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Ultraviolet–visible absorption spectra of solid hydrogen sulphide under high pressure

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Abstract

Ultraviolet–visible absorption spectra of solid hydrogen sulphide (H₂S) were measured at various pressures from 0.3 to 29 GPa. The absorption edge observed around 4.8 eV at 0.3 GPa indicated a red-shift with increasing pressure, and positioned below 3 eV at 29 GPa. On the basis of the spectra obtained, the energy gap was determined as a function of pressure. The transition to phase IV at 11 GPa was found to lead to a small jump in its pressure dependence and to yield an Urbach tail in the absorption edge.

1. Introduction

The decrease in the intermolecular distance arising from pressurization causes an overlap in the molecular orbitals, giving rise to a drastic change in the electronic properties. High-pressure research on molecular solids has recently provided us with various novel phenomena—superconductivity in O₂ [1], covalency in solid CO₂ [2], electrical conductivity of Xe [3] and so on. These are believed to arise directly or indirectly from the drastic changes in the electronic states at high pressures. In obtaining evidence of the change in electronic properties such as metallization, measurements of electrical conductivity are straightforward, but optical measurements are of importance as a simple probe for exploring the novel phenomena related to the electronic states.

Hydrogen sulphide (H₂S), which is a typical molecular solid, is known to undergo a phase transition from liquid to cubic disordered phase I (*Fm* $\bar{3}$ *m*) at 0.5 GPa, to cubic disordered phase I' (*P*2₁3) at 8 GPa and to tetragonal ordered phase IV (*I*4₁/*acd*) at 11 GPa [4–7]. The solid phase IV, which is initially transparent at 11 GPa, changes in colour from pale yellow to deep brown and finally to black above 30 GPa [7, 8], suggesting that the energy gap in the UV region for a free molecule drastically decreases to or to just below the visible region. As far as the authors are aware, however, there has been no experimental investigation focused on the UV–visible absorption band and its pressure dependence.

In this paper, we present a systematic high-pressure study of the optical absorption of H₂S from the mid-UV to the near-IR region using a diamond anvil cell (DAC). It was found that the absorption edge observed around 4.8 eV at 0.3 GPa shifts to lower energies with increasing pressure, and finally to below 3 eV at 29 GPa. At the transition to phase IV at 11 GPa, a small jump was observed in its pressure dependence, and an Urbach tail ranging to the visible region was found to appear.

2. Experimental details

A DAC with a metal gasket was used for the high-pressure experiments. A hole of 50 μm in diameter served as the sample chamber. The thickness of the chamber, which varies with compression, was initially about 30 μm . The loading of a sample of H₂S into the DAC was performed by spraying its vapour into the chamber in the DAC cooled in a liquid N₂ bath. The solidified H₂S was sealed by translating one of the diamond anvils. To avoid inclusion of contamination, the loading was done in a glove box filled with dry N₂ gas.

Natural diamonds (type Ia) commonly used as anvils are known to show a strong impurity absorption, which prevents us from measuring in the UV region above 4.0 eV. Since the H₂S molecule shows its intrinsic absorption band above 4 eV, UV measurements are important for following the change of the absorption spectrum from low pressure. Therefore, we used synthetic type-IIa diamonds, transparent up to 5.5 eV.

Figure 1 shows schematically the optical system of the absorption measurements for the spectral range from mid-UV to near-IR using a DAC. The use of quartz optical fibres, transparent to 5.5 eV, allows the optics to be very simple. The optical fibres for input and output are typically 50 and 800 μm in core size, respectively. The white light from the 50 μm fibre is focused onto the specimen using a reflecting objective ($\times 10$) without chromatic aberration. The other reflecting objective focuses the transmitted light onto the 800 μm fibre connected to a single monochromator. The images of the specimen and the illuminated spot can be monitored with a CCD camera. The diameter of the focused spot, which depends on the size of the optical fibre used, was about 30 μm smaller than the sample chamber. The white-light source covering a wide spectral range was achieved by the combination of a deuterium lamp and a tungsten lamp.

To deduce the absorption spectra of the specimen itself, the transmittance of the empty cell was measured prior to the loading of the specimen. The spectrum was used as the reference, to cancel out the diamond's signal. From the transmissivity (T) of the specimen, the absorption coefficient was approximately obtained from $-\ln(T)/d$ (d : thickness of the specimen).

The specimen thickness, which varies with increasing pressure, was estimated as follows. The quantity of nd (n : refractive index of the specimen) can be obtained from the interference spectra shown in figure 2, which were measured without focusing the white light. Since the data on n have already been determined in the previous study up to 7 GPa [9], the thickness can be deduced for pressure lower than 7 GPa. For higher pressures, the thicknesses were estimated by linear interpolation between the value obtained at low pressure (<7 GPa) and the final value that was measured for the empty chamber after the pressurization to the highest pressure in each experimental run.

3. Results and discussion

Figure 3 shows the absorption spectra obtained at various pressures from 0.3 to 29 GPa. In the liquid phase at 0.3 GPa, the absorption edge corresponds to the electronic transition

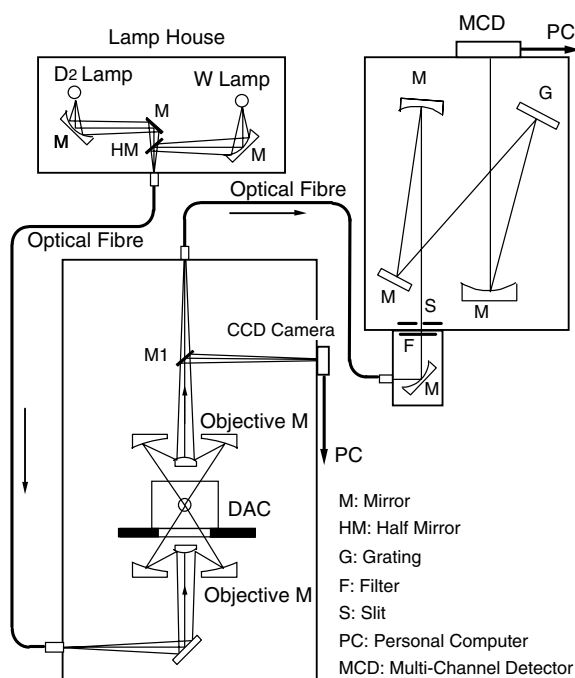


Figure 1. The optical system for UV-visible absorption measurements using a DAC. The use of quartz optical fibres, transparent to 5.5 eV, allows the optics to be very simple.

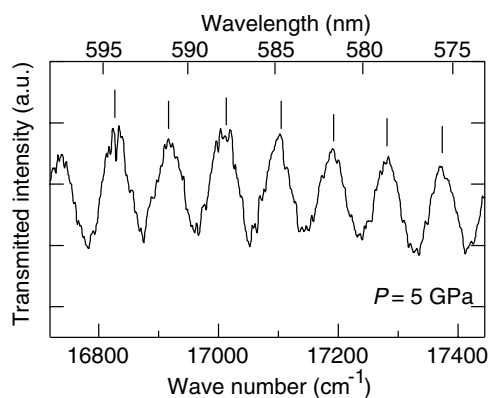


Figure 2. The interference spectrum obtained without focusing the white light. From the spectrum, the thickness was estimated.

between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). With increasing pressure, the absorption edge shifts to the lower-energy side, suggesting a decrease in the energy gap resulting from the changes in electronic structure to a band-like state.

To allow further discussion, we estimated the band gap (E_g) under the assumptions that (1) the electronic transition is direct and (2) the valence and conduction bands are parabolic. Under these assumptions, the absorption coefficient ($\alpha(h\nu)$) near the edge can be represented using $\alpha(h\nu) = A(E_g - h\nu)^{1/2}/h\nu$, where A is a constant. As shown in the inset of figure 4,

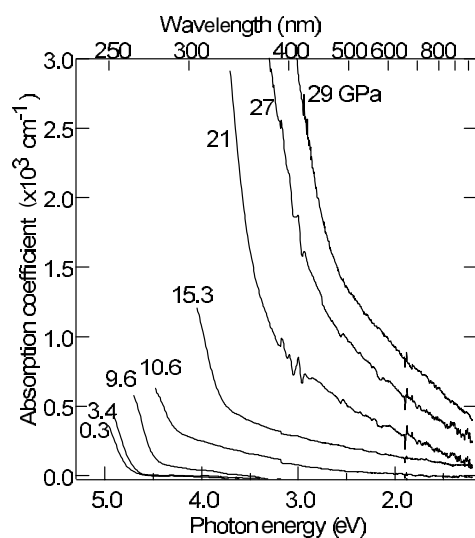


Figure 3. Absorption spectra of H₂S obtained for various pressures from 0.3 to 29 GPa. At the transition to phase IV (10.6 GPa), a tail ranging to the lower-energy side suddenly appears.

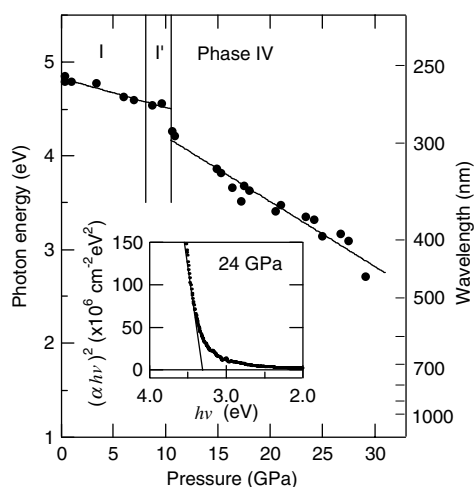


Figure 4. The pressure dependence of the absorption edge of solid H₂S. The absorption edge is given by the intersection between the horizontal axis and a line obtained from the $(\alpha hv)^2 - hv$ plot shown in the inset.

E_g is given by the intersection between the horizontal axis and a line obtained from the plot of $(\alpha hv)^2$ versus hv . The E_g obtained is indicated as a function of pressure in figure 4. The small jump of E_g can be found at 11 GPa, corresponding to the phase transition from the plastic phase (phase I') to the ordered phase (phase IV). According to the recent x-ray diffraction experiment [6], the nearest-neighbour S–S distance drastically decreases on transition to phase IV. The drastic decrease in the S–S distance seems to give rise to a discontinuous decrease in the energy gap.

As reported in the previous paper [7], solid H₂S was coloured pale yellow at the transition to phase IV and changed in colour to dark brown with increasing pressure. Nonetheless, the

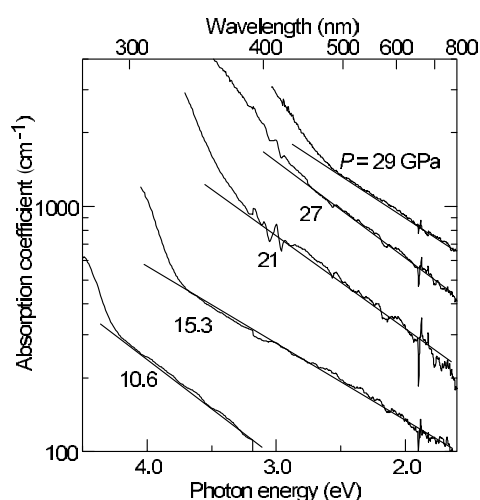


Figure 5. Absorption spectra of solid IV plotted with a logarithmic scale. Straight lines are guides to the eye. The exponential absorption edge implies an Urbach tail, suggesting that there is disorder and/or distortion in solid phase IV.

energy gap shown in figure 4 is still in the UV region even at 27 GPa. It should be noted from figure 3 that a tail ranging to the visible region appears suddenly at the transition to phase IV (10.6 GPa). The absorption tail seems to be responsible for the colour observed with the naked eye. From the plot of the spectra with a logarithmic scale (figure 5), the absorption tail was found to be expressible with an exponential function. The exponential absorption tail, known as the Urbach tail, implies that there is some disorder or distortion in the solid. According to a molecular dynamics theoretical study [10], the H_2S molecules in phase IV show large fluctuations around the average positions. The fluctuation of the molecules is possibly responsible for the disorder, leading to the Urbach tail.

4. Conclusions

We have measured UV–visible absorption spectra of solid hydrogen sulphide (H_2S) under high pressures up to 29 GPa at room temperature. The absorption edge observed around 4.8 eV at 0.3 GPa was found to decrease almost linearly with increasing pressure and to shift below 3 eV at 29 GPa. In the pressure dependence of the absorption edge, a discontinuous decrease was found on phase transition to phase IV, corresponding to the drastic decrease in the intermolecular distance reported in a previous x-ray study.

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