Properties and phase diagram of (H$_2$S)$_2$H$_2$


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By combining hydrogen and sulfur within diamond-anvil cells we synthesize (H$_3$S)$_2$H$_2$ at 5 GPa and 373 K. Through a series of Raman spectroscopy, infrared spectroscopy, and synchrotron x-ray diffraction experiments we have constrained the phase diagram of (H$_2$S)$_2$H$_2$ within a wide P-T range. On compression we observe the phase transition sequence of I-II-II′-III, where II′ is a previously unreported phase; at room temperature this sequence spans from 5 to 47 GPa, while the application of low temperatures stabilizes this sequence to 127 GPa (< 80 K). Above these pressures we propose that phase III of (H$_2$S)$_2$H$_2$ transforms to a nonmolecular H$_3$S network. Our Raman and infrared measurements indicate that the transition from (H$_2$S)$_2$H$_2$ to H$_3$S is reversible at room temperature. X-ray diffraction reveals that the symmetry of the underlying S lattice of (H$_2$S)$_2$H$_2$ and H$_3$S is retained along this compression path up to at least 135 GPa.

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I. INTRODUCTION

The report of high-temperature superconductivity in dense H$_2$S has galvanized studies of the high-pressure sulfur-hydrogen system [1], yet the composition and nature of bonding in the superconducting phase remain disputed [2–11]. Prior to experimental measurements, two separate theoretical studies predicted abnormally high critical temperatures $T_c$ to emerge from the H$_2$S ($T_c = 80$ K) [12] and (H$_2$S)$_2$H$_2$ ($T_c = 200$ K) [13] systems at very high densities. The latter study predicted a pressure-driven reaction between the molecular H$_2$ and H$_2$S components of (H$_2$S)$_2$H$_2$ (phase III, $\bar{C}m\bar{m}$) [13]: on compression we observe the H-H bond softens and then breaks at 111 GPa, reacting with H$_2$S to form a new phase composed solely of individual H$_2$S units ($R\bar{3}m$). At even higher pressure, it was predicted that H$_2$S would become a nonmolecular, highly symmetrical cubic structure ($Im\bar{3}m$), with a calculated maximum $T_c$ of 204 K at 200 GPa [13,14].

Given the intense interest in the sulfur-hydrogen system, there are surprisingly few direct experiments on (H$_2$S)$_2$H$_2$ [6,15–17]. The first experimental observation of superconductivity in this system used pure H$_2$S as a precursor but claims a maximum $T_c$ of 203 K [1]. However, producing the high-$T_c$ phase required following a convoluted P-T path, leading the authors to suggest a decomposition mechanism: 3H$_2$S $\rightarrow$ 2H$_3$S + S. Furthermore, H$_2$S decomposition models have found competitive H-S stoichiometries (e.g., H$_2$S$_2$) present with H$_3$S, close to the pressures where the highest $T_c$ is claimed [1,11]. Disproportionated S and other by-products imply that the H$_3$S product from H$_2$S is impure, which may account for inconsistent $T_c$ measurements (ranging from 110 to 203 K) reported in experiments using H$_2$S as a precursor [1,18–21].

Powder x-ray diffraction (XRD) studies of the high-$T_c$ sample detected the disproportionation product S ($\beta$-Po type) alongside a bcc lattice of S atoms, attributed to $Im\bar{3}m$ H$_3$S [2]. The pattern can also be better described by S with $Cccm$ symmetry [suggested for (H$_2$S)$_2$H$_2$], accounting for unidentified “impurity” peaks, which the $Im\bar{3}m$ structure does not do [2,6,22]. Although the volume per S atom of the fitted bcc phase (and also $Cccm$) does give an H:S ratio of 3:1, the weak interaction of x rays with hydrogen means there is no information regarding hydrogen atom positions or how S and H are bonded. Indeed, the small distortions between $R\bar{3}m$ and $Im\bar{3}m$ H$_3$S structures are indistinguishable under the challenging experimental conditions.

In (H$_2$S)$_2$H$_2$ the underlying S-atom configurations are similar across all known experimental and predicted phases, making them difficult to distinguish on the basis of diffraction alone [13,15]. Transitions between high-pressure phases in (H$_2$S)$_2$H$_2$ at room temperature are primarily driven by hydrogen bonding (H bonding) and are characterized by the orientation of H$_2$S molecules and the nature of the H$_2$ sites within the structure, producing unique vibrational spectra [6,15–17]. In particular the number of H$_2$ vibrational modes (vibrons) and the effect of compression on their respective frequencies can be utilized to distinguish phase changes and shifts in bond orientation of the surrounding H$_2$S molecules.
Therefore Raman spectroscopy combined with infrared (IR) spectroscopy presents a powerful diagnostic combination for (H_2S)_2H_2 at high pressure [15,16], being sensitive to both inter- and intramolecular interactions [23–25].

In this study, we synthesize (H_2S)_2H_2 by combining S and H_2 directly in controlled ratios within diamond-anvil cells (DACs). On compression at 300 K, we observe the phase sequence I-II-III, where phase II’ is previously unreported. We map out the solid phases of (H_2S)_2H_2 from 15 to 300 K, up to 185 GPa. From phase III of (H_2S)_2H_2 we observe substantial softening and weakening of the ν_{H2} H_2 vibron, with a complete loss of intensity above 50 GPa (300 K) and 127 GPa (80 K); this suggests a reaction between H_2S and H_2 forming an extended sulfur-hydrogen network (H_3S), retaining the initial stoichiometry of 1S:3H but with no H_2 molecules, predicted to occur upon compression of (H_2S)_2H_2 [13]. At 300 K we report the reversibility of this transition from both Raman and IR spectroscopy studies. From XRD studies we find that the same S lattice is retained on compression through the H_3S transition, at least up to 135 GPa.

II. EXPERIMENTAL METHODS

DACs with culets of 50–200 μm, containing crystalline sulfur suspended in fluid H_2, were heated to 373 K for 1 h (below 0.5 GPa), then cooled to 300 K, producing discrete fluid domains of H_2S and H_2. Samples were then compressed above 4.8 GPa to form phase I of (H_2S)_2H_2 [15,16] in the same manner used to produce (H_2Se)_2H_2 [26]. The ratio of H_2S was controlled by varying the amount of sulfur used, relative to the size of the gasket chamber; we find that (H_2S)_2H_2 requires an initial atomic ratio in excess of 3:1 H:S in order to form (equivalent to 3:2 H_2:S). Ratios between 2:1 and 3:1 H:S formed samples of H_2S with excess H_2 but did not tend to transform to (H_2S)_2H_2 on further compression, instead behaving in the same manner as pure H_2S. Because of the rich vibrational spectra produced in these experiments we name and number the individual Raman and IR vibrational modes arising from different H_2 environments from (H_2S)_2H_2: apart from phase I, all solid phases exhibited two discrete sets of H_2 Raman modes which are herein referred to as a (lower frequency) and b (higher frequency). Therefore each H_2 vibron \nu from (H_2S)_2H_2 is denoted by the phase from which it originates (i.e., I, II, II’, III), followed by a or b. For example, the single H_2 vibron from phase I (H_2S)_2H_2 is referred to as \nu_{Ia}, and phase II exhibits a high-frequency vibron doublet labeled \nu_{IIb} and a lower frequency doublet labeled \nu_{IIa}; \nu_I refers to only pure bulk H_2.

Raman spectroscopy measurements from 17 different samples of (H_2S)_2H_2 were collected in a wide temperature range (15–300 K) up to 184 GPa, using 180° backscattering geometry [27]; room temperature experiments were performed with a 514.5-nm Ar^+ excitation laser, and low-temperature experiments were performed using a 532-nm solid-state excitation laser, controlling temperature with a modified continuous-flow cryostat using liquid-N_2 (80 K) or liquid-He (< 80 K) cryogens, coupled with two thermostat heaters and proportional-integral-derivative controllers. (H_2S)_2H_2 samples were always formed prior to initial cooling. Pressure was calibrated for Raman and IR experiments with a combination of ruby fluorescence [28,29] and Raman shift of the diamond edge [30]. The mid-IR spectra were collected in transmission mode with a Bruker Vertex 80v Fourier transform IR spectrometer and a Hyperion 2000 IR microscope equipped with a nitrogen-cooled mercury cadmium telluride detector. Synchrotron XRD data were collected up to 135 GPa (300 K) from four separate runs. Angle dispersive XRD measurements were recorded at room temperature at the following beamlines and synchrotrons (wavelengths): P2.02 at PETRA III (Germany; 0.2922 Å), GSECARS at Advanced Photon Source (United States; 0.3344 Å), and I-15 at the Diamond Light Source (United Kingdom; 0.4246 Å). XRD experiments utilized a combination of ruby fluorescence, the Raman diamond edge, and Au pressure markers, calibrated using the Vinet equation of state [31].

III. RESULTS

Phase I was identified upon compression of H_2S and H_2 between 4.7 and 5.3 GPa (300 K) from a single additional H_2 Raman vibron at 4140 cm\(^{-1}\) (\nu_{Ia}), redshifted relative to H_2 \nu_I [Figs. 1, 2(a), and 3]. An IR absorption attributed to the guest H-H stretch was also observed at a frequency very close to the \nu_{Ia} Raman mode [Figs. 2(a) and 3]. A Rietveld refinement of diffraction data collected at 6.1 GPa confirmed the tetragonal I4/mcm structure [a = 7.183(1), c = 5.902(1) Å], in agreement with a previous study [15,22].
FIG. 2. (a) Raman frequencies (relative cm$^{-1}$; solid triangles) and infrared absorption frequencies (cm$^{-1}$; darker circles) for H$_2$ vibrons from (H$_2$S)$_2$H$_2$, plotted as a function of pressure (GPa) at 300 K, showing transitions between phases I (purple), II (green), II$'$ (magenta), and III (blue). Free molecular H$_2$ vibron frequencies from the (H$_2$S)$_2$H$_2$ samples (solid gray triangles) are shown alongside data from pure H$_2$ (open gray triangles). Data replotted from other studies are represented by cross symbols for (H$_2$S)$_2$H$_2$ (Raman) [15] and plus symbols for pure H$_2$ (IR) [32]. (b) Raman frequencies (relative cm$^{-1}$) for S-H stretching modes from (H$_2$S)$_2$H$_2$, plotted as a function of pressure (GPa) at 300 K. Different symbols refer to different experimental runs, while cross symbols are replotted from a previous study [15].

Phase II can be reached on cooling below 173 K (10 GPa) or on compression above 16.7 GPa at room temperature, resulting in a negative slope between the I-II transition pressure at room temperature and lower temperatures (Fig. 4). Phase II is identified by the characteristic splitting of the S-H Raman vibrational stretching mode ($\sim$2400 cm$^{-1}$) and splitting of $\nu_{IIa}$ into $\nu_{IIa}$ and $\nu_{IIb}$ [Figs. 1, 2(a), 5, and 6]. No change was observed in atomic volume by diffraction at room temperature, in agreement with a previous study [15]. Phase II is easily recognized by the emergence of lattice modes (Figs. 1 and 5) arising from the orientational ordering of H$_2$S molecules; the strengthening of H bonding between neighboring H$_2$S molecules restricts their free rotation, which also breaks the degeneracy of the symmetric and asymmetric S-H stretches. A comparable effect is observed in Raman studies on compression of pure H$_2$S (and D$_2$S) from phase I-I$'$-IV [33–35]. We also observe a large increase in the IR absorption of the S-H stretching mode ($\sim$2300 cm$^{-1}$) at the phase transition (I-II), reflecting the change in dipole moment of the S-H bonds [22]. For (H$_2$S)$_2$H$_2$, at room temperature we observe two H$_2$ Raman vibrons ($\nu_{IIa}$ and $\nu_{IIb}$) and four broad S-H stretching modes (between 2200 and 2600 cm$^{-1}$; Figs. 1; [15,16] at low temperatures we find at least seven narrow S-H stretching modes ($\sim$2250-2580 cm$^{-1}$) and observe two doublets of H-H Raman vibrons ($\nu_{IIa}$ and $\nu_{IIb}$, Figs. 5 and 6). On compression of phase II at room temperatures and below, the S-H stretching modes rapidly broaden and decrease in frequency [Fig. 2(b)], indicating a significant enhancement of the H-bond strength between neighboring H$_2$S molecules. From IR spectroscopy, we observe a reduction in the FWHM of the H-H IR vibron at the transition pressure from phase I to 174511-3
FIG. 4. Proposed phase diagram for the solid phases of \((\text{H}_2\text{S})_2\text{H}_2\). Symbols represent different experimental runs, while their colors represent different phases: purple, I; green, II; magenta, II'; blue, III; and black, H\(_3\text{S}\). The dotted line outlines a translucent yellow area indicating the stability field of II': The overlapping colors from phases II and III within this stability field indicate the phase overlap. The white region indicates where nonmolecular H\(_3\text{S}\) is stable.

phase II (Fig. 3), while its frequency retains the same pressure dependence of \(v_{\text{IIa}}\). This reduction in IR bandwidth, coupled with the positive slope of the \(v_{\text{IIa/b}}\) Raman mode frequencies, reflects a reduced interaction between H\(_2\) and H\(_2\text{S}\) within phase II of the compound; this is due to an enhanced interaction between the H\(_2\text{S}\) molecules themselves upon orientational ordering, as H bonding strengthens until it overcomes the energy of rotation, which then induces the lattice modes.

Above 25 GPa (300 K) and 39 GPa (> 80 K) we observe new lattice modes and previously unidentified H-H Raman vibrons \(\nu_{\text{IIa}}\) and \(\nu_{\text{IIb}}\), magenta open triangles in Fig. 1), which we attribute to a previously unreported \((\text{H}_2\text{S})_2\text{H}_2\) phase, II', which coexists with phases II and III. The H:S stoichiometry of II' is assumed to remain 3:1, as no change was observed in the atomic volume at the transition (Fig. 7). It should be noted that at 300 K only two II' vibrons are visible [Figs. 1 and 2(a)], but \(\nu_{\text{IIb}}\) exhibits a high-frequency shoulder below 80 K (Figs. 5 and 6). IR measurements detect only one vibron with a frequency very close to \(\nu_{\text{IIa}}\). Phase II' also exhibits the following distinct Raman characteristics at 300 K: development of a librational mode (460 cm\(^{-1}\) at 25 GPa), one S-H stretching mode (highlighted in the middle panel of Fig. 1), with a change in pressure dependence [Fig. 2(b)]; and a further increase in the bandwidth and marked decrease in overall intensity for all S-H stretching modes (Fig. 1; note scaling of first two spectra in middle panel). Increasing pressure above 25 GPa (300 K) sees the continued broadening of the S-H stretches.

We observe Raman vibrons \(\nu_{\text{IIIa}}\) and \(\nu_{\text{IIIb}}\) from 34.0 GPa (300 K), with one IR active vibron with a frequency similar to \(\nu_{\text{IIa}}\). The corresponding phase III lattice modes appeared from 31.4 GPa at 300 K (Fig. 1) and 53 GPa below 80 K (Fig. 5). At 300 K the phase overlap after the II' to III transition was around 10 GPa: this phase overlap increases at lower temperatures such that phase II' is stable up to 42 GPa at 300 K, 99 GPa at 80 K, 105 GPa at 45 K, and 112 GPa at 25 K (Fig. 4), which we use to map a straight phase boundary with a slope of approximately \(-4\) G Pa\(^{-1}\) (rightmost dotted line Fig. 4).

Figure 2(b) shows a marked increase in the slopes of three S-H stretching modes (around 1775, 2375, and 2500 cm\(^{-1}\), at 34 GPa), around the phase II-III transition pressure. This indicates that the intermolecular interactions are greater in phase III of \((\text{H}_2\text{S})_2\text{H}_2\) and that the S-H bonds are longer and weaker than in the previous phases. This could be interpreted as the H bonds approaching symmetrization in phase III, whereby the H atom becomes equidistant between the two S atoms [17]. A similar shift in the pressure dependence of the \(\nu_{\text{IIa}}\) Raman mode and the sole IR mode is shown in Fig. 2(a) (marked with a star). On further compression, the frequency of \(\nu_{\text{IIa}}\) steadily decreases with a gradual reduction in intensity, up to a maximum pressure of 46 GPa (300 K) and 127 GPa (80 K), above which it was no longer observed. The IR mode exhibits the same behavior (Fig. 3), and the lattice modes also disappear around the same pressures (Figs. 1 and 5). We interpret these observations as a transition from \((\text{H}_2\text{S})_2\text{H}_2\) to an extended sulfur-hydrogen network following the loss
of molecular integrity from the H-H bond breaking and symmetrization from H-bonding between the H$_2$S molecules [13]. We observe no evidence that the stoichiometric ratio of H:S changes from 3:1; therefore we refer to the sulfur-hydrogen network as H$_3$S. Indeed, the change in the $\nu_{IIIa}$ and $\nu_{IIIb}$ stretching mode frequencies aligns well with previous theoretical calculations for the internal H-H bond lengths within the Cccm structure (phase III) [13]. In addition, at 300 K we find the transition to a nonmolecular network to be reversible, with the Raman and IR signatures of (H$_2$S)$_2$H$_2$ returning on decompression (Figs. 3 and 8).

In contrast to the rich Raman and IR spectra arising from the reorientation of H$_2$S and rearrangement of H$_2$ molecules, diffraction studies show almost no changes to the underlying sulfur lattice throughout the solid phases of (H$_2$S)$_2$H$_2$, and H$_3$S. Figure 7 shows a plot of atomic volume per S atom as a function of pressure; we observe no sudden volume decreases at any of the transition pressures observed in our Raman and infrared experiments. This indicates that the stoichiometry remains 3H:1S. The inset plot of diffraction peaks vs pressure shows no obvious splitting or merging of peaks due to the solid phases of (H$_2$S)$_2$H$_2$ and H$_3$S. Figure 4 shows our proposed phase diagram of (H$_2$S)$_2$H$_2$ based on our Raman and IR data points. The significant phase overlap of phases II and III with II’ is represented by the stability field of II’, surrounded by dotted black lines. The white region indicates the proposed stability field of the H$_3$S phase, where no vibrational modes from H$_2$ molecules are observed by either Raman or IR spectroscopy. The phase diagram highlights the significant enhancement of the stable pressure ranges at low temperatures; most notably, the difference in the H$_3$S transition pressure moves from 47 GPa at 300 K to 127 GPa at 80 K. The expansion of the respective stability fields of the (H$_2$S)$_2$H$_2$ phases at low temperatures also reflects the overall stability of the compound with respect to decomposition at high pressures.

In some room temperature studies we observe partial decomposition from laser overexposure in samples of (H$_2$S)$_2$H$_2$ and H$_3$S (and pure H$_2$S). This is evidenced by a broad Raman excitation at 475 relative cm$^{-1}$ (Fig. 1), which we attribute to the formation of an S-S bond within amorphous sulfur, from degradation of the H$_2$S molecules. Previous Raman studies have also reported a broad peak at the same frequency, attributed to the formation of S-S bonds on compression of D$_2$S [36–38]. We find that laser-induced decomposition is more sensitive at higher pressures and was observed only at room temperature. Throughout the phase sequence I-II-II’-III, (H$_2$S)$_2$H$_2$ progressively loses molecular integrity of both H$_2$S and the H$_2$ $\nu_a$ environments, which could explain the increased sensitivity at higher pressures with respect to decomposition (at 300 K). This sensitivity appears restricted to...
wavelengths around the visible spectrum, as S was observed in only one diffraction study where the sample was also probed with a Raman laser. We previously reported sensitivity to only one diffraction study where the sample was also probed with both Raman (Fig. 8) and IR measurements (Fig. 3). In a prior study of \((\text{H}_2\text{S})_2\text{H}_2\), decomposition of the compound above the metallization pressure of Se was misinterpreted as metallization of \(\text{H}_3\text{Se}\) [39,40].

Although we were able to synthesize single crystals of \(\text{H}_2\text{S}\) from \(\text{S}\) and \(\text{H}_2\), upon formation of \((\text{H}_2\text{S})_2\text{H}_2\) the sample tended to break up into a small number of crystalites, resulting in poor powder diffraction patterns, an issue that was also raised in a previous study of \((\text{H}_2\text{S})_2\text{H}_2\) [15]. Given that the transition from \((\text{H}_2\text{S})_2\text{H}_2\) to \(\text{H}_3\text{S}\) from diffraction would be if the \((131/311)\) peak in \(\text{Cccm}\) up to 50 GPa. The same volumes could hence be obtained from either \(I4/mcm\) or \(\text{Cccm}\).

From XRD we can detect only the relative positions of the S atoms, and therefore the primary evidence for \(\text{Cccm}\) in phase III or \(\text{H}_3\text{S}\) from diffraction would be if the \((131/311)\) peak split; this would signify that the unit cell dimension \(a\) was no longer equal to \(b\), as it is for the tetragonal \(I4/mcm\) symmetry. We do not clearly observe any peaks visibly splitting in our diffraction data (or in data from other studies of \(\text{H}_3\text{S}\) [6,17]), yet the differences between our refined values of \(a\) and \(b\) are statistically significant (Fig. 9). Despite the fact that competitive \(\text{H}_3\text{S}\) structures have been reported in the relevant pressure ranges (e.g., \(C2/c\)) [11], \(\text{Cccm}\) still presents the best stable structural candidate for phase III, which agrees with the experimental Raman data [13,41]; \(\text{Cccm}\) has two \(\text{H}_2\) environments compared to the single environment of \(I4/mcm\) [15], and the predicted \(\text{H}-\text{H}\) bond lengths as a function of pressure for \(\text{Cccm}\) also correspond very well to the observed frequency dependences of \(\nu_{\text{H}-\text{H}}\) [13] [Figs. 1, 2(a), 5, and 6]. Although none of the structures can be claimed to be explicitly true, \(\text{Cccm}\) remains the best approximation of the phase III structure from an assessment of all existing studies.

Given that the transition from \((\text{H}_2\text{S})_2\text{H}_2\) to \(\text{H}_3\text{S}\) appears to result from a gradual lengthening of the internal chemical bonds of \(\text{H}_2\text{S}\) and \(\text{H}_2\), the \(\text{H}_3\text{S}\) structure is likely to be very similar to phase III of \((\text{H}_2\text{S})_2\text{H}_2\) but with slightly shifted \(\text{H}\) atomic positions. At the very least, our diffraction data can discern the difference between orthorhombic-based (\(\text{Cccm}\) or equivalent) and a more symmetrical bcc cubic \(\text{S}\) lattice (i.e., \(I\text{m}3\text{m}\) or \(R\text{3}3\text{m}\)). Although the orthorhombic-based and cubic-based symmetries have common peaks, the bcc pattern produces far fewer reflections. Previously, both \(\text{Cccm}\) [6] and \(I\text{m}3\text{m}\) [17] structures were reported as stable crystalline...
phases after laser heating S in H₂. Similarly, the first structural study of the high-\( T_c \) phase (from decomposition of H₃S) claims the pattern is bcc S but has impurity peaks which match the orthorhombic-based structure, alongside the additional reflections from the excess by-product of pure S [2]; at the least, it cannot be said to be purely bcc S. Recently, it was shown that subsequent laser heating of the poorly crystallized mixture produces a much cleaner bcc S phase, without any of the orthorhombic peaks and only minor impurities [42]. Theoretical calculations find a high kinetic barrier between the phase with an orthorhombic-based S lattice and a cubic-based S lattice [13]. Given both structures are reported from compression of (H₂S)₂H₂, would become the high-\( T_c \) cubic phase if heated. A wide range of \( T_c \) values is reported across multiple studies of the high-\( T_c \) phase where H₂S is used as a precursor, and the samples are only “annealed” at room temperature [1,18–21]; it is possible that the pressure-induced decomposition of H₂S produces a mixture of orthorhombic, cubic, and pure S phases. While it remains experimentally unfeasible to determine the atomic positions of hydrogen in (H₂S)₂H₂ and H₃S phases, our spectroscopic data offer substantial insight into their behavior. An important question is raised by the observation that the detected IR absorption frequencies of the H-H stretch in (H₂S)₂H₂ are nearly identical to the Raman excitation frequencies of H₂ \( v_a \) vibrators as functions of pressure, from all of the solid phases, I-II-II’-III (Fig. 3); the IR frequencies even match subtle shifts in pressure dependence, for example, in \( v_{1\text{iii}} \) [indicated by a star in Fig. 2(a)], as well as mirroring a slight increase in frequency of \( v_{1\text{iii}} \) around 30 GPa [Fig. 2(a)]. It is reasonable to assume that this is not coincidental and that the IR absorptions also occur from the same \( v_a \) vibrational modes. Because the selection rules for I-4/mcm and Cccm forbid the same IR and Raman lattice vibrational modes, it could be interpreted that the H₂ \( v_a \) molecules are aligned such that their vibration becomes coupled to the lattice phonons of the compound and hence are only observed by Raman spectroscopy and not in the IR spectra. This in turn would imply the internal vibrations of H₂ \( v_a \) molecules remain uncoupled to the lattice vibrations, possibly due to rotation, and hence the symmetry based selection rules do not apply. The lower frequency of \( v_a \) indicates these H₂ molecules experience more local interaction with the H₂S molecules themselves. Perhaps this is due to a greater dipole moment on each H₂S, as the H bonding becomes enhanced at higher pressures, which in turn contributes to the weakening of the \( v_{1\text{iii}} \) Raman mode at higher pressures, facilitating the subsequent transformation to an extended sulfur-hydrogen H₃S network. These results provide a benchmark for future studies of the sulfur-hydrogen system. The enhanced stability of (H₂S)₂H₂ and H₃S at low temperatures and the retention of the S lattice structure contribute to understanding the mechanisms by which other sulfur-hydride phases are adopted at high pressures.

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