



岐阜大学機関リポジトリ

Gifu University Institutional Repository

Title	Pressure-Induced Molecular Dissociation and Metallization in Hydrogen-Bonded H ₂ S Solid(本文(Fulltext))
Author(s)	SAKASHITA, M; YAMAWAKI, H; FUJIHISA, H; AOKI, K; SASAKI, S; SHIMIZU, H
Citation	[Physical Review Letters] vol.[79] no.[6] p.[1082]-[1085]
Issue Date	1997-03-03
Rights	Copyright ©1997 American Physical Society
Version	出版社版 (publisher version) postprint
URL	http://hdl.handle.net/20.500.12099/24103

この資料の著作権は、各資料の著者・学協会・出版社等に帰属します。

Pressure-Induced Molecular Dissociation and Metallization in Hydrogen-Bonded H₂S Solid

M. Sakashita, H. Yamawaki, H. Fujihisa, and K. Aoki

National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305, Japan

S. Sasaki and H. Shimizu

Department of Electronics and Computer Engineering, Gifu University, Gifu 501-11, Japan

(Received 3 March 1997)

Infrared spectra at high pressure and room temperature reveal that molecular dissociation and metallization occur in solid H₂S near 46 and 96 GPa, respectively. The disappearance of SH stretching bands in the 2300–2500 cm⁻¹ region and simultaneous appearance of a lattice vibrational mode around 1300 cm⁻¹ signal the molecular dissociation. At higher pressures, a low-energy electronic absorption band develops and eventually extends throughout the infrared region studied (700–6000 cm⁻¹). Thus, metallization seems to occur by closing a band gap originating from S-S bond formation in the dissociated phase. [S0031-9007(97)03782-4]

PACS numbers: 64.70.Kb, 62.50.+p

Pressure-induced molecular dissociation provides crucial insights into chemical bonding. Atomic and molecular solids are extremes. When molecules consisting of atoms connected by strong covalent bonds condense, van der Waals forces and other weak intermolecular interactions govern the physical properties of the resulting molecular solids. Characteristics of individual atoms are buried in the molecules. Molecular dissociation releases atoms to form an "atomic solid" whose physical properties depend more directly on characteristics of constituent atoms. Thus, atomic and molecular solids with the same composition may behave very differently. The molecular dissociation of solid hydrogen, predicted to occur at several megabars accompanied by metallization [1,2], is one representative example of this behavior.

Hydrogen sulfide H₂S is a hydrogen-bonded molecular solid at ambient pressure and low temperatures. Hydrogen bonds align the molecules in this solid just as they orient H₂O molecules in the ices. By destroying the source of these hydrogen bonds at high pressures, molecular dissociation should take place with change in the structure of solid H₂S.

Molecular dissociation in H₂O ice at high pressures was very recently identified by optical reflection [3] and absorption measurement [4]. For water, dissociation coincides with symmetrizing the hydrogen bond. That is, above 60 GPa, the protons in solid H₂O move midway between neighboring O atoms, and intact H₂O molecules are no longer obvious. This dissociation and hydrogen-bond symmetrization is well characterized as a displacive phase transition with soft-mode behavior for the proton-related vibrations. These results for H₂O suggest that its sister molecule H₂S also might dissociate at high pressures. However, it is not evident *a priori* whether the dissociation mechanisms would be similar or which dissociation pressure would be higher.

Phase transitions in solid H₂S have been studied by Raman [5,6] and Brillouin scattering [7], x-ray diffraction [8], and infrared absorption [9] to 50 GPa from 30 to 300 K. All of the phases studied are molecular, differing by arrangements of molecular orientations. No experimental evidence for molecular dissociation has been reported. A dramatic change in the electronic state of H₂S accompanied by the IV-V transition was recently observed at 27 GPa and ambient temperature [8]. The transparent, colorless IV phase becomes black and opaque, suggesting an apparently large decrease of the band-gap energy. This possible precursor of metallization motivated us to study H₂S to 100 GPa, in search of what might be a *metallic hydrogen-bonded system*.

Infrared spectra of solid H₂S were measured with a diamond-anvil cell [10]. The 30- μ m diameter, 20- μ m thick sample chamber was machined in the metal gasket by electrical-discharge methods. When the H₂S filled the chamber, the spectra were saturated, which prevents determining the positions and intensities of the peaks. We, therefore, prepared thin films of H₂S by packing most of the sample chamber with potassium bromide KBr, cooling the cell with liquid nitrogen below 170 K, and condensing gaseous H₂S (purity 99.999%) on the surface of the KBr. These operations were done in a nitrogen-purged glove box [11]. KBr is transparent from 700–6000 cm⁻¹ at these pressures.

Infrared spectra were measured with a microscope Fourier-transform infrared spectrometer with 4 cm⁻¹ spectral resolution. A reference spectrum of the empty cell at atmospheric pressure corrected for absorption by the diamond anvils. Pressures were determined from fluorescence spectra of a ruby chip buried in the KBr [12]. A thin film was studied to 100 GPa and 297 K, and a rather thick film was examined to 50 GPa.

All three fundamental vibrational modes of the H_2S molecule are infrared active. In the gas phase, these are at: ν_1 (symmetric stretch), 2615 cm^{-1} ; ν_2 (bending), 1183 cm^{-1} ; and ν_3 (antisymmetric stretch), 2623 cm^{-1} . Hydrogen bonding and other solid phase effects slightly modify the wave numbers of these bands; for instance, at 140 K and ambient pressure, ν_1 , ν_2 , and ν_3 are 2550, 1770, and 2562 cm^{-1} , respectively.

Figure 1 shows spectra of a thin film measured to 100 GPa. At pressures below 42 GPa, the strong ν_1 and ν_3 peaks appear between 2300 and 2500 cm^{-1} while the weak ν_2 bending peak is missing. The ν_1 and ν_3 peaks disappear at higher pressures, and a new broad peak appears around 1300 cm^{-1} . We interpret the disappearance of the SH stretching peaks as showing a phase transition involving dissociation of H_2S molecules. Above the transition pressure, an absorption band starting around 6000 cm^{-1} (0.74 eV) also develops gradually. The absorption extends toward lower energies with pressure and by 90 GPa covers the entire spectral region measured. This phenomenon suggests band-gap closure or metallization.

Spectra of a thick H_2S film (Fig. 2) to 50 GPa more clearly show the character of the transition near 40 GPa. The ν_1 and ν_3 stretching peaks occur near the diamond absorption and are saturated. They provide little useful information about the phase transition pressure. We used the appearance of the new peak at lower wave numbers than the stretching peaks in the 46.0-GPa spectrum to locate the V-VI phase boundary.

Figure 3 shows the pressure dependences of the vibrational frequencies of H_2S . ν_1 and ν_3 decrease by -3.5 to $-5.3\text{ cm}^{-1}\text{ GPa}^{-1}$, suggesting the SH covalent bonds

weaken slightly and the hydrogen bonds become slightly stronger as the molecules approach each other. The frequency of the ν_2 bending mode increases slightly up to 46 GPa.

The 46 GPa transition can be interpreted in terms of molecular dissociation. The disappearance of the SH stretching vibrations implies the SH bonds have ruptured, dissociating the molecules into H and S atoms, which probably have significant ionic character. We interpret the new strong broad band near 1300 cm^{-1} as a lattice vibrational mode of the atomic solid, although we cannot assign this mode more definitely until the crystal structure of phase VI is known. However, this mode may correspond to the distortional vibration of the OH_4 tetrahedron in symmetric ice [3,4] which derives from the OH bending mode when $\text{OH} \cdots \text{O}$ hydrogen bonds symmetrize. In parallel with the H_2O case, the ν_2 mode of H_2S seems to convert to a lattice mode without changing frequency at the V-VI transition. However, both the intensity and width of this peak change across the phase boundary. The ν_2 mode of the molecular phase is very weak and narrow [9], while the lattice mode of the dissociated phase is broad and strong.

At about 96 GPa, the entire specimen becomes opaque, even in the infrared, and vibrational spectrum cannot be detected. We interpret this as a transformation to a metallic phase. Although we have no information on the location and bonding state of the H atoms in the metallic state, we believe that a segregation into atomic hydrogen and sulfur phases does not take place at the transition.

A likely mechanism for the molecular dissociation transition of H_2S is displacement of the protons from the hydrogen-bonded axes, as depicted in Fig. 4(a). H and S

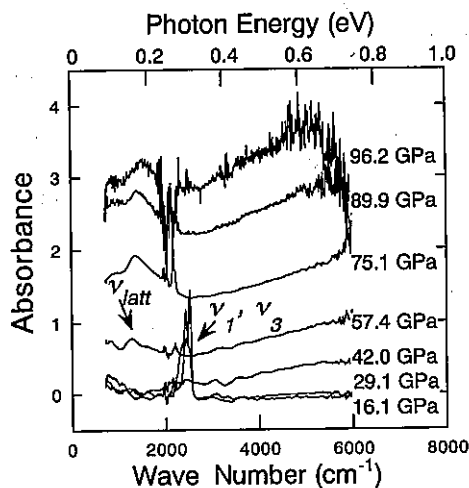


FIG. 1. Absorption spectra measured for a thin film of H_2S to 100 GPa. The strong ν_1 and ν_3 stretching peaks around 2300 cm^{-1} almost disappear at pressures above 40 GPa, where a lattice vibrational peak (ν_{latt}) begins to appear around 1300 cm^{-1} . An absorption edge attributed to electronic transitions arises at about 0.7 eV at 46 GPa. This edge moves to lower energies at higher pressures. The specimen transmits no light at pressures above 96 GPa.

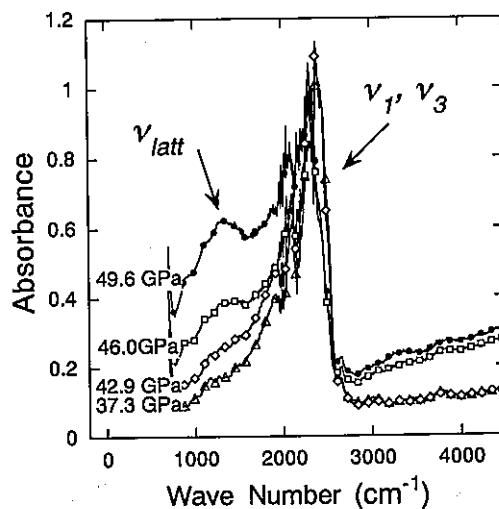


FIG. 2. Infrared absorption spectra measured for a thick film of H_2S to 50 GPa. At 46 GPa, a lattice peak definitely appears. The ν_1 and ν_3 peaks decrease in intensity at higher pressures, although measurements of these peaks are not quantitative because the diamond absorption cannot be completely subtracted.

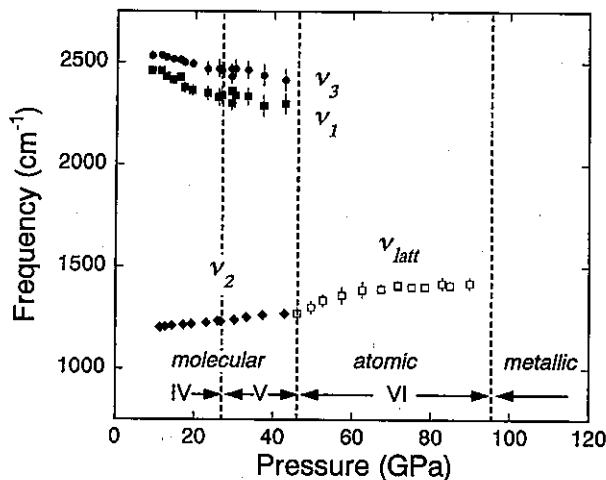


FIG. 3. The frequencies of the peaks of the infrared spectrum of solid H_2S are plotted vs pressure to 96 GPa. The bond-stretching frequencies (ν_1 and ν_3) decrease by about 10% up to 46 GPa and do not tend toward zero near the dissociation pressure. The frequencies of both the bending mode of the molecular phase (ν_2) and the lattice mode of the dissociated phase increase with pressure.

atoms are in line and connected by hydrogen bonds in the molecular phase V. Beyond 46 GPa, the H atoms move from the hydrogen-bond axes in forming an atomic solid. Because H atoms are much smaller than S atoms (the ratio of atomic radii r_H/r_S is roughly 0.3), the H atoms can occupy the interstices among the S atoms. This atomic arrangement in the dissociated solid brings each S atom in contact with many neighboring S atoms, forming many S-S bonds. This mechanism differs from the dissociative transition in H_2O which proceeds continuously without changing the molecular arrangement. The H atoms remain between O atoms in the atomic phase of H_2O , precluding direct O-O bonds, as shown in Fig. 4(b).

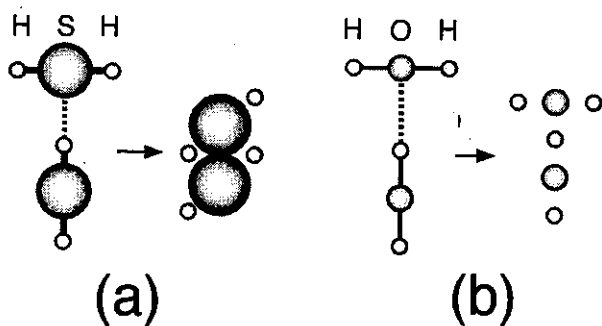


FIG. 4. In this schematic representation of the molecular dissociation processes for (a) H_2S and (b) H_2O , the molecules are shown as simple linear species to show clearly the differences between the transition mechanisms. In (a), the H atoms are pushed from the hydrogen-bond axes into the interstitial spaces among the bonded S atoms. In (b), the dissociation of H_2O molecules occurs by hydrogen-bond symmetrization; the H atoms remain aligned between neighboring O atoms, preventing formation of O-O bonding.

Similarities of the optical properties between solid H_2S and sulfur at very high pressures also support the proposed interpretations of the 46 and 96 GPa transitions of H_2S . The absorption edge of solid sulfur decreases linearly with pressure from 1.1 eV at 40 GPa to 0.65 eV at 70 GPa, and the reflectivity of sulfur suddenly increases at 95 GPa, where it metallizes [13]. Solid H_2S is already black at 40 GPa, with an absorption edge well below 1 eV. As shown in Fig. 1, the electronic absorption spectrum of H_2S extends across the infrared at about 96 GPa. The parallel behavior suggests that S-S bonds form in the dissociated phase of H_2S just as they do for the high pressure atomic phase of S. That is, S-S bonds may determine the electronic states of both solids with the H atoms having only a slight influence, if any, on the electronic states of H_2S near 100 GPa.

The vibrational spectra of H_2O and H_2S also behave differently near their dissociation transitions. For ice, the frequencies of the ν_1 and ν_3 stretching modes decrease very rapidly from 3000 cm^{-1} to nearly 0 just below the transition pressure, about 60 GPa. Beyond the transition, the frequency of the lattice mode of the dissociated phase which develops from these stretching modes gradually increases from zero. That is, for H_2O , the proton-related vibrations show soft-mode behaviors across this second-order-like dissociation process. H_2S shows no similar soft-mode behavior. The ν_1 and ν_3 modes of H_2S decrease by less than 300 cm^{-1} up to the pressure of the abrupt, first-order-like dissociation transition.

Hydrogen atoms determine the molecular arrangements in solid H_2S to 46 GPa through forming hydrogen bonds. Above 46 GPa, S atoms determine the electronic properties and crystal structure of the atomic phase. The continuous metallization of H_2S , which follows this molecular dissociation transition at higher pressures, presents a new aspect of dissociation-metallization processes in simple molecular solids. The behavior of H_2S differs from the (nearly) continuous changes of structure and electronic states observed for ice [3,4] and halogens [14–16]. Precise structural studies, including atomic positions and even electron densities, will be required to clarify the mechanisms of molecular dissociation and metallization.

This work was supported by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation.

- [1] Russel J. Hemley and Neil W. Ashcroft, *Nature (London)* **380**, 671 (1996).
- [2] S. T. Weir, A. C. Mitchell, and W. J. Nellis, *Phys. Rev. Lett.* **76**, 1860 (1996).
- [3] A. F. Goncharov *et al.*, *Science* **273**, 218 (1996).
- [4] K. Aoki *et al.*, *Phys. Rev. B* **54**, 15 673 (1996).
- [5] H. Shimizu, Y. Nakamichi, and S. Sasaki, *J. Chem. Phys.* **95**, 2036 (1991).
- [6] H. Shimizu *et al.*, *Phys. Rev. B* **51**, 9391 (1995).

- [7] H. Shimizu and S. Sasaki, *Science* **257**, 514 (1992).
[8] S. Endo *et al.*, *Phys. Rev. B* **54**, 717 (1996).
[9] H. Shimizu *et al.*, *Phys. Rev. B* **55**, 5538 (1997).
[10] K. Aoki *et al.*, *Jpn. J. Appl. Phys.* **26**, 2107 (1987).
[11] K. Aoki, H. Yamawaki, and M. Sakashita, *Phys. Rev. Lett.* **76**, 784 (1996).
[12] H. K. Mao *et al.*, *J. Geophys. Res.* **91**, 4673 (1986).
[13] Huan Luo *et al.*, *Phys. Rev. Lett.* **67**, 2998 (1991).
[14] K. Takemura *et al.*, *Phys. Rev. Lett.* **45**, 1881 (1980).
[15] Y. Fujii *et al.*, *Phys. Rev. Lett.* **63**, 536 (1989).
[16] H. Fujihisa *et al.*, *J. Phys. Chem. Solids* **56**, 1439 (1995).