High-pressure phase transitions of solid H_2S probed by Fourier-transform infrared spectroscopy

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Infrared-absorption spectra of solid H_2S have been measured at high pressures up to 50 GPa and room temperature. The symmetric stretching overtone vibration $2\nu_1$ shows a redshift in frequency with increasing pressure, and changes into two components at about 11 GPa for the II-IV phase transition. The pressure dependence of the observed $2\nu_1$, $\nu_2+\nu_3$ (bending plus asymmetric-stretching combination bands), and ν_2 vibrations shows strongly the existence of the phase transition from IV to V at about 30 GPa, which is consistent with a recent high-pressure x-ray study. The derived frequencies of fundamental ν_1 and ν_3 vibrations continue to decrease with pressure up to the IV→V phase transition, and show small jumps at its point and moreover decrease slightly up to 45 GPa. The S-H- - -S hydrogen-bond system still exists up to at least 45 GPa; however, its bonding is very weak. [S0163-1829(97)02810-5]

I. INTRODUCTION

Hydrogen sulfide (H_2S) is a typical molecular solid showing the hydrogen bond which is a very important interaction in nature.[1] It is well known that H_2O ices can exist in many different phases at various pressures and temperatures,[2–5] however, the pressure-temperature (P-T) phase diagram of solid H_2S is still little known, despite its many similarities to H_2O. We have studied Raman spectra,[6,7] Brillouin scattering,[8,9] and x-ray diffraction[10] of solid H_2S under high pressures. At room temperature, orientationally disordered phase I exists at pressures from 0.47 to about 8 GPa, and more compression of solid H_2S leads to the phase transition from phase II (or I′) to phase IV at about 11 GPa. This phase IV persists to at least 23 GPa.[6]

Recently, we have determined the P-T phase diagram of H_2S at high pressures up to 20 GPa and at temperatures from 300 to 30 K, by using Raman spectroscopy with a high-pressure diamond-anvil cell.[11] The triple point between the II, III, and IV phases of solid H_2S exists at about 3.1 GPa and 153 K. Phase IV is stable in the wide P-T region. The conclusive phase diagram of H_2S is simple in comparison with that of H_2O ice.

Very recently, we have found a high-pressure phase at 300 K and at pressures above about 30 GPa by x-ray measurements.[12] This phase V appeared with an accompanying color change from a thin yellow to black.

In this paper, we present an infrared-absorption measurement of solid H_2S at pressures up to 50 GPa and 300 K. The remarkable change in infrared spectra indicates clearly the pressure-induced phase transition at about 30 GPa, which is consistent with our recent x-ray result.[12] The analyzed fundamental frequencies of symmetric and asymmetric S-H stretching vibrations decrease with pressure up to the IV→V phase transition, and then show small jumps and moreover gradual decrease up to 45 GPa. The slight pressure dependence of their frequencies implies that the S-H- - -S hydrogen-bond system still exists up to at least 45 GPa; however, its bonding is very weak.

II. EXPERIMENT

Infrared spectra of solid H_2S were measured with a diamond-anvil cell (DAC) at various pressures and 300 K. The system for the loading of H_2S gas into DAC is the same as in our previous reports on H_2S.[6–12] The sample chamber was approximately 60 μm in diameter and 40 μm thickness in a metal gasket between two type II-A diamonds. Spectra were measured with a microscope Fourier-transform infrared spectrometer with 4 cm^{-1} resolution.[13] Since diamond itself has strong absorption in the range from 2400 to 1800 cm^{-1}, absorption spectra were normalized by the measurement of the empty DAC as a reference. Pressure was measured by the ruby-scale method.[14]

III. RESULTS AND DISCUSSION

Infrared-absorption measurements of solid H_2S have been made at high pressures from 2 to 50 GPa. Figure 1 shows a typical absorption spectrum of crystalline H_2S phase IV at 13.6 GPa and room temperature. The H_2S molecule has three normal vibrational modes, the symmetric S-H stretching mode ν_1, the S-H bending mode ν_2, and the asymmetric S-H stretching mode ν_3. All modes are infrared active in a molecular solid. Since absorptions associated with ν_1 and ν_3 vibrations around 2500 cm^{-1} were too strong, their band positions were unable to be determined due to saturation. However, to assign the observed bands, we made one measurement of fundamental ν_1 and ν_3 modes at about 11 GPa by the use of transparent CsI for the compensation of sample thickness in a DAC chamber. As seen in Fig. 1, the difference in frequency between ν_3 and ν_1 vibrational modes shows a large value of about 70 cm^{-1} at about 11 GPa. Therefore, this observation gives strong support for making the mode assignment for combination bands. For four
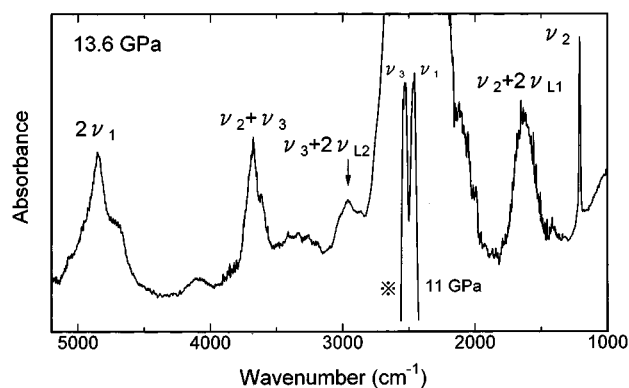
FIG. 1. Infrared-absorption spectrum of H_2S solid phase IV measured at 13.6 GPa and room temperature. Approximate locations are 4848 and 4715 cm^{-1} ($2\nu_1$), 3674 and 3614 cm^{-1} ($\nu_2+\nu_3$), 2960 ($\nu_3+2\nu_{L2}$), 1633 ($\nu_2+2\nu_{L1}$), and 1209 cm^{-1} (ν_2). * The ν_3 and ν_1 fundamental absorption spectrum at about 11 GPa (ν_3; 2520 cm^{-1} and ν_1; 2449 cm^{-1}): This spectrum was measured for mode assignment, by using the transparent CsI for the compensation of sample thickness in a DAC chamber.
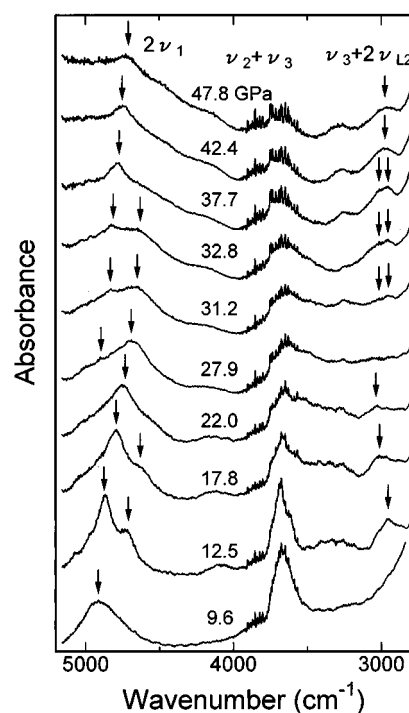

FIG. 2. Infrared-absorption spectra of solid H_2S in the $2\nu_1$, $\nu_2+\nu_3$, and $\nu_3+2\nu_{L2}$ vibrational regions at various pressures and room temperature.

combination[15] and ν_2 fundamental bands observed with adequate absorption intensities, the vibrational frequencies were observed over the whole pressure range measured. Judging from the fundamental ν_1 and ν_3 frequencies observed above, we identified reasonably two bands around 4800 and 3700 cm^{-1} as the overtone band of $2\nu_1$ and combination band $\nu_2+\nu_3$, respectively. Furthermore, the combination bands of $\nu_3+2\nu_{L2}$ and $\nu_2+2\nu_{L1}$ (ν_{L1} and ν_{L2} are lattice vibrational modes) were assigned from the feature of a broadband and the self-consistent set of each vibrational frequency. These will be described below in detail.

In Figs. 2 and 3, infrared spectra in the frequency regions from 5200 to 2800 cm^{-1} and from 2000 to 800 cm^{-1} are shown under various pressures, and their frequencies are plotted as a function of pressure in Fig. 4. The overtone mode $2\nu_1$ shows a redshift in frequency, and changes into two components at the II-IV phase transition. The half of their frequencies are also plotted by solid circles in Fig. 4. Their values around 11 GPa are very close to the experimental value of the fundamental ν_1 frequency measured. The behavior of the ν_1 frequency is consistent with the result of the fundamental ν_1 vibration observed by our Raman study up to 23 GPa.[6] Moreover, a discrete change in the $2\nu_1$ frequency at about 30 GPa is clearly seen in Figs. 2 and 4. This result strongly indicates the pressure-induced phase transition at about 30 GPa, which supports our recent x-ray study showing the transition from phase IV to a solid phase V.[12] The large interval of two peaks around the phase transition indicates the coexistence of phase IV and a phase V up to at least 37 GPa. The negative slope of $2\nu_1$ (or ν_1) frequency over the whole pressure range measured, i.e., the softening of the S-H stretching vibration indicates the existence of the S-H- - -S hydrogen-bond system up to at least 45 GPa. However, the slight pressure dependence of its frequency implies that its bonding is very weak.

For the bending vibrational ν_2 mode near 1200 cm^{-1} in Fig. 3, the characteristic feature of the spectra is the extreme

sharpness of the lines ascribable to the fundamental. As seen in Fig. 4, the ν_2 mode shows a slight increase in frequency with pressure, because the atomic motions are close to being perpendicular to the direction of hydrogen bonds which are
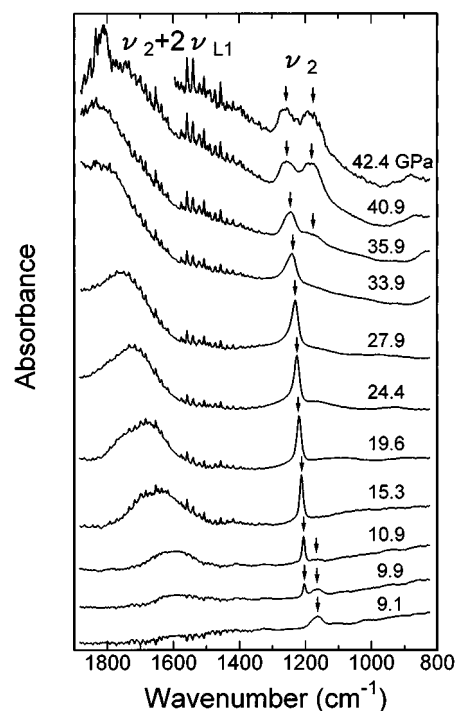

FIG. 3. Infrared-absorption spectra of solid H_2S in the $\nu_2+2\nu_{L1}$ and ν_2 vibrational regions at various pressures and room temperature.
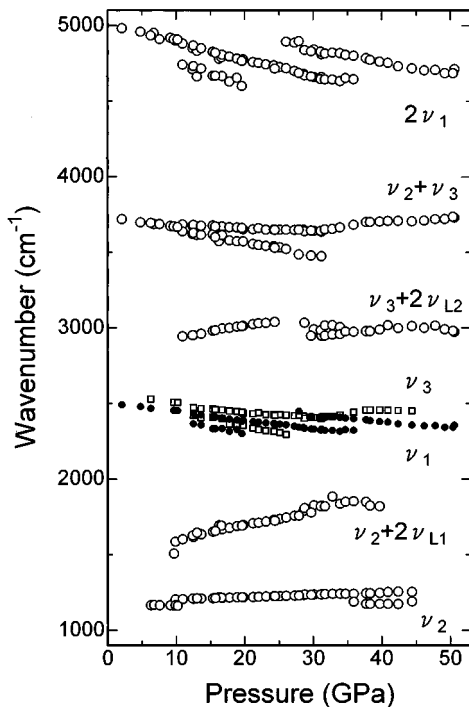
FIG. 4. Pressure dependence of the infrared-absorption frequencies for the $2\nu_1$, $\nu_2+\nu_3$, $\nu_3+2\nu_{L2}$, $\nu_2+2\nu_{L1}$, and ν_2 vibrational bands in solid H_2S at room temperature. The frequencies measured on loading process are plotted. The derived frequencies of fundamental ν_3 and ν_1 modes are shown as a function of pressure by open squares and solid circles, respectively.
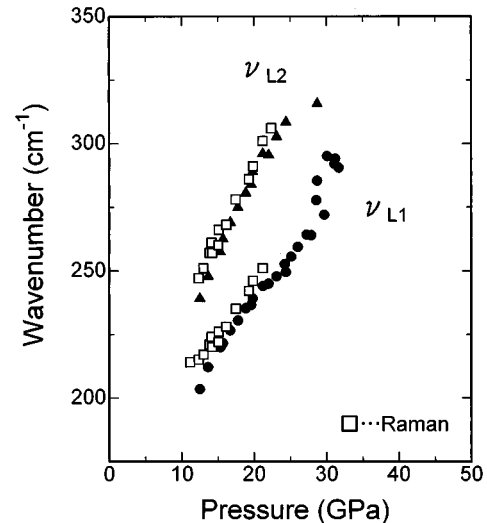

FIG. 5. The derived frequencies of lattice vibrational modes, ν_{L2} and ν_{L1} are plotted as a function of pressure by solid triangles and solid circles, respectively. The results from Raman measurements, (Ref. 6) are shown by open squares for comparison.

dominantly under the influence of pressure effect on crystalline H_2S. At the II to IV phase-transition point around 11 GPa, the ν_2 frequency shows a jump of about 50 cm^{-1}, and around 30 GPa the spectra show the asymmetric broad profile and, moreover, split to two broad peaks in the phase V.

For the combination bands $\nu_2+\nu_3$ near 3700 cm^{-1} in Figs. 2 and 4, it shows a gradual decrease in frequency with increasing pressure up to about 30 GPa. At the highest pressures, the scratchiness probably due to H_2O contamination makes this band difficult to resolve. By using measured ν_2 frequencies, we can plot the derived ν_3 frequencies by open squares as a function of pressure in Fig. 4. Their values around 11 GPa are very close to the experimental value of the fundamental ν_3 frequency measured. The frequencies of two ν_3 modes show the redshift up to the II-IV phase-transition point. Their pressure derivatives are approximately the same as those of ν_3 modes in phase IV observed by our high-pressure Raman measurements up to 23 GPa.[6] Furthermore, a slight decrease in ν_3 frequency against pressure in the phase V suggests that the S-H- - -S hydrogen bond exists up to at least 45 GPa, but its bonding is very weak.

Two broadbands near 3000 and 1700 cm^{-1} in Figs. 2 and 3 appear at pressures above 11 GPa, i.e., in the IV phase. These broad absorptions are due to the combination bands with lattice vibrational modes which appear just in the IV phase.[6] Judging from the lattice phonon modes studied by our Raman measurements[6] and the frequencies of ν_3 and ν_2 modes obtained above, two bands can be assigned to the

combination bands of $\nu_3+2\nu_{L2}$ and $\nu_2+2\nu_{L1}$ with ν_{L2} and ν_{L1} phonon modes, respectively. The pressure dependence of their frequencies is shown in Fig. 4. At a higher pressure range, the data from the spectra are not clear due to the weak signal and the broadband. From the frequencies of the ν_3 and ν_2 modes, therefore, we could determine the ν_{L2} and ν_{L1} frequencies as a function of pressure in phase IV (see Fig. 5), which show excellent agreement with those observed by our previous Raman measurements.[6]

The opaque nature of the phase V means that the optical absorption occurs in the whole region of the visible wavelength below 1 μm ($=10\,000$ cm^{-1}). There is no evidence for metallization, but the rising absorption at higher frequencies can be seen at the highest pressures in Fig. 2. This feature will be connected with the color change to black opaque. Namely, the tail of the absorption edge will develop gradually toward the lower frequency region.

IV. CONCLUSION

We have studied high-pressure phase transitions of solid H_2S by using Fourier-transform infrared spectroscopy. The absorption spectra for $2\nu_1$, $\nu_2+\nu_3$, $\nu_3+2\nu_{L2}$, $\nu_2+2\nu_{L1}$, and ν_2 vibrational bands have been measured as a function of pressure in the 2–50 GPa range at room temperature. The pressure-induced phase transition has been found at about 30 GPa, in close agreement with our recent x-ray results. This phase transition from IV to V occurs with an accompanying color change from a thin yellow to black. The softening of the symmetric and asymmetric S-H stretching vibrations with pressure suggests the existence of the S-H- - -S hydrogen-bond system up to at least 45 GPa and 300 K; however, the slight pressure dependence of their frequencies implies that its bonding is very weak. The opaque nature of the phase V is investigated with the concept of optical absorption.

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