solids. This technique is applied to H_2 in a modest pressure range up to 28 GPa. The fact that the diamonds in a DAC form a Fabry-Perot étalon, filled with the sample under study, has been used earlier by van Straaten *et al.*[6] and Besson *et al.*[7] to study the index of refraction of the sample as well as its thickness as a function of pressure. Here we show that by measuring the fringe position over a broad spectral region, the dispersion of the index of refraction can be determined and from this the ATE can be calculated. This is applied to H_2 in which the dispersion of the index is observed to increase implying a decrease of the ATE with pressure.

In order to relate the index n to the gap, we note that the real part of the dielectric constant can be written

$$\epsilon_1(\omega)=1+\omega_p^2\sum_n f_n/(\omega_n^2-\omega^2) , \tag{1}$$

where ω_p is the plasma frequency, ω_n is an electronic transition frequency, and f_n is the associated oscillator strength. Wemple and DiDomenico[8] showed, based on empirical data, that at low frequencies ($\omega<\omega_n$), a large class of solids can be represented by a single oscillator model

$$n^2-1\equiv\epsilon_1(\omega)-1=F_1/(\omega_1^2-\omega^2) . \tag{2}$$

Here F_1 is an effective oscillator strength and $E_1=\hbar\omega_1$ is an "average electronic transition energy." For some solids, deviations from this simple formula occur at high frequency due to the proximity of the band edge or excitonic absorption. The largest deviations occur when strong exciton peaks are present below the band edge. Further they found empirically that $E_1\approx1.5E_t$ where E_t is the ATE. Differentiating Eq. (2) yields

$$n(\partial n/\partial\omega)/(n^2-1)=\omega/(\omega_1^2-\omega^2) . \tag{3}$$

Using Eq. (3) we can determine the pressure dependence of ω_1 from our measurements of the dispersion of n.

Our experimental DAC–Fabry-Perot optical system is shown schematically in Fig. 1. The spectrum of the collimated white light passing through the DAC is analyzed by a spectrometer. For H_2 under pressure a series of about 50–70 fringes is observed in the 13 000–21 000-cm^{-1} spectral region. The fringe pattern is measured as a function of pressure which is determined from the ruby fluorescence spectrum[9] arising from a few small grains of ruby embedded in the H_2. The method of loading the H_2 into the DAC is described in detail elsewhere.[10] The DAC gasket which radially confines the sample was made of T301 stainless steel.

For a DAC, the usual Fabry-Perot equations require a modification due to deformation of the mirror surface under pressure. The normalized transmitted light intensity for a Fabry-Perot étalon with flat mirrors is

$$I/I_0=1/[1+G\sin^2(\delta/2)] , \tag{4}$$

where $G=4R/(1-R)^2$, R is the reflectance of the diamond-sample interface, $\delta/2=2\pi nd/\lambda$, λ is the wave-

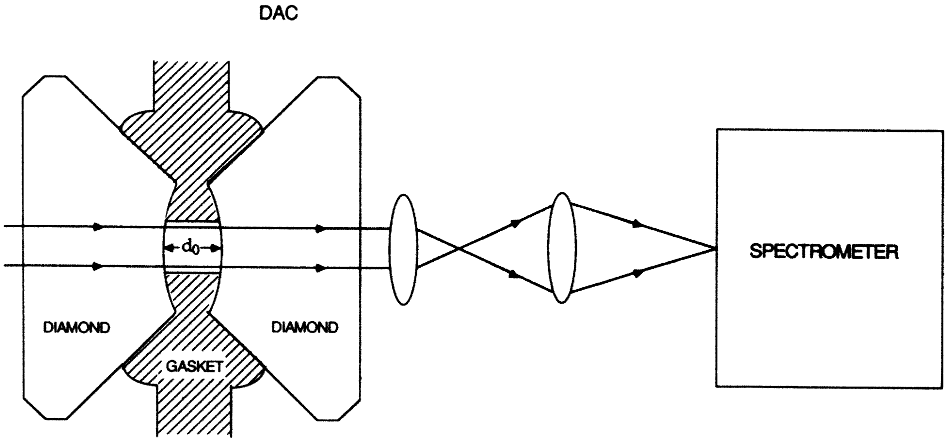

FIG. 1. Schematic diagram of the experimental setup. The components are not drawn to scale.

length of light, and n is the index of refraction of the sample which is a function of λ. Under pressure, the diamonds will cup as shown in exaggeration in Fig. 1, so that the distance between diamonds is a function of r, the distance from the center of the hole. In order to understand the effect of the cupping on the transmission, we expand Eq. (4) for the case of low contrast to obtain the transmission as a function radius,

$$I/I_0=1-\tfrac{1}{2}G+\tfrac{1}{2}G\cos\delta \ . \tag{5}$$

A Taylor-series expansion of $d(r)$ yields

$$d\simeq d_0+\tfrac{1}{2}(\partial^2 d/\partial r^2)r^2 \ . \tag{6}$$

From this expansion, we see that Eq. (5) for the transmission is a function of r. We now find the transmission through the cupped Fabry-Perot étalon to be

$$I_{\text{tot}}=\int_0^{r_0} 2\pi I(r)r\,dr \tag{7}$$

which gives

$$I_{\text{tot}}/I_0\simeq 1-\frac{G}{2}g_{\text{mod}}\cos\left[4n\pi\sigma\left[d_0+\frac{\partial^2 d}{\partial r^2}\frac{r_0^2}{4}\right]\right] , \tag{8}$$

where r_0 is the sample radius and σ is the wave number of the light. We shall call the quantity in parentheses the distance $\bar{d}$; $g_{\text{mod}}=(\sin\bar{\delta})/\bar{\delta}$ is a modulation function of the contrast due to cupping, where $\bar{\delta}=\pi n\sigma(\partial^2 d/\partial r^2)r_0^2$, so that the fringe envelope is modulated with periodicity $2n\bar{d}$. The cupping thus produces a decrease in the contrast as well as a slow modulation.

The dispersion of the index of refraction, $(1/n)\partial n/\partial\sigma$, is determined by noting that the frequency spacing between two extrema of order m and m' is

$$\Delta\sigma=\sigma_m-\sigma_{m'}=m/2n_m d-m'/2n_{m'}d \ . \tag{9}$$

Using $n_m\simeq n_{m'}+\Delta\sigma\,\partial n/\partial\sigma$ in Eq. (7) gives

$$\Delta\sigma\simeq[(m-m')/2n_{m'}d][1-\sigma_m(1/n_{m'})\partial n/\partial\sigma] \ . \tag{10}$$

We can now assign m' an arbitrary integral value associated with a particular fringe and plot $\Delta\sigma$ versus σ_m; the slope and intercept determine the dispersion. However, since for H_2 the dispersion is very small the statistical error is large. A substantial increase in precision is attained by extrapolating the spectrum to zero frequency in such a way that the orders of the extrema are known. From Eq. (9) one finds

$$(m'/m)(\sigma_m/\sigma_{m'})=1+(1/n_m)(\partial n/\partial\sigma)\Delta\sigma \ . \tag{11}$$

A plot of the left-hand side versus $\Delta\sigma$ now directly gives the dispersion as the slope of the straight line.

Great care must be taken in identifying the order, or a systematic error can occur. First one must note that identification of minima and maxima depends on the sign of g_{mod}. For g_{mod} positive, maxima are at $m/2n\bar{d}$ and minima at $(m+2)/2n\bar{d}$, whereas for g_{mod} negative, the identification is reversed. In Fig. 2(a) we plot the fringe intensity ratio $I_{\max}/I_{\min}$ as a function of frequency for two pressures. This clearly has a period of approximately 10 000 cm^{-1} so that the sign of g_{mod} must be negative.[11]

To further reduce the possibility of systematic error due to incorrect identification of orders we correlated interference patterns at different pressures. The difference between extrema of the same order taken at pressures P_1 and P_2 is $\Delta\sigma=m(\frac{1}{2}n_1d_1-\frac{1}{2}n_2d_2)$, where n_i,d_i correspond to pressure P_i. This difference is proportional to m and therefore the wave number of m. By taking small pressure steps the order could be followed and correlated to remove uncertainties. In Fig. 2(b) we plot our findings for the dispersion for 31 values of pressure using the two methods described. We find $(1/n)\partial n/\partial\sigma=(0.649+0.04P)\times10^{-6}$ cm (P in GPa), the result of the second method.

Before considering the ATE, it is useful to compare our results to known dielectric properties. The Lorentz-Lorentz relation is

$$(n^2-1)/(n^2+2)=\tfrac{4}{3}\pi N_A\alpha/V \ , \tag{12}$$

where N_A is Avogadro's number, α the polarizability, and V the molar volume. One can use a single oscillator model of the polarizability, $\alpha(\omega)=F_0/(\omega_0^2-\omega^2)$. Substituting into (10) and differentiating yields

$$[6n/(n^2+2)(n^2-1)]\partial n/\partial\omega=2\omega/(\omega_0^2-\omega^2)\ . \quad (13)$$

It is noted[8] that a single oscillator description of α cannot be distinguished from the Wemple-DiDomenico model of (n^2-1). Using our results for the dispersion and the value of n for H_2 as determined by Shimizu *et al.*[12] at room temperature, we determine ω_0 as a function of pressure, shown in Fig. 3(a). We compare this to the gas phase value[13] of 114 200 cm^{-1}. With increasing pressure ω_0 decreases.

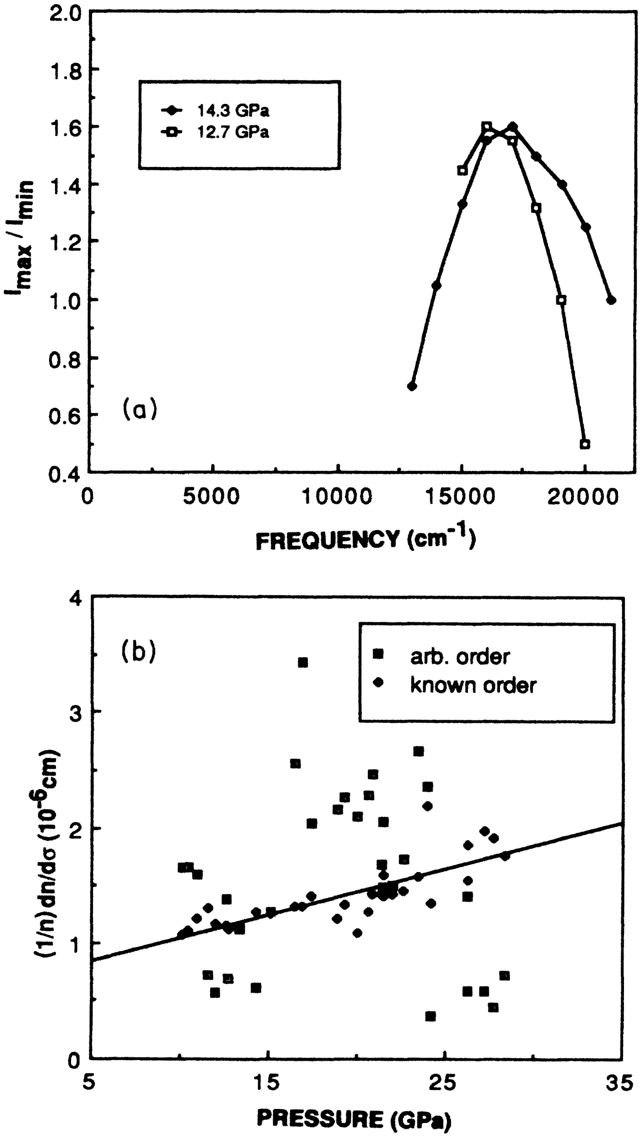

FIG. 2. (a) Fringe intensity ratio as a function of frequency for two pressures. (b) Experimentally determined dispersion of H_2 as a function of pressure. Data points are shown for two methods of analysis described in the text, with arbitrary fringe order and known fringe order. The line is a linear fit to the latter data.

In Fig. 3(b) we plot the pressure dependence of ω_1 as points determined from Eq. (3), the dielectric model of the solid.[8] We also plot a point at $P=0$ which we did not measure, but calculated by combining Eqs. (3) and (13) to find $\omega_1^2=3\omega_0^2/(n^2+2)$; using the zero-pressure value of ω_0 gives $\omega_1=103\,000$ cm^{-1}. Wemple and DiDomenico suggest the relation $E_t=\hbar\omega_1/1.5$, however, this has not been established for H_2. The experimental spectrum of H_2 in the uv as measured by Inoue *et al.*[14] has two principal bands with obsorption onsets at about 89 000 and 124 000 cm^{-1}. The lower band is attributed to excitonic absorption, whereas the higher band is identified as the threshold for valence-conduction transitions. Thus at zero pressure we find $E_t=\hbar\omega_1/1.16$.

In Fig. 3(b) we also show the band gap of H_2 from Min *et al.* who calculate E_g, the valence-conduction band

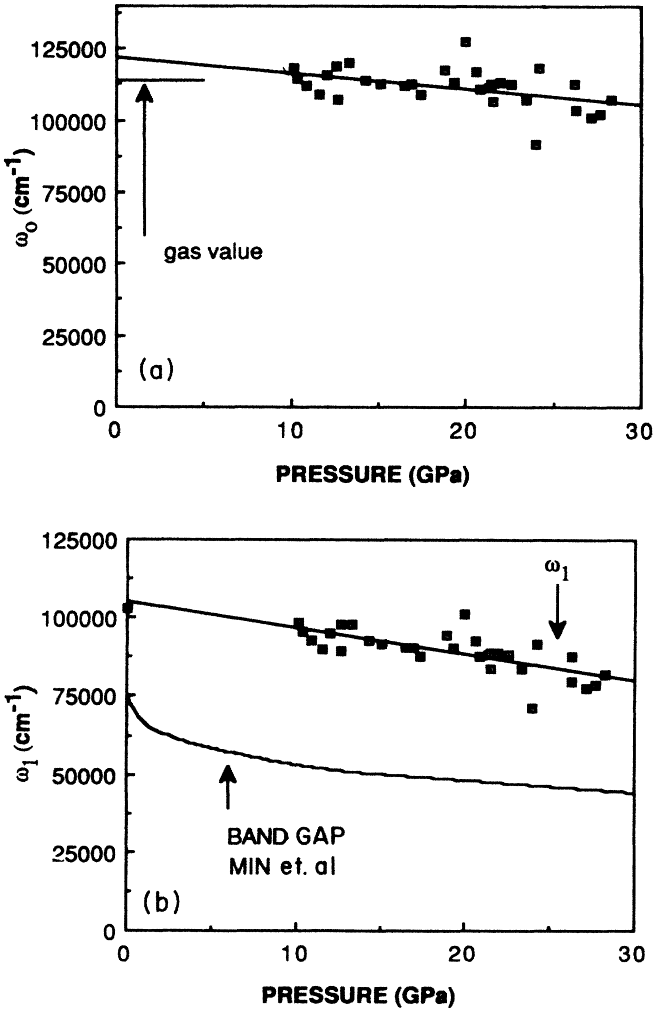

FIG. 3. (a) Data points analyzed to determine ω_0 as a function of pressure. The point at $P=0$ is calculated. The line is a linear fit with $\omega_0=(1.22\times10^5-541P)$ cm^{-1}. (b) ω_1 as a function of pressure. The line through the data points is a linear fit. We also show a solid line representing the band gap from calculations of Min *et al.* (Ref. 2).

gap, versus r_s, the Wigner-Seitz radius. For the plot, we convert to molar volume and then to pressure using the experimental equation of state.[6] The slope of ω_1 and E_g are quite similar, however, we note that the local density approximation used by Min *et al.* usually underestimates the magnitude, E_g. A Hartree-Fock band calculation for zero pressure H_2 by Giannozzi and Baroni[15] is in better agreement with experiment, as is the calculation of Ceperley and Alder.[2] Extending the plot of E_g of Min *et al.* in Fig. 3(b) to very high pressures shows that E_g versus P can be fitted remarkably well with a straight line, above 10 GPA.

Our measurements show that, to within the validity of the dielectric model, the ATE of H_2 decreases under pressure. A linear fit gives $\omega_1 = 105\,300 \pm 3093 - (845 \pm 689)P$, which gives $\omega_1 = 0$ at 124 GPa. The most desired experimental information is to determine the pressure dependence of E_g, so that a prediction of the metallization pressure can be made. However it is clear that measurements to higher pressure and a theoretical study or model of the pressure dependence of the exciton absorption edge as a function of density are needed. An experimental estimate of the critical pressure can be found[6] using the Herzfeld[16] dielectric model combined with the equation of state of H_2 of van Straaten and Silvera.[6] We predict a metallization pressure of 280 GPa.

The experiments reported here were limited to modest pressures as we optimized the system for developing the technique and our diamonds had large culets (~250 μm). For megabar experiments, smaller culets are required. Further, with increasing pressure the index of refraction of H_2 approaches that of diamond and therefore the fringe contrast becomes small. This can be overcome by depositing a partially transmitting metallic surface on the diamonds.[6]

We would like to thank J. Eggert, K. Goettel and N. Ashcroft for useful discussions. The support of the National Science Foundation (NSF) under Grant No. DMR-86-00955 and the Harvard University Materials Research Laboratory under NSF Grant No. DMR-86-14003 is acknowledged.

---

[1] E. P. Wigner and H. P. Huntington, J. Chem. Phys. **3**, 764 (1935).

[2] B. I. Min, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **33**, 6383 (1986); D. M. Ceperley and B. J. Alder, Phys. Rev. B **36**, 2092 (1987).

[3] J. Oliva and N. W. Ashcroft, Phys. Rev. B **23**, 6399 (1981).

[4] H. K. Mao, P. M. Bell, and R. J. Hemley, Phys. Rev. Lett. **55**, 99 (1985).

[5] See, for example, J. van Straaten and I. F. Silvera, Phys. Rev. Lett. **57**, 766 (1986).

[6] J. van Straaten, R. J. Wijngaarden, and I. F. Silvera, Phys. Rev. Lett. **48**, 97 (1982); J. van Straaten and I. F. Silvera, Phys. Rev. B **37**, 1989 (1988).

[7] J. M. Besson, J. P. Itie, G. Weill, and I. Makarenko, J. Phys. (Paris) Lett. **43**, L-401 (1982).

[8] S. H. Wemple and M. DiDomenico, Jr., Phys. Rev. B **3**, 1338 (1971).

[9] H. K. Mao, P. M. Bell, J. Shaner, and D. Steinberg, J. Appl. Phys. **49**, 3276 (1978).

[10] I. F. Silvera and R. J. Wijngaarden, Rev. Sci. Instrum. **56**, 121 (1985).

[11] From this we can determine that $d_0 \simeq 25$ μm and decreases by about 0.3 μm from center to edge at 35 μm.

[12] H. Shimizu, E. M. Brody, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. **47**, 128 (1981).

[13] E. R. Peck and S. Huang, J. Opt. Soc. Am. **67**, 1550 (1977).

[14] K. Inoue, H. Kanzaki, and S. Suga, Solid State Commun. **30**, 627 (1979).

[15] P. Giannozzi and S. Baroni, Phys. Rev. B **30**, 7187 (1987).

[16] K. F. Herzfeld, Phys. Rev. **29**, 701 (1927).