Structural and dynamical properties of H$_2$S under high pressure: *ab initio* molecular dynamics studies

Structural and dynamical properties of H_2S under high pressure: *ab initio* molecular dynamics studies

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Abstract
The structural and dynamical properties of H_2S in the region $0 \text{ GPa} < P < 4.3 \text{ GPa}$ and $T = 80$ K are investigated extensively by *ab initio* molecular dynamics (MD) simulations. Our results indicate that the hydrogen bonding is very weak and the intermolecular interaction is mainly contributed by the van der Waals force below 3.3 GPa. When the pressure reaches 3.8 GPa, the intermolecular covalent hydrogen bond forms, causing a phase transition between the phases III′ and IV′. No evidence of short S–S contact is found; the H_2S maintains very good characteristics of single molecules. The hydrogen-bonded network does not change in our research range. There is no sign that a new phase of hydrogen sulfide exists in this P–T range.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Hydrogen sulfide shows very complicated behavior under extreme conditions, especially at high pressure and low temperature. At ambient pressure, there are three solid phases at low temperature, which are phase I (cubic $Fm\bar{3}m$), phase II (cubic $Pa\bar{3}$) and phase III (orthorhombic $Pbcm$) [1]. The S–H bond orientations in phase I and phase II are disordered, while they are ordered in phase III. Using a diamond anvil cell, the properties of H_2S under high pressure have been investigated [1–12]. Up to 8 GPa and 11 GPa at room temperature, hydrogen sulfide transforms to phase I′ (cubic $P2_13$) [3] and phase IV with the symmetry of tetragonal $I41/acd$ [2, 8] suggested by Fujihisa or monoclinic Pc [9] suggested by Endo, respectively. Sulfur atoms in I′ (IV-$I41/acd$, IV-Pc) slightly dislocate from the face-centered cubic (fcc) structure of phase I. Phase IV transits to phase V [5, 6] under 27 GPa at room temperature and phase VI [7] under 46 GPa, which is the highest pressure phase of hydrogen sulfide ever

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known. When the pressure is even higher, molecular dissociation and metallization occur in solid H_2S near 27 GPa [12, 16] and 96 GPa [7] at room temperature, respectively. Raman and infrared scattering studies show that D_2S dissociates to form sulfur at pressures above 27 GPa at room temperature. At low temperature, the phase diagram of hydrogen sulfide is even more complicated. When the system is compressed, the lowest phase, phase III, experiences a very different phase transition compared with the case at room temperature. Two new phases, phase III′ (*pcca*) and phase IV′ (orthorhombic *Ibca*) [12], appear between phase III and phase IV. Phase IV is stable in a wide *P–T* region at both room temperature and low temperature.

However, from these experiments based on x-ray diffraction, Raman spectra and infrared-absorption spectra, not enough information about the position of hydrogen atoms could be obtained. Neutron diffraction techniques have been used to totally determine the structure of phase I′: partial molecular orientation rotationally disordered about the ⟨111⟩ axes is found (as in phase II at ambient pressure), but with markedly greater nonuniformity of the toroidal D distribution [11]. An alternative is the *ab initio* method, which can provide detailed information on the positions and thermal motions of both S and H atoms [13–15]. 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 partial rotational disorder with a crystal structure of approximate symmetry $P42/ncm$ at 17 GPa [13]. They also studied the structure and stability with respect to the dissociation of phases V and VI at room temperature. They found the formation of H_3S^+ and HS^- ionic species and fluctuating S–S chains in phase V. The H_2S molecules lose their identity, and S–S bonding in hexagonal sheets appears [14]. At low temperature, Takashi Ikeda studied the nature of the transition between phases IV′ and IV by using a constant-pressure MD simulation and suggested that the formation of short S–S contacts and the reformation of a hydrogen-bonded network are possible driving forces of the IV′/IV transition.

There is a remarkable difference between Rousseau and Takashi's results. The former suggests that phase IV has a partial rotational disorder, while the latter does not, even when the temperature is raised to room temperature. In Rousseau's simulation, they constructed their initial model from experimental results with position information for both H and S atoms [8]. In contrast, in Takashi's paper they started from an experimental structure without information on the hydrogen atoms. They put hydrogen atoms at the general symmetry site of phase IV′, with the constraint of a 1.3 Å S–H bond length and a 92° H–S–H bond angle. This would produce only a few configurations. After optimizing the geometry and calculating the total energy, they picked up the most stable one as a starting structure in their further simulations. This carefully selected configuration may have a much lower energy.

However, following the same procedure as used for phase IV′, Takashi failed to uncover the nature of phase III′. Their constant-pressure MD simulation of phase III′ showed reorientational motion even at 100 K. This may be because the *P–T* phase diagram of H_2S in the regime 0 GPa < *P* < 3 GPa and *T* < 150 K is more complicated than the present one, and the stable region of phase III′ could be much narrower than expected from the x-ray analysis. Anderson *et al* reported the Raman spectra of solid H_2S in the pressure range from 0 to 3 GPa at 25 K and suggested one or more phase changes as a result of molecular reorientation in the research range [17].

In this paper, using a constant-pressure *ab initio* MD calculation, we investigate the relationship between the low-temperature phases of hydrogen sulfide. Ten pressure–temperature points have been calculated by changing the pressure by ∼0.5 GPa from ambient pressure to 4.3 GPa at a temperature of 80 K. This rather small increasing step in pressure is used for searching for the complex structure of the hydrogen sulfide system at low temperature. A 4 ps long simulation time is employed to obtain good convergence of the static structural and

dynamical properties. *Ab initio* generalized gradient approximation (GGA) pseudo-potential calculations are performed on the electron densities and the band structures at some equilibrium configurations, in order to uncover the detailed bond information at different P–T points.

Section 2 covers the methodology of our work. In section 3, we show the details of our simulation results and discussions. Conclusions are given in section 4.

2. Model and methods

Ab initio constant-pressure molecular dynamics have been performed using the Car–Parrinello scheme [18, 19]. The GGA by Perdew *et al* [20, 21] is used for dealing with the electron correlations. The valence-core interaction is described by norm-conserving pseudo-potentials of Troullier–Martins type [22]. The valence orbits are expanded in plane waves with an energy cutoff of 40 Ryd. Periodic boundary conditions have been imposed. Brillouin zone sampling is restricted to the supercell Γ point. The electron densities and band structures are calculated by using the CASTEP program [23]. We chose the structure of phase IV′ at 3.8 GPa and 100 K from a theoretical result in [15] as our start-up structure, from which sequential lowering and increasing of the sample pressure at $T = 80$ K are used in our simulations with a pressure step of ∼0.5 GPa.

3. Results and discussion

The effect of low temperature as well as high pressure is to lower the disorder of hydrogen orientation. At ambient conditions, the hydrogen atoms are completely disordered and rotate around sulfur atoms as a center, so the H_2S molecule behaves like a sphere on average. The sub-Bravais lattice of sulfur atoms in phase I of hydrogen sulfide, which is the stable phase at ambient conditions, has the fcc structure. When the temperature is lowered, the rotational movement of hydrogen gets slower and slower and finally an ordered phase III is formed. When the pressure becomes higher, the separation between the H_2S molecules becomes smaller, so the rotational movement of hydrogen becomes slower and the orientation of the H_2S molecule is ordered as well as in the low-temperature case. But the effect of pressure has a remarkable difference with temperature, because pressure provides energy for the formation of chemical bonds. As the pressure increases, the total energy of the system becomes higher. This energy can be stored in both hydrogen bonds and the S–S covalent bonds, which are significant in determining the whole phase diagram of hydrogen sulfide.

Hiroshi Fujihisa obtained the sulfur sub-lattice by x-ray diffraction experiments [12]. Their results indicate that all phases at low temperature (phase III, III′, IV′, IV) are orientationally ordered. Using *ab initio* simulations, Ikeda [15] clarified the position of hydrogen atoms of phase IV′ and gave an ordered form of phase IV which differs from Rousseau's results [13]. However, following the same process, they failed to uncover the nature of phase III′. They suggested that the phase diagram in the range 0 GPa $< P <$ 3 GPa and $T <$ 150 K may be more complicated than the present one. We focus on the complexity in this regime. We perform constant-pressure molecular dynamics with a trajectory time of 4 ps.

The structure is monitored by the radial distribution function (RDF), which shows the number of molecules that are at a distance R from a given molecule statistically. We calculate both the S–S and the S–H radial distribution functions. The S–H RDF is shown in figure 1(b); its first and second peaks indicate the covalent bonding of S and H atoms in an individual molecule and the hydrogen bonding between sulfur and hydrogen atoms from different molecules, respectively. The locations of both peaks do not change too much compared with the large volume compression. The maximum of the first peak remains 1.40 Å in spite of the
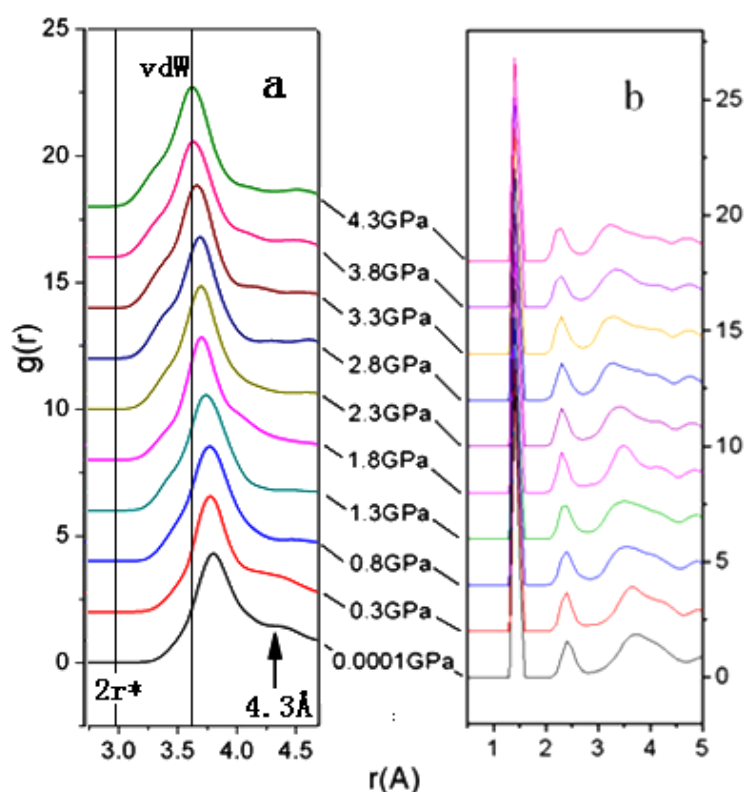
Figure 1. The radial distribution functions are analyzed from our 4 ps long trajectories. The periodic boundary condition is used. The upright arrows represent twice the sulfur van der Waals radius (vdW) and twice the sulfur constant-energy radius ($2r^*$).

increasing pressure, indicating that the covalent bonding within molecules is incompressible, while the maximum of the second peak decreases from 2.39 Å at ambient pressure to 2.23 Å at 4.3 GPa. This change causes significant variety in hydrogen bonding, which we will discuss later. The equation of states shown in figure 4 indicates that, at 4.3 GPa, the supercell volume decreases to 79% compared with the volume at ambient pressure. From the curve, we can see that there are two discontinuities in volume, changing at about 0.3 and 3.8 GPa, indicating that the crystal experiences two transitions during the increase in pressure, which can be explained by the change in separation between S atoms from the RDF of S–S in figure 1(a) in which the first main peak of S–S distance is shown. Compared with the S–H part, it is much broader. This is due to the multiple types of interaction between S atoms, for they can be covalent, vdW or through H bonds. Each type has its own main peaks and superposes on the $g(r)$. Another reason is the presence of a large fluctuation between weakly interacting S atoms. At ambient pressure, the distribution of neighboring S–S distances is even more dispersed. When the pressure is increased, the separation between S atoms which are vdW interacting must be easily compressed. From figure 1(a) we can see that the value of $g(r)$ at about 4.3 Å under ambient pressure and 0.3 GPa (shown with arrows) is much bigger than those at higher pressure. This implies efficient compression of neighboring S atoms. Both the constant-energy radius and the van der Waals radius of sulfur, which can shed light on the type of interaction between S atoms, are also shown in figure 1. Twice the sulfur constant-energy radius of 2.92 Å [24] is a criterion
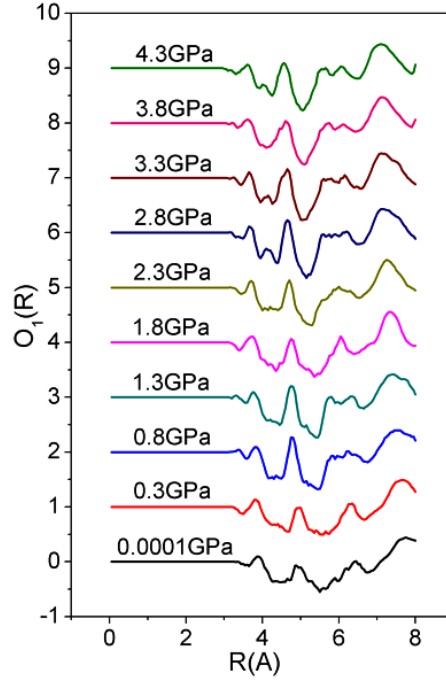
Figure 2. Orientational correlation function $O_1(R)$, defined in equation (1).

for the existence of an overlap in molecular orbitals or covalent S–S bond formation [9, 10], while twice the van der Waals radius is 3.60 Å. It can be seen from the RDF of S–S that there is no evidence of S–S close contact. With an increase in pressure, the first main peak of the S–S RDF moves left, but it stops at twice van der Waals radius of 3.8 GPa. To form the S–S covalent band, a much higher pressure is needed.

To investigate the correlations in molecular orientations, we define two orientation vectors: vector 1 starts at the S atom and ends at the middle of two H atoms and vector 2 starts at one hydrogen atom and ends at another H atom within one molecule. Two kinds of two-body correlation function $O(R)$ are defined as [25]:

$$O_1(R) = \left\langle \frac{\sum_{i<j} \cos\theta_1 \delta(R_{ij} - R)}{\sum_{i<j} \delta(R_{ij} - R)} \right\rangle \tag{1}$$

$$O_2(R) = \left\langle \frac{\sum_{i<j} (2(\cos\theta_2)^2 - 1)\delta(R_{ij} - R)}{\sum_{i<j} \delta(R_{ij} - R)} \right\rangle \tag{2}$$

where θ_1 is the polar angle between the orientation vector 1 of the molecules located at R_j and R_i, and θ_2 is the polar angle between the orientation vector 2 of the two molecules, respectively. If θ has a uniform distribution between 0 and π, the value of the functions will be zero. These two functions can be used to monitor efficiently the orientational order or the change in the hydrogen bonding network. The calculated $O_1(R)$ and $O_2(R)$ are shown in figures 2 and 3. According to the results, the hydrogen distribution is ordered and does not change in the pressure range 0–4.3 GPa and at $T = 80$ K, thus the hydrogen bonding network remains unchanged.

In general, the main reasons causing phase transitions in the hydrogen sulfide system are the formation of covalent bonds between sulfur atoms, hydrogen bonds between molecules,
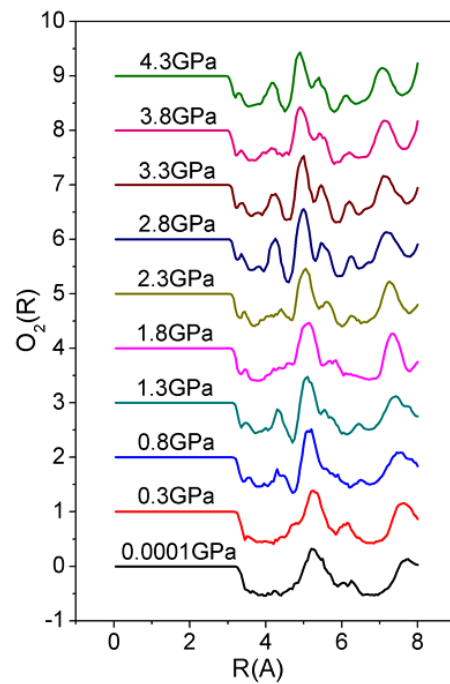
Figure 3. Orientational correlation function $O_2(R)$, defined in equation (2).
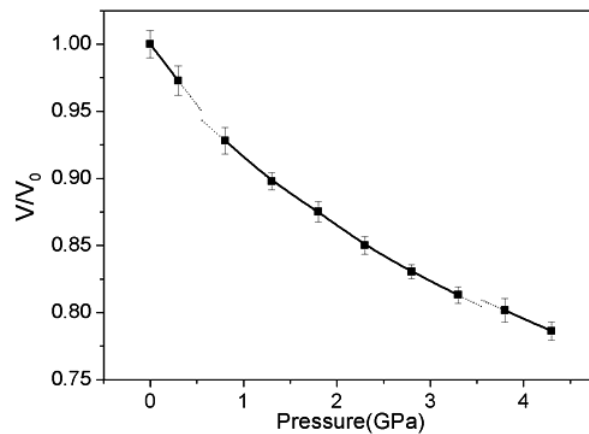

Figure 4. The equation of state of H_2S by averaging the volume of the supercell after equilibrium at each pressure point.

and rearrangements of hydrogen bonding networks. In our simulation, no hydrogen bonding rearrangement has been found in the range from 0 to 4.3 GPa at 80 K, which is in agreement with the experimental results [12]. The electronic densities and the partial densities of solid H_2S are calculated to understand the chemical bonding in the system. The partial density of electronic states (PDOS) is shown in figure 5. In our model, only the outermost electrons have been considered for bonding. That means that two s electrons of hydrogen and two s and four p electrons of sulfur participate in the formation of chemical bonds in a single molecule. Since
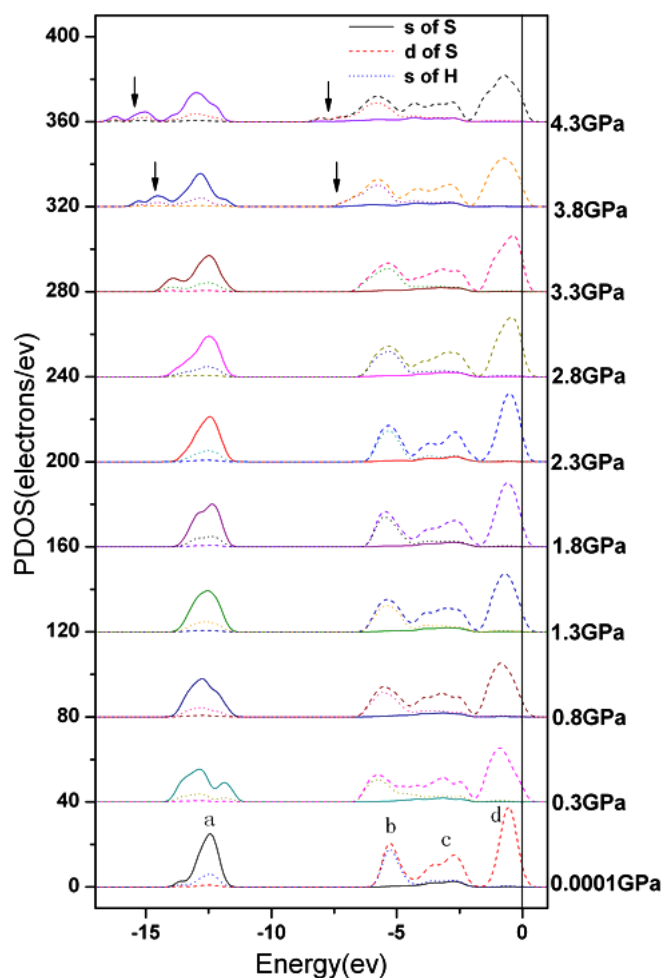
Figure 5. The calculated PDOS at different pressure. The vertical line indicates the Fermi level.

H_2S is an insulator, we only focus on those occupied bands below Fermi levels. The left-hand parts, which have lower energies, are mainly contributed by s electrons from both sulfur and hydrogen atoms, while the right-hand parts, which have higher energies, are mainly contributed by p electrons of sulfur and s electrons of hydrogen. It is beneficial to compare the PDOS of H_2S solid with those of an isolated single H_2S molecule, to clarify the changes in electronic densities from isolated molecules to solid. The PDOS of an isolated single molecule is shown in figure 6. The van der Waals forces between molecules affect the electron density and, as a result, we can see the overlap of outer orbits (b, c, d, shown in figure 6) in the PDOS of the H_2S solid (figure 5). The total PDOS of H_2S solids does not change too much until the pressure is increased to 3.8 GPa. Below 3.3 GPa, the hydrogen bonding between S and H atoms is mainly contributed by coulomb attraction, while above 3.8 GPa the energy levels corresponding to orbit-a and orbit-b (which are labeled by arrows in the figure 5) reduce, indicating a strong electronic overlap between orbit-a and orbit-b. This is a signal of the formation of covalent hydrogen bonds. It means that the lone pairs of electrons of S atoms begin to occupy the intermolecular 1s orbits of H atoms which have not been fully occupied by the intramolecular
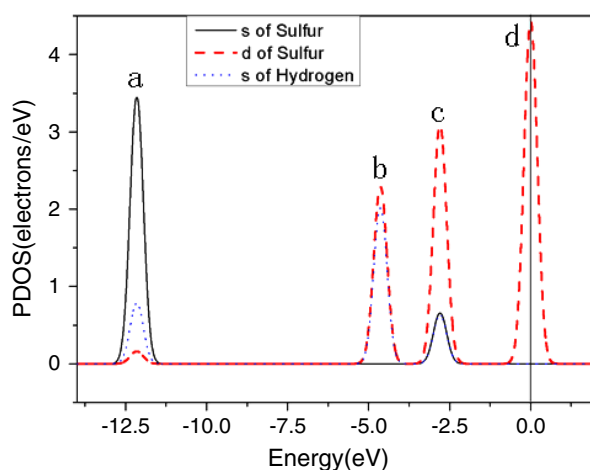
Figure 6. The PDOS of an isolated H_2S molecule. The vertical line indicates the Fermi level.

S–H covalent bond. Since compression between vdW interacting S atoms becomes harder, the compression effect between hydrogen-bonded atoms become significant. This may cause phase transition between phase III′ and phase IV′.

4. Conclusion

We have performed *ab initio* constant-pressure molecular dynamics simulations to understand the solid H_2S crystal structures under high pressure, discovered recently by x-ray diffraction experiment. The hydrogen-bonded network does not change in our investigated range. The equation of state shows two step changes at 0.3 GPa and 3.8 GPa. The radial distribution function of S–S at about 4.3 Å decreases rapidly when the pressure changes from 0.3 to 0.8 GPa. The transition between phase III and phase III′ can be explained by the efficient compression of distances between neighboring S atoms without intermediate H atoms. The formation of covalent-like hydrogen bonding may be the driving force for the III′ → IV′ transition. The transition pressures from our simulation are about 0.3 and 3.8 GPa, which are in quantitative agreement with experimental results [12]. In our research region of 0 GPa $< P <$ 4.3 GPa and $T = 80$ K, no new solid H_2S phase and covalent S–S bond is found.

Acknowledgments

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