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Pressure-induced phase transition of hydrogen sulfide at low temperature: Role of the hydrogen bond and short S-S contacts

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New phase transitions have recently been observed experimentally for H_2S in the low-temperature and high-pressure regime. In this paper the nature of the transition between phases IV′ and IV is elucidated using *ab initio* constant pressure molecular-dynamics simulations. We show that the cell parameters do not show discontinuity at the phase boundary between phases IV′ and IV consistent with the experimental results. The present analysis suggests that the formation of short S-S contacts and the reformation of hydrogen-bonded network are the possible driving force of the IV′→IV transition. Implications to the phase IV structure at room temperature will also be given.

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I. INTRODUCTION

Hydrogen sulfide (H_2S) is, at the molecular level, an analog of water, but its properties and behavior are significantly different in the condensed phases. Whereas water is strongly hydrogen bonded, hydrogen sulfide appears to be very weakly hydrogen bonded at ambient pressure. It is known that H_2S shows three molecular solid phases at low temperature under ambient pressure. The high-temperature phase I ($126.2 < T < 187.6$ K) has the space group of cubic $Fm\overline{3}m$; S-H bond orientations are disordered and symmetric about all four C_3 axes. The intermediate phase II ($103.5 < T < 126.2$ K) is orientationally disordered with anisotropic distributions and has cubic $Pa\overline{3}$. The lowest-temperature phase III ($T < 103.5$ K) has orthorhombic $Pbcm$ with the orientational order arranged in a quasi-two-dimensional hydrogen-bonded network.[1] Thus, H_2S is a good simple molecular system for exploring intermolecular interactions in the very weakly hydrogen-bonded regime.

The transition sequence of hydrogen sulfide found on compression is similar to that found on cooling; the structural behavior is dominated by increasing orientational ordering. Phase I is formed above 0.47 GPa at room temperature. Further compression above 9.1 GPa results in the primitive cubic phase I′ which then transforms to phase IV at 11 GPa.[2,3] The structures of these pressure-induced phases are still a matter of debate. Particularly, there have been several arguments on the structure of phase IV. Two x-ray diffraction experiments reported so far suggest different structures of sulfur sublattice.[3,4] Furthermore, *ab initio* molecular dynamics (MD) simulation for room temperature using the experimental structure as an initial configuration showed, contrary to experiment, the existence of partial orientational disorder and emphasized the importance of dynamical fluctuation in the analysis of x-ray diffraction patterns.[5]

So far, the Raman scattering and IR absorption techniques have usually been employed for the study of the pressure-temperature phase diagram in the low-temperature and high-pressure regime. Whereas diffraction experiment is able to offer more direct information on crystal structure, only one neutron experiment has been reported around the region of phases I′ and II.[6] Recently, Fujihisa *et al.* performed an x-ray powder diffraction experiment in the lower-temperature and higher-pressure region of phases III and IV using a diamond-anvil cell.[7] They successfully obtained the diffraction images of good quality in the conditions of low temperature ($T < 150$ K) and high pressure ($P > 1$ GPa). Careful analysis of the diffraction patterns suggests that there exist two new phases tentatively called phases III′ and IV′ in addition to phases III and IV known so far. However, since the x-ray diffraction cannot determine the hydrogen positions, the basic nature of the structures and the phase transitions at low temperature is not clear.

In this paper, using *ab initio* electronic state calculations we examine possible hydrogen positions for the low-temperature phases of hydrogen sulfide based on the structure of sulfur sublattice determined experimentally. Then, the relation among the structures of the low-temperature phases are clarified using *ab initio* constant pressure MD simulations.

II. METHODS

The present study of solid hydrogen sulfide was performed using the density-functional theory in the generalized gradient approximation by Perdew, Burke, and Ernzerhof.[8] This choice of the exchange-correlation functional is justified by the excellent agreement of hydrogen bond energy for H_2S dimer (-6.91 kJ/mol) with the experimental estimate[9] (-7.1 kJ/mol). The valence-core interaction was described by norm-conserving pseudopotentials of Troullier-Martins type.[10] The valence orbitals were expanded in plane waves with an energy cutoff of 70 Ry. This rather high energy cutoff is required to achieve the convergence of stress tensor included in the constant pressure algorithm. Brillouin zone sampling is restricted to the supercell Γ point unless mentioned otherwise. For constant pressure MD simulation we used the *ab initio* MD implementation of the Parrinello-Rahman approach.[11] Nosé-Hoover chain thermostat[12,13] for the simulation box was introduced so as to minimize the

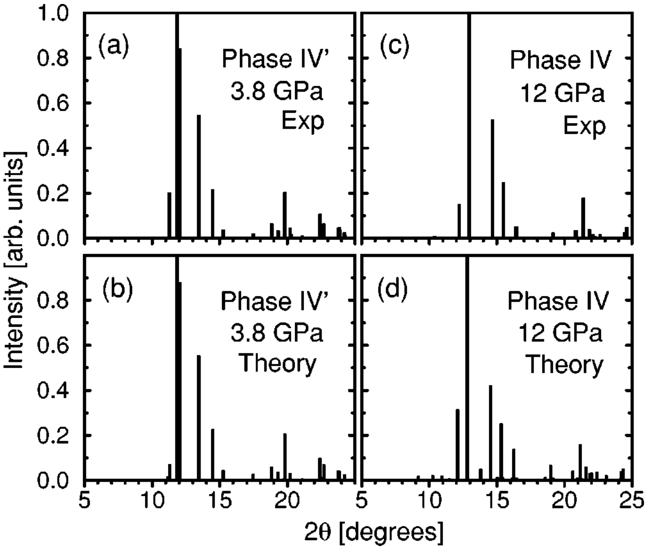

FIG. 1. The theoretical and experimental x-ray powder diffraction patterns of H_2S obtained with $\lambda = 0.6198$ Å at 3.8 and 12 GPa. The experimental x-ray patterns are shown after Rietveld refinement. The theoretical patterns were calculated using the static structural models shown in Fig. 3.

relaxation time to equilibrium state. Temperature was also maintained by introducing Nosé-Hoover chain thermostat coupled to the nuclear degrees of freedom. The simulations were performed using the CPMD package.[14]

III. RESULTS AND DISCUSSION

The x-ray experiment suggests that phase IV′ has the space group of orthorhombic *Ibca* and the unit cell contains sixteen sulfur atoms. To construct structural model for phase IV′, we examined the possible hydrogen positions in the following way. First, we put hydrogen atoms at the general symmetry site of the space group of phase IV′ in the experimental sulfur sublattice under the constraint of the molecular shape of S-H bond length (1.3 Å) and H-S-H bond angle (92°). It turned out that only a few configurations can satisfy the above criteria; when a hydrogen atom is put at the general symmetry site, the position of another hydrogen atom forming a H_2S molecule together with a given hydrogen is automatically determined by the symmetry operation. Secondly, the geometry optimization was done with lattice parameters fixed to experimental ones at 3.8 GPa. In this calculation $4\times4\times4$ Monkhorst-Pack mesh was utilized for Brillouin zone sampling to calculate accurately the difference of total energies for generated configurations. We picked up the lowest energy configuration as a candidate of structural model for phase IV′. Finally, the x-ray powder diffraction patterns were compared between the theoretical and experimental structures; the results for $\lambda = 0.6198$ Å are shown in Fig. 1. The theoretical structure reproduces the experimental ones very well, suggesting the validity of our structural model.

The transition from phase IV′ to phase IV was observed experimentally at around 12 GPa and 100 K by increasing pressure. To investigate the nature of this phase transition and hopefully obtain the information of crystal structure after the phase transition, we carried out *ab initio* constant pressure MD simulations at 100 K. Our sample consists of 32 H_2S molecules in a periodic box defined as

$$\mathbf{a}' = \mathbf{a} + \mathbf{b}, \quad \mathbf{b}' = -\mathbf{a} + \mathbf{b}, \quad \mathbf{c}' = \mathbf{c}, \tag{1}$$

where **a**, **b**, and **c** are the translation vectors of the phase IV′ structure. Six pressure-temperature (P-T) points were explored by increasing pressure by ~2 from 3.8 GPa to 14.0 GPa. For each P-T point trajectories of 4 ps long were generated after an initial equilibration. Figure 2 shows the pressure dependence of the supercell dimensions obtained by statistical averaging. The distinction between orthorhombic and tetragonal unit cell manifests itself in the deviation of γ' from 90° because of our choice of supercell given in Eq. (1). The error bars on the data points were roughly estimated as 0.08 Å and 0.05° for the length and the angles, respectively. Therefore, the length of a' and b' is the same within computational accuracy at each pressure point. The angles of α' and β' are virtually 90°, while the angle of γ' varies with pressure and becomes 90° at around 12.0 GPa. Thus, the orthogonal unit cell of phase IV′ where the length of a and b is slightly different from each other transforms to the tetragonal unit cell with increasing pressure around 12.0 GPa. This characteristic behavior of lattice parameters is in qualitative agreement with the experimental results.

In addition to the change of crystal system close examination of atom positions generated by our constant pressure MD simulations suggests the change of space group at around 12 GPa. As shown in Fig. 3 hydrogen-bonded network is distorted above ~12 GPa with the slight shift of the positions of sulfur atoms. The resultant space group above ~12 GPa is identified as *Pbca* rather than *Ibca*. The structural parameters that we obtained for 3.8 and 12.0 GPa are

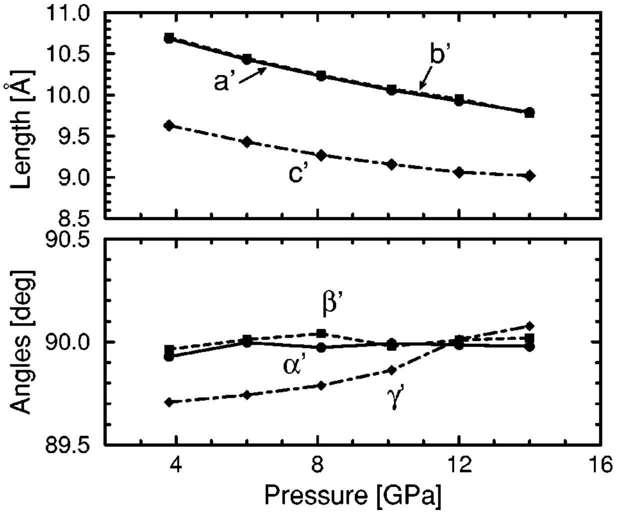

FIG. 2. Pressure dependence of the simulation box defined in the text. The distinction between orthorhombic and tetragonal unit cell manifests itself in the deviation of γ' from 90° because of our choice of supercell given in Eq. (1). The error bars on the data points were roughly estimated as 0.08 Å and 0.05° for the length and the angles, respectively.

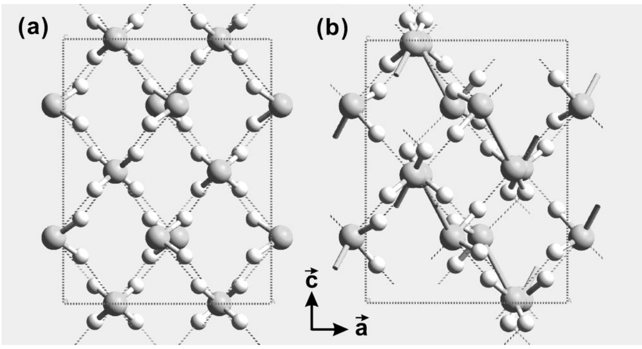

FIG. 3. Static structural models of H_2S at (a) 3.8 GPa and 100 K and (b) 12.0 GPa and 100 K obtained by identifying equilibrium atom positions from our constant pressure MD simulations. Shown are the projections onto *ac* plane.

summarized in Table I. In addition to the reformation of hydrogen-bonded network the structure above ~12 GPa has another unique feature of the static formation of short S-S contact (~2.9 Å) represented by sticks in Fig. 3(b). This contrasts strikingly with the dynamical formation of short S-S contact reported in Ref. 5. Very recent high pressure experiments[15,16] observed that molecular dissociation of H_2S and D_2S occurs at ~30 GPa and room temperature as opposed to the previous reports of molecular phase V.[17,18] Although the stabilization of phases V and VI was predicted with respect to phase separation or even coexistence of H_2S with elemental S and H below ~80 GPa,[19] x-ray experiments on H_2S suggested that above ~30 GPa several phases coexist such as phase IV of H_2S, phase II of sulfur, amorphous, and undefined crystalline phase; phase II of solid sulfur[20] is dominant among these phases.[21] Therefore, the formation of short S-S contact seen in our simulation might trigger molecular dissociation in solid hydrogen sulfide under high pressure.

TABLE I. Structural parameters of solid hydrogen sulfide at 3.8 and 12.0 GPa obtained by statistical averaging of atom positions generated by our constant pressure MD simulations at 100 K. The space group is identified as *Ibca* and *Pbca* at 3.8 and 12.0 GPa, respectively. Both the cases sixteen molecules are included in unit cell.

Atom	Cite	*X*	*Y*	*Z*
		3.8 GPa and 100 K		
S(1)	8*c*	−0.02	0.00	1/4
S(2)	8*d*	1/4	0.29	0.00
H(1)	16*f*	0.10	0.10	0.18
H(2)	16*f*	0.15	0.34	0.43
		12.0 GPa and 100 K		
S(1)	8*c*	0.43	0.02	0.25
S(2)	8*c*	0.23	0.29	0.49
H(1)	8*c*	0.43	0.40	0.31
H(2)	8*c*	0.11	0.17	0.41
H(3)	8*c*	0.29	0.36	0.07
H(4)	8*c*	0.05	0.09	0.15

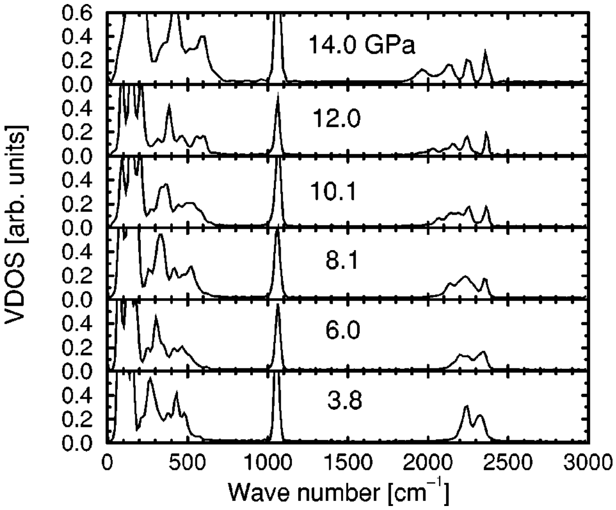

FIG. 4. Pressure dependence of vibrational density of states (VDOS) of solid hydrogen sulfide calculated from velocity autocorrelation functions using the data of our constant pressure simulations.

It is natural to expect that x-ray diffraction patterns above ~12.0 GPa may have many peaks compared to those below ~12.0 GPa because reflection conditions of $h+k+l=$odd are also allowable in the *Pbca* lattice. Nevertheless, the calculated x-ray patterns with the static model shown in Fig. 3(b) are very similar to the observed ones except for the small features around 10° and 14° as shown in Fig. 1(d). Such small features could be considerably diminished in intensity by the large thermal fluctuation of sulfur atoms as well as hydrogens as actually seen in our simulations even at 100 K.[22] Another possibility is that the *Pbca* structure we obtained does not correspond to the final structure of this phase transition but to the intermediate one; duration of our MD runs of picoseconds is not long enough to complete the phase transition at low temperature. Despite of this shortcoming and a part of disagreement with the experimental result still we can safely conclude that the IV′→IV transition of H_2S at ~12 GPa and ~100 K could be driven by the two factors: reformation of hydrogen-bonded network and the formation of short S-S contact.

Pressure dependence of vibrational frequencies is a useful phenomenon for the study of phase transition under pressure; actually the *P*-*T* phase diagram of H_2S by Shimizu *et al.* was constructed based on the Raman scattering data.[23] Figure 4 shows the vibrational density of states for H_2S calculated from velocity autocorrelation functions using the data of our constant pressure simulations. The bending mode located at ~1050 cm^{-1} in Fig. 4 shows almost no pressure dependence in frequency in this pressure regime, while the stretching modes at ~2300 cm^{-1} show a pronounced splitting above 12 GPa indicating that the intramolecular stretching modes are strongly coupled to each other between neighboring molecules. It is worth while noticing that two higher frequency peaks of the stretching modes have little pressure dependence in frequency. Both the experiments of IR absorption and Raman scattering observe two strong peaks in stretching region and those peaks show little frequency shift in this pressure region. Hence, the structural change at ~ 12 GPa is reflected with high probability in the appearance of additional peaks in the lower frequency tail of the two strong stretching peaks.

Rousseau *et al.* studied the structure and dynamics of H_2S in phase IV at room temperature using *ab initio* MD simulations and suggested that phase IV has a partial rotational disorder with a crystal structure of approximate symmetry $P4_2/ncm$ at 17 GPa.[5] Before arriving at this conclusion, they compared the pressure dependence of intramolecular vibrational modes and the x-ray diffraction patterns computed from their constant-volume simulations with the available experimental data. The computed stretching and bending modes reproduce a pronounced splitting of these modes seen in Raman spectra associated with the $\mathrm{I}' \rightarrow \mathrm{IV}$ transition at room temperature. The simulated structure factor also reproduces quite well the peak positions and relative intensities of the experimental x-ray diffraction patterns when taking into account the contribution of diffuse scattering which exhibits important structures according to their analysis. Although the agreement of the two quantities with the experimental data seems to be satisfactory, we should point out that the Raman scattering experiment observed clearly the sudden appearance of lattice modes in addition to a splitting of intramolecular modes when the $\mathrm{I}' \rightarrow \mathrm{IV}$ transition occurs at room temperature.[2] This suggests strongly that H_2S molecules form the ordered structure above ~ 12 GPa even at room temperature. Contrary to the result of Rousseau *et al.*, our phase IV structure does not show a rotational disorder even when the temperature is raised to room temperature. However, our simulation time of 4 ps is insufficient to obtain reliable Raman or infrared spectra in the region of lattice modes ($\leqslant 300\ \mathrm{cm}^{-1}$). It is not surprising that our calculations give so different results from those of Ref. 5; Rousseau *et al.* used the structural model for phase IV proposed by Fujihisa *et al.*[3] as an initial configuration. We noticed that this model has very high energy even compared to disordered configurations occupying very wide configuration space. Therefore, the simulations of Rousseau *et al.* correspond to the study of ordering process because the system becomes disordered immediately after the MD simulation is started. On the other hand, in this work an initial configuration is carefully selected so as to ensure that the selected configuration has lower energy than the disordered one. This selection enables us to avoid disordering of the system and reach the other ordered structure.

Finally, we describe briefly the current understanding of phase III′ from theoretical calculations. We performed geometry optimization following the same procedure as used for phase IV′. We were able to find a possible structure compatible with the space group $Pcca$ suggested experimentally. It also reproduces quite well the observed x-ray diffraction patterns. However, our MD simulations for 100 K starting from the optimized structure showed reorientational motion even at 100 K.[24] This may imply that the unit cell of phase III′ must contain more independent symmetry sites for hydrogen atoms than those assumed in our calculation (two $8f$ sites). Anderson *et al.* reported the Raman spectra of solid H_2S in the pressure range of between 0 and 3 GPa at 25 K.[25] Their observed Raman spectra seem to suggest that one or more phase changes occur as the result of molecular reorientation under pressure before the stable structure is realized above ~ 3 GPa. Combining the result of ours with that of Anderson *et al.*'s, we can expect that the P-T phase diagram of H_2S in the regime of $0 < P < 3$ GPa and $T < 150$ K may be more complex than the present one and the stable region of phase III′ could be much narrower than the present expectation from the x-ray analysis.

IV. CONCLUSIONS

We have performed *ab initio* calculations of solid H_2S to obtain the crystal structures for low-temperature and high-pressure phases discovered recently by x-ray diffraction experiment. Then we have examined the nature of the transition between phases IV′ and IV using *ab initio* constant pressure MD simulations. Our simulations suggested that the cell parameters do not show discontinuity at the phase boundary between phases IV′ and IV being consistent with the experimental results. We also suggested that the formation of short S-S contacts and the reformation of hydrogen-bonded network are the possible driving force of the $\mathrm{IV}' \rightarrow \mathrm{IV}$ transition. Whereas the stable structures at ~ 100 K were successfully obtained for phases IV′ and IV, the same procedure as used for phase IV′ failed to predict stable structure for phase III′. This implies that the phase diagram may be more complex than the present one and the stable region of phase III′ could be much narrower than the present expectation from the x-ray analysis.

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