Favored decomposition paths of hydrogen sulfide at high pressure

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Abstract

Sulfur trihydride (H₃S) is a theoretically predicted high-pressure superconductor and has been experimentally confirmed to have the highest superconducting transition temperature T_c. Solid H₂S decomposition is considered as the primary source of H₃S, however, it is complex and controversial how H₂S is transformed into H₃S. Herein, we employ the density functional theory augmented with many-body dispersion interactions (DFT+MBD) to study a full path of H₂S decomposition at pressure of 20–260 GPa. We find that H₂S starts to decompose into H₃S and other H–S compounds from about 20 GPa, in which the MBD interactions can decrease both the phase transition pressure of H–S compounds and the reaction transition pressure of H₂S decomposition. H₃S₂, H₄S₃, H₅S₅, sulfur and HS₂ are byproducts of H₂S decomposition with increasing pressure. Our results provide a complete phase diagram of H–S compounds during H₂S decomposition, and clarify the pressure range of each product and favored paths of H₂S decomposition.

Introduction

Metallic hydrogen considered as a room-temperature superconductor is an important physical problem in high-pressure research [1, 2], however, still under debate [3, 4]. Hydrogen-rich compounds such as sulfur trihydride (H₃S) [5], GeH₄ [6] and LaH₆ [7] are extensively explored as potential superconductors due to their relative lower pressure of metallization. H₂S is a predicted high-pressure superconductor through ab initio calculations [3] and has been proved to have a superconducting transition temperature T_c of 203 K at 155 GPa in experiments [8]. This is the highest T_c reported for any superconductor so far, even exceeding the nitrogen boiling point and breaking the long-standing record of 160 K in a mercury cuprate [9]. Therefore, understanding the origin of H₃S is crucial in sufficiently utilizing its superconductivity. Many researches from both experimental and theoretical sides have confirmed that H₃S is one of the decomposition products of H₂S solids (or mixing with H₂) at high pressure [5, 8, 10–17]. However, it is complex and controversial that how solid H₂S is transformed into H₃S, including the full reaction path, the intermediates and exact transition pressure of H₂S decomposition.

As a typical molecular crystal, solid H₂S at high pressure has attracted great interests regarding its decomposition [10–18] and metallization [19–27]. Initially, solid H₂S was believed to dissociate into sulfur and hydrogen at 46 GPa due to the disappearance of the S–H stretching vibrations by infrared spectra, and experienced metallization at 96 GPa [19]. But subsequent theoretical study by Li et al [23] found several thermodynamically stable H₂S phases up to 200 GPa to refute the earlier decomposition of solid H₂S and predicted the potential superconductive of metallic H₃S through the electron–phonon coupling calculations. High-pressure experiments on H₂S solids [8] found the precipitation of sulfur and the formation of H-rich compounds, the latter of which can be considered as the stoichiometry H₃S according to the theoretical study of Duan et al [5]. This proposal by Duan et al [5] was supported by numerous first principles studies and Raman spectroscopy experiments which suggested different decompositions of solid H₂S, such as H₂S → H₃S + S [10–12] above 43 GPa [10], H₂S → S + H₂S + H₅S₅ above 27 GPa [13], and H₂S → H₃S + H₃S₂ (H₅S₅) at 25–150 GPa [14]. In the latest work on H₂S decomposition [28], the path of H₂S → H₃S + H₂S₂ at low pressure...
properties of H\textsubscript{2}S and the components of the stress tensor to DFT calculations were performed with the CASTEP Method and structure has been predicted due to discovering a new stable semiconducting phase of H\textsubscript{3}S\textsubscript{2}. Despite many efforts to H\textsubscript{2}S body dispersion converged to better than 1 anharmonicity of vibrational zero-point energy can lower the superconducting transition of 5H\textsubscript{2}S decomposition and generate several compounds, that is, the major product H\textsubscript{3}S and the by product H\textsubscript{3}S\textsubscript{2}, H\textsubscript{4}S\textsubscript{3}, H\textsubscript{5}S\textsubscript{2}, H\textsubscript{3}S\textsubscript{5} and H\textsubscript{5}S\textsubscript{8}. Each compound has different phases, shown in table 1.

Table 1. Phases of H\textsubscript{2}S and its decomposition products.

| Compounds | Phases |
|-----------|--------|
| H\textsubscript{2}S | Cmca, Ibca, P-1, P21/c, Pmc2\textsubscript{1}, [23] |
| H\textsubscript{3}S | Cccm, Im-3m, P1, R3m [5]; C2/c [13]; Cm, 14mm [14] |
| H\textsubscript{3}S\textsubscript{2} | P-1, P212\textsubscript{1}, Pnm\textsubscript{a} [13] |
| HS\textsubscript{2} | C\textsubscript{2}/c, C\textsubscript{2}/m [11]; P4/nmm [13]; Pbcm [28] |
| S | C\textsubscript{2}/m [42]; I\textsubscript{2}/m [43]; I\textsubscript{4}\textsubscript{1}-acd, R-3m [12] |
| H\textsubscript{4}S\textsubscript{3} | P1, C\textsubscript{m} [13]; P2\textsubscript{1}, [28] |
| H\textsubscript{5}S\textsubscript{2} | C\textsubscript{2}m, P1 [15] |
| H\textsubscript{3}S\textsubscript{5} | C\textsubscript{2} [13] |
| H\textsubscript{5}S\textsubscript{3} | C\textsubscript{2}/m [14] |
| H\textsubscript{5}S\textsubscript{8} | P1 [14] |

has been predicted due to discovering a new stable semiconducting phase of H\textsubscript{3}S\textsubscript{2}. Despite many efforts to H\textsubscript{2}S decomposition, it is still urgently needed to perform a comprehensive study to thoroughly understand the evolution of H\textsubscript{2}S decomposition, for which the previous studies provide a basis.

First principles calculations have identified several key factors that can significantly influence the physical properties of H–S compounds. Errea et al [29] indicate that quantum nuclear motion of hydrogen and anharmonicity of vibrational zero-point energy can lower the superconducting transition (R3m → Im-3m) pressure by up to 70 GPa for H\textsubscript{2}S. The inclusion of anharmonic zero-point motion above 200 GPa results in a decomposition of 5H\textsubscript{2}S → 3H\textsubscript{3}S + HS\textsubscript{2}, where both H\textsubscript{3}S and HS\textsubscript{2} are metallic and show superconducting behavior [11]. However, widely adopted density functional theory calculations with local and semilocal functionals, suffers from the electron self-interaction error and misses dispersion interactions. In particular, high-pressure solids often undergo insulator-metal transition under the influence of pressure, in which MBD energies can experience pronounced change and consequently modify the phase behavior of high-pressure solids [30].

Here, we employ the density functional theory augmented with many-body dispersion interactions (DFT + MBD) [31, 32] to study the decomposition behavior of solid H\textsubscript{3}S at high pressure. By investigating the phase transition and thermodynamic stability of seven H–S compounds, we present a full decomposition path of solid H\textsubscript{2}S from 20 to 260 GPa. We find that starting from about 20 GPa, H\textsubscript{3}S solids experience a series of decompositions and generate several compounds, that is, the major product H\textsubscript{3}S and the by product H\textsubscript{3}S\textsubscript{2}, H\textsubscript{4}S\textsubscript{3}, H\textsubscript{5}S\textsubscript{2}, sulfur and HS\textsubscript{2}. The MBD effects are found to quantitatively influence the phase transition pressure of H–S compounds and the reaction enthalpy of H\textsubscript{3}S decomposition. A complete phase diagram of H–S compounds during H\textsubscript{2}S decomposition is put forward, which clarifies the pressure range of each product and favored paths of H\textsubscript{2}S decomposition.

Method and structure

DFT calculations were performed with the CASTEP [33] code using an ultrasoft pseudopotential, and Perdew–Burke–Ernzerhof (PBE) [34] functionals. We adopt a plane-wave cutoff energy of 1200 eV and a M-P Brillouin zone sampling grid of spacing 2\pi × 0.02 Å\textsuperscript{-1} for PBE calculations to ensure that the total energies can be well converged to better than 1 × 10\textsuperscript{-5} eV/atom. The setups converge the energies on the atoms to <0.001 eV Å\textsuperscript{-1} and the components of the stress tensor to <0.01 GPa. vdW interactions were calculated by non-local many body dispersion (MBD) method [35, 36] using the Pymbd program [37]. In the scheme of MBD approach, the valence electronic response is projected onto a set of N interacting atomic response functions, which allows an efficient and accurate treatment of the valence electronic response in terms of coupled atomic dipolar fluctuations [35, 38]. Within its framework, the long range many-body electronic correlation energy E\textsubscript{MBD} is a random-phase approximation method for accounting the many-body correlation energy and goes beyond the pairwise approximations through diagonalization of the Hamiltonian corresponding to a system of coupled fluctuating dipoles [39].

Besides the experimentally known H\textsubscript{3}S and sulfur [8, 16], we test seven candidate products for H\textsubscript{2}S decompositions: HS\textsubscript{2}, H\textsubscript{3}S\textsubscript{3}, H\textsubscript{4}S\textsubscript{3}, H\textsubscript{5}S\textsubscript{2}, H\textsubscript{3}S\textsubscript{5} and H\textsubscript{5}S\textsubscript{8}. Each compound has different phases, shown in table 1.
Result and discussion

We first study the phase transition of H$_2$S, sulfur, HS$_2$, H$_3$S$_2$, H$_4$S$_3$, H$_5$S$_4$, H$_6$S$_5$, H$_7$S$_6$, H$_3$S$_5$, H$_5$S$_8$ and H$_3$S (the candidate intermediates and products of H$_2$S decomposition) at the pressure of 20–260 GPa by calculating the static-lattice enthalpies with PBE and PBE+MBD. H$_2$S solids experience the phase transition of P2$_1$/c $\rightarrow$ Pc (28 GPa) $\rightarrow$ P-1 (80 GPa) $\rightarrow$ Cmca (140 GPa) at the PBE level (structures of H$_2$S phases shown in figure 1(a)). P2$_1$/2$_1$/2$_1$ phase is stable at lower pressure (<20 GPa) and Pmc2$_1$ phase and Pc phase are almost thermodynamically identical, which are consistent with previous results [23, 28]. PBE+MBD gives rise to the same transition order as PBE, however, the transition pressure of each step decreases by different degrees. The inclusion of MBD interactions lowers the transition pressure of P2$_1$/c $\rightarrow$ Pc by only 4 GPa, but decreases the transition pressure of Pc $\rightarrow$ P-1 (72 GPa) and P-1 $\rightarrow$ Cmca (130 GPa) by up to 10 GPa. This phenomenon can be rationalized by the differences and similarities of geometric configurations of each H$_2$S phase.

Absolute MBD energies of H$_2$S phases increase sub-linearly with pressure due to gradual compression of structures, shown in figure 1(b). However, these four considered phases exhibit distinct relative MBD energies and respond differentially towards pressure (see figure 1(c)). At low pressure, the difference of intermolecular distance between P2$_1$/c phase and Pc phase is increased from 0.049 Å at 20 GPa to 0.117 Å at 60 GPa, generating the differences of MBD energies by less than 10 meV/H$_2$S (−446.3 meV/H$_2$S for P2$_1$/c and −457.3 meV/H$_2$S for Pc at 60 GPa). Nevertheless, these two phases remain the structures of typical vdW molecule crystal with four H$_2$S molecules per unit cell [23] and exhibit a slight distortion on the configurations of H$_2$S molecules (see figure 1(a)), towards the increase of pressure. The similar geometric structures of P2$_1$/c phase and Pc phase result in minor change of transition pressure (∼4 GPa) of P2$_1$/c $\rightarrow$ Pc under the inclusion of MBD interactions. As pressure increases to 71 GPa, Pc phase transforms into polymerized P-1 phase. P-1 phase, which has longer lengths of intramolecular H–S bonds than Pc phase (1.473 Å for P-1 and 1.444 Å for Pc at 80 GPa), forms dumbbell-like H$_3$S–SH$_3$ units and edge-shared S$_6$H$_4$ quasi-rectangles in one directional arrangement [23] (see figure 1(c)).
figure 1(a). The significant geometrical variation from Pc phase to P-1 phase leads to the differences of MBD energies by up to 25 meV/H$_2$S at 100 GPa, thereby decreases transition pressure by 8 GPa. Upon further compression, P-1 phase transforms into Cmca phase at 128 GPa. Compared with P-1 phase, Cmca phase shows the S$_6$H$_4$ quasi-rectangles distributing in two orientations, and all H atoms in Cmca phase bond with two S atoms [23] (see figure 1(a)). The difference of S–S bond length between P-1 phase and Cmca phase increases from 0.012 Å at 80 GPa to 0.041 Å at 140 GPa. Notably, the length difference of intramolecular H–S bonds between P-1 phase and Cmca phase is maximum at 80–100 GPa (~0.022 Å), at which pressure these two phases have the most significant difference of MBD energies (about 10 meV/H$_2$S). This difference of geometric structures between P-1 phase and Cmca phase results in the decline of transition pressure of P-1 → Cmca by 10 GPa. Under each pressure, phase with diverse structures, such as P2/c phase and Cmca phase at 80 GPa, can yield the difference of MBD energies up to 40 meV/H$_2$S (see figure 1(c)).

Compound with stoichiometry of H:S = 3:1 (H$_3$S) is considered as the major product of H$_2$S decomposition at high pressure, however, with the geometry and symmetry undergoing substantial change as the increased pressure. In the phase transition of H$_3$S, we find C2/c structure which consists of weakly bonded H$_2$S and H$_3$ molecules, is more stable than the previously predicted Cccm phase [5] at pressure of 20–101 GPa by PBE+MBD, consistent with [13, 28]. Moreover, we have noticed that distorted Cm and I4mm structures were considered more thermodynamically stable than R3m phase and Im-3m phase in previous study [14]. Our calculations find that Cm phase is the most thermodynamically stable at pressure of 148–230 GPa, but with the enthalpies difference (relative to R3m phase) of ~0.2 meV/molecule by PBE+MBD, within the error bar. Thus, we take the zero-temperature phase order of H$_3$S as C2/c (2 GPa) → R3m (101 GPa) → Im-3m (230 GPa), in which the R3m phase and Im-3m phase are considered as metallic and superconductive phases, respectively. The phase transition of high-pressure H$_5$S is P4/nmm (35 GPa) → Pbcm (128 GPa) → C2/c (223 GPa) → C2/m, in which Pbcm phase is the newly predicted phase of Kruglov’s study [28]. In the phase transition of sulfur we consider four phases I41/acd, R-3m, I2/m and C2/m [40–43]. We find that I2/m and C2/m phases have the same structure and are unstable at considered pressure, and I41/acd transforms into R-3m above 61 GPa by PBE+MBD, which is in agreement with previous study [28]. Different from previous studies [13, 28], phase transition of H$_4$S$_3$ is P-1 → P2$_1$2$_1$2$_1$ at 25 GPa, and Pnma phase is almost thermodynamically identical with P2$_1$2$_1$2$_1$ phase. Considering the latest research of H$_4$S$_3$ [28], our calculations confirm P2$_1$ phase is more thermodynamically favorable than Cm phase predicted by Li et al [13]. For H$_5$S$_2$, C2/m phase transforms into P1 phase above 63 GPa.

The inhomogeneous roles of MBD interactions are found also held in the phase transition of the candidate products of H$_3$S decomposition. We find that MBD interactions quantitatively decrease the pressure of phase transition for H$_3$S, sulfur and H$_2$S by 5–15 GPa. However, other H–S compounds (H$_4$S$_3$, H$_5$S$_2$ and H$_6$S$_2$) exhibit negligible MBD effects on their phase transitions. Moreover, MBD interaction decreases the pressure of phase transition C2/c → R3m by 7 GPa, but has almost no influence on the pressure of phase transition R3m → Im-3m. MBD interaction can make roles in varying degrees on the phase transition pressure of H–S system, thereby influencing the decomposition characters of H$_3$S solids.

Next, we investigate the thermodynamic stability of H$_3$S by the convex hull diagram at the given pressure and 0 K, which is defined as the formation enthalpy of per atom of the most stable phases at each stoichiometry (obtained by PBE+MBD):

$$h_f(H_3S) = \frac{h_{H_3S} - xh_{H_2S} - yh_S}{x + y},$$

(1)

where $h_f$ is the formation enthalpy of per atom and $h_{H_3S}$ is the enthalpy of the most stable phase of each stoichiometric H–S compound at each pressure (results are shown in figure 2). Any stoichiometric compound on the convex hull diagram is considered to be thermodynamically stable and experimentally achievable [44]. Our results can declare that the most stable products always contain the compounds with the stoichiometry of H:S = 3:1 in the H$_2$S decomposition. At 40 GPa, H$_3$S$_2$ is thermodynamically stable and coexists with C2/c H$_3$S. As pressure is increased to 100 GPa, H$_3$S$_2$ and H$_5$S$_2$ become stable on the convex hull and coexist with R3m H$_3$S. With further increasing pressure, R-3m S appears and coexists with R3m H$_3$S at 140 GPa, while H$_5$S$_2$ is competitive with Im-3m H$_3$S at 260 GPa.

According to the implication of convex hull diagram, we calculate the reaction enthalpies of H$_3$S decompositions as a function of pressure. For reaction aH$_2$S → bH$_3$S$_{y}$ + eH$_2$S$_{2}$, the reaction enthalpy $h_r$ is defined as:

$$h_r = (bh_{H_3S_y} + eh_{H_2S_2} - ah_{H_2S})/a,$$

(2)

where $h_{H_3S_y}$ is enthalpy of each stoichiometric H–S compound using PBE+MBD. These calculations allow us to predict five reaction paths at considered pressure range (figure 3). Solid H$_3$S starts to decompose at about 20 GPa, in accord with [10, 13, 14, 24, 28], and the compounds with stoichiometry of H:S = 3:1 are the major
products up to 260 GPa. Meanwhile there are several products co-existed with H$_3$S, such as H$_3$S$_2$, H$_4$S$_3$, H$_3$S$_5$, sulfur and HS$_2$, forming a full decomposition path: H$_2$S $\rightarrow$ H$_3$S$_2 +$ H$_3$S (20–57 GPa) $\rightarrow$ H$_3$S$_3 +$ H$_3$S (57–96 GPa) $\rightarrow$ H$_3$S$_5 +$ H$_3$S (96–103 GPa) $\rightarrow$ S + H$_3$S (103–230 GPa) $\rightarrow$ HS$_2 +$ H$_3$S (above 230 GPa) (figure 3(a)). H$_3$S$_2$ was considered to have very narrow pressure range of stability in previous study [13], however, we put forward a pressure range of more than 30 GPa for H$_3$S$_2$ based on a more stable P$_{2_1}$ phase suggested by Kruglov et al [28]. The identification of H$_4$S$_3$ is in agreement with Li’s finding [13], but we find a more energetically favorable path of H$_2$S $\rightarrow$ H$_4$S$_3 +$ H$_3$S (without sulfur) than Li’s decomposition of H$_2$S $\rightarrow$ H$_4$S$_3 +$ S + H$_3$S at pressure of 57–96 GPa. Our finding that H$_3$S$_5$ is a by-product in H$_3$S decomposition is consistent with Goncharov’s experimental results [14], and we further specify the pressure range of H$_3$S$_5$. The formation of sulfur and H$_3$S at high pressure has been confirmed by plenty of theoretical and experimental reports [8, 10, 12, 16, 17], and HS$_2$ is considered as a product co-existed with H$_3$S in experiments at pressure above 200 GPa [11], which are all in good agreement with our calculations. MBD interactions do not change decomposition paths of H$_3$S solids, but can decrease the transition pressure of decomposition paths by 5–10 GPa (see figure 3(b)). Meanwhile, the MBD effects increase the reaction enthalpies by $\sim$25 meV/molecule (absolute value is decreased) at 60–100 GPa, but have negligible influences on the reaction enthalpies at higher pressure (>100 GPa).

As it follows from the convex hull diagram and the reaction enthalpies of H$_3$S decompositions, we can obtain a complete phase diagram of H$\textsubscript{x}$–S compounds during H$_3$S decomposition, shown in figure 4. Why the H$_3$S decomposition prefers different reaction path towards the increase of pressure? This can be understood from the corresponding structural evolution of H$_3$S decomposition products with increasing pressure. As the pressure increases, the intramolecular interactions and intermolecular interactions are well reflected by the bond length of molecules and the volume of unit cell, respectively. The coupling of these two effects determines the enthalpy of each product by the formula of $H = U + PV$, where $H$, $U$, $P$ and $V$ are enthalpy, internal energy, pressure and volume of a matter, respectively. At each pressure, the reaction enthalpies $h_r$ of H$_3$S and its products with the lowest $h_{H_3S}$ govern the decomposition path.

We have noted that Li et al [13] proposed the stoichiometric H$_4$S$_3$ coexisting with H$_3$S is thermodynamically stable at pressure of 25–113 GPa and suggested a reaction path of 8H$_2$S $\rightarrow$ H$_3$S$_5 +$ 4H$_2$S + S at this pressure. However, 5H$_2$S $\rightarrow$ H$_4$S$_3 +$ 2H$_3$S is a more competitive path at 57–96 GPa in our calculations. To ensure whether decomposition products contain sulfur or not, we test several potential decompositions with various proportionalities of H$_4$S$_3$, H$_3$S and sulfur (figure 3(c)). We find that the reaction enthalpy of

![Figure 2](image_url)

**Figure 2.** The formation enthalpies of the most stable phase of H$_x$S, with respect to decomposition into sulfur and hydrogen at 40, 100, 140 and 260 GPa. Convex hulls are shown as continuous lines using PBE+MBD.
Figure 3. Reaction enthalpies of five energetic decomposition paths for H₂S using (a) PBE+MBD and (b) PBE. Inserts are the magnifying pictures of reaction enthalpies at 95–105 GPa using PBE+MBD and those at 98–115 GPa using PBE, respectively. (c) Comparison of reaction enthalpies of H₂S decomposition products with or without sulfur. (d) Reaction enthalpies of H₄S₃ decomposition. Insert is the reaction enthalpies of H₃S₅ decomposition.

Figure 4. Composition-pressure phase diagram for stoichiometric H–S compounds as a function of pressure by PBE+MBD method.
8H₂S → H₅S₃ + 4H₂S + S is significantly higher than that of 5H₂S → H₅S₃ + 2H₂S (−93.7 meV/molecule versus −100.7 meV/molecule at 70 GPa). Furthermore, if the yield of sulfur is gradually decreased, the reaction enthalpies become closer to that of 5H₂S → H₅S₃ + 2H₂S, as shown in figure 3(c). In particular, when the proportion of H₅S₃, H₃S, H₂S, and sulfur is 503:20:100:1, the reaction enthalpy of 503H₂S → 202H₂S + 100H₂S + S is almost the same as that of 5H₂S → H₅S₃ + 2H₂S. These results confirm the robustness of our proposals. Actually, there is a debate about whether sulfur is one of H₂S decomposition products at low pressure. Previous theoretical studies declared that H₃S and sulfur were the products of H₂S decomposition [10–12] and some experiments proposed sulfur by x-ray measurements [8, 16, 18, 24]. However, these results are mostly obtained at the higher pressure (>100 GPa). The main evidence for the presence of sulfur is the observation of spiral chains of S atoms [16, 24], which also appear in H₂S and H₂S₂ [13, 14].

Remarkably, in the study of Li et al [13], the XRD profile of sulfur is not clear enough at 46 GPa and even disappears at 66 GPa. Though they interpreted this as a reaction of 4H₂S + 5 S → 3H₂S₉, our thermodynamic calculations indicate that above reaction is endothermal (reaction enthalpy h is positive) below 96 GPa (figure 3(d)). One possible reason for this divergence is that we study the phase stability of sulfur with several phases including I₄₁/a, R-3m, I₂/m and C₂/m. In our calculation, phase transition of I₄₁/a → R-3m occurs at around 60 GPa, but [13] always took I₄₁/a as the most stable phase of sulfur. Moreover, Alexander et al [14] confirm that sulfur has not been clearly detected at 34–110 GPa and put forward a S-rich compound, which has the density of S between H₂S and sulfur to balance with the H-rich H₂S. Thus, we propose a supposition that H₂S decomposition at low pressure (<103 GPa) cannot yield sulfur, expecting further experimental verification. Notably, the above-mentioned products H₂S₉ and H₂S₇ gradually decompose into H₂S and sulfur above 103 GPa (figure 3(d)), indicating that neither H₂S₉ nor H₂S₇ can exist at 140 GPa (figure 2). Overall, we provide an accurate division of H₂S decomposition in a wide range of pressure and propose a new opinion that there is no sulfur in H₂S decomposition at low pressure.

Conclusion

In conclusion, our DFT + MBD calculations put forward a full path of solid H₂S decomposition at 20–260 GPa, which is H₂S → H₅S₃ + H₂S₂ (20–57 GPa) → H₂S + H₂S₂ (57–96 GPa) → H₂S + H₂S₃ (96–103 GPa) → H₂S + S (103–230 GPa) → H₂S + HS₂ (above 230 GPa). We propose a supposition that H₂S decomposition at low pressure (<103 GPa) cannot yield sulfur and find that many-body vdW interactions play various roles on the phase transitions of H₂S and its decomposition products with pressure. Our results provide a complete phase diagram of H–S compounds during H₂S decomposition, and clarify the pressure range of each product and favored paths of H₂S decomposition.

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