Article

Effect of Pressure on the Distribution of Electrons in a Cluster of H₂S

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ABSTRACT: We carry out a theoretical study of the effect of pressure on the atomic and electronic distribution of a cluster made of 155 H₂S molecules. The pressure was modeled by bringing the cluster into a spherical container made of 500 helium atoms and reducing the diameter of the container. We did *ab initio* molecular calculations using DFT. At the lowest pressure, the S−H−S angle between two neighboring H₂S molecules has a distribution with a mean value of 167.1°. This angle will be shorter as pressure increases, reaching a distribution with a mean value of 125.5° at the highest pressure. Changes in this angle result from a strong S−S interaction, displacing the H atoms from the line joining the sulfur atoms. This rearrangement of the atomic distribution generates hydrogen-rich spatial regions. We analyzed the evolution of Mulliken charges on S and H atoms in the cluster with pressure, finding that electrons move from S to H atoms, suggesting that these hydrogen-rich regions should be responsible for the electrical conductivity and, consequently, also for the superconductivity in solid H₂S under pressure.
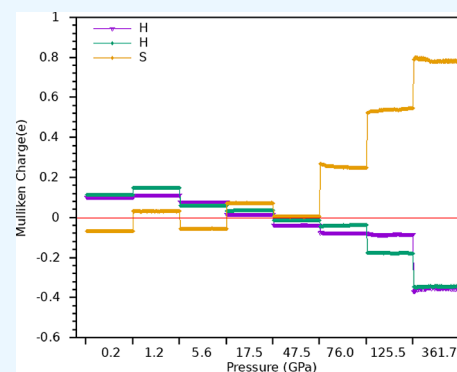
INTRODUCTION

For decades, people have been interested in obtaining metallic, superconducting hydrogen. In 1935, Wigner and Huntington[1] believed that crystalline hydrogen could be metallic. Therefore, they theoretically studied the electrical conductivity of hydrogen in a body-centered cubic crystalline structure. At that time, however, they argued that the experimental conditions did not exist to obtain the necessary pressure to generate this crystalline hydrogen. Through analysis of this cubic crystalline phase of hydrogen, Ashcroft[2] predicted that it would be a super-conductor.

Wigner and Ashcroft's reports inspired people to search for the synthesis of metallic hydrogen[3−6] and its possible behavior as a superconductor. The reported studies inferred that pure hydrogen under pressure would likely be metallic but not superconducting.[6]

As an alternative to looking for hydrogen-based super-conductors, the researchers looked to hydrides. This search culminated in the discovery of the superconducting behavior of sulfur hydride at high pressures with a transition temperature of 203 K,[7] which was increased to 287.7 K by photochemically transforming a mixture of H₂S, H₂, and CH₄ subjected to high pressures.[8] Following this finding, the search for new super-conducting hydrides led to the discovery of high-pressure lanthanum hydrides with a transition temperature to the superconducting state of 260 K,[9] also discovering that high-pressure yttrium hydrides have a superconducting transition temperature of 262 K.[10]

The atomic distribution of some of these high-temperature superconducting hydrides has been identified by X-ray diffraction experiments,[11,12] but almost nothing has been studied about changes in the electronic distribution with pressure.[13,14] Superconducting H₂S is a simple system that makes it well suited to study these changes. Understanding them would help elucidate the superconducting behavior of this hydride.

In the present manuscript, we describe the changes, with pressure, in the atomic distribution and the electron distribution of a 155H₂S cluster. The manuscript completes previously reported properties for this cluster.[15] We describe in detail how, with pressure, hydrogen atoms redistribute in space and, through an analysis of the Mulliken charges,[16] how electrons redistribute in the atoms of the cluster.

RESULTS AND DISCUSSION

We built an atomic cluster of 155 H₂S molecules; the cluster morphology approximated a sphere. To build the cluster, we made a small crystallite using the crystallography reported for the tetragonal phase of H₂S obtained under pressure.[17] The crystallite could be built with any crystallography reported for H₂S, because for our pressure simulations, the initial atomic distribution of the cluster was expanded and subjected to molecular dynamics at 300 K.

To model the pressure in the 155H$_2$S cluster, we built a spherical container made of He atoms. The coordinates of He atoms in the initial container corresponded to those reported for the carbon atoms in the spherical fullerene that has 500 carbon atoms and a radius of 9.973 Å.[18]

This container was large enough to contain the 155H$_2$S cluster inside. The H–He and S–He distances were large enough to achieve SCF convergence during DFT calculations. By embedding the cluster in the container, its atomic coordinates were moved to match its centroid with the centroid of the container. For each pressure, during geometry optimization, the coordinates of the He atoms remained fixed.

In order to lose the initial atomic distribution in the cluster, after incorporating it into the container, the radius of the container was expanded by 1.8 times its initial value. After that, we performed molecular dynamics calculations at 300 K for 2.7 ps with a time step of 1 fs. We then reduced the container radius to 1.6 of its initial value and performed molecular dynamics calculations at 300 K for 1.0 ps with a time step of 1 fs.

Following these molecular dynamics calculations, the final atomic distribution of the cluster was used as the initial atomic distribution to study the evolution of its properties with pressure. This study was carried out by optimizing the geometry of the cluster in the container of He.[15]

The different pressures were implemented by reducing the radius of the container (Table 1). Reference 15 gives details on the calculation of the static pressure on the 155H$_2$S cluster due to the variation of this radius.[15]

Table 1. Container Radius and the Corresponding Pressure on the 155H$_2$S Cluster

radius (Å)	pressure (GPa)
13.962	0.2
12.965	1.2
11.968	5.6
10.971	17.5
9.973	47.5
9.475	76.0
8.976	125.5
8.477	208.3
7.979	361.7

For the lowest pressure (0.2 GPa), the H$_2$S molecules interact with each other through hydrogen-type interactions. At this pressure, each H atom is between two sulfur atoms forming S–H–S angles with a distribution that has a mean value of 167.1° with a standard deviation of 6.8° (Figure 1). For the highest pressure (361.7 GPa), the S–H–S angles had a distribution with a mean value of 125.5° and standard deviation of 9.5° (Figure 1).

As pressure increases, the S–S pair distribution function (Figure 2) shows that sulfur atoms move closer to each other, displacing H atoms to positions outside the line joining two sulfur atoms. This displacement gives rise to hydrogen-rich spatial distributions.

The previous results suggest revising the crystalline phases reported for superconducting H$_2$S,[11,19] some of which propose that the H atoms are found between two sulfur atoms forming S–H–S angles of 180°.

In the atomic arrangement of the 155H$_2$S cluster at high pressures, the H atoms move closer to each other. For example, for the pressure of 361.7 GPa, 86 of the 310 hydrogen atoms have a H–H bond length smaller than 1.0 Å. These H atoms are
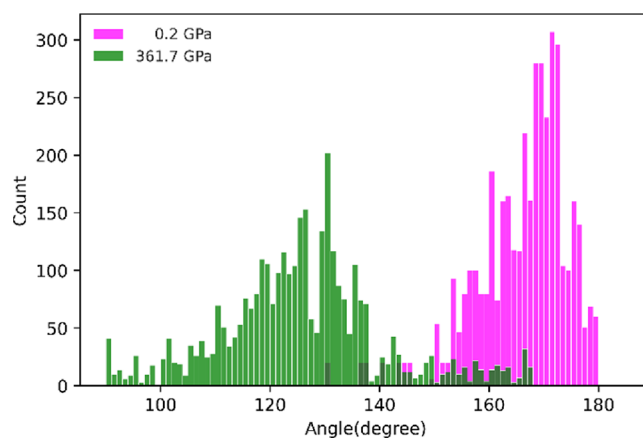

Figure 1. Histogram for the S–H–S angle. The magenta curve corresponds to the atomic distribution for 0.2 GPa; the green curve corresponds to the atomic distribution for 361.7 GPa.
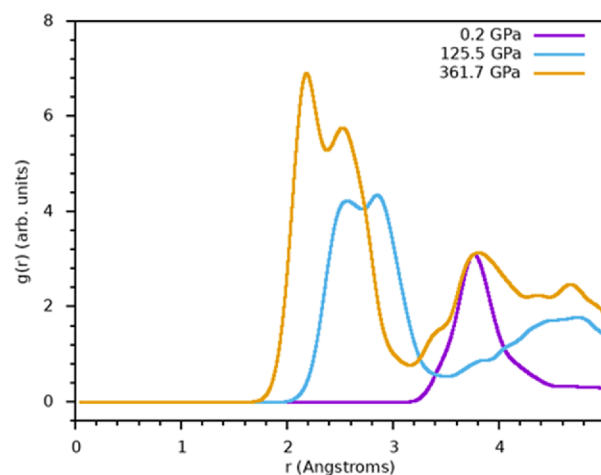

Figure 2. S–S pair distribution function for different pressures.

identified in the H–H pair distribution function (Figure 3) by the presence of the peak centered at 0.75 Å. It is to remark that this atomic distribution was generated through geometry optimization calculations on the 155H$_2$S–500He cluster.

In the literature,[12] the formation of the short H–H bonds with pressure has been interpreted as dissociation of the solid
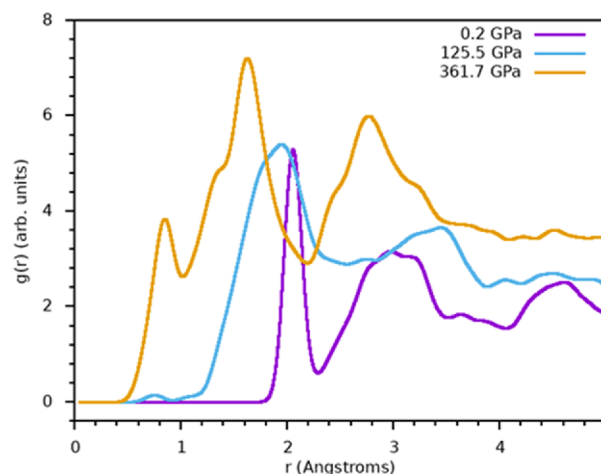

Figure 3. H–H pair distribution function for different pressures.

H_2S forming H_2 molecules, but, in the present work, a detailed analysis of the images of the spatial atomic distribution obtained at the highest pressure shows the presence of hydrogen atoms with more than two other hydrogen atoms as neighbors at distances smaller than 1.0 Å.

Interestingly, as the pressure increases, the distribution function of the S−H pairs remained almost constant (Figure 4); this fact shows that S−H bonds do not change significantly
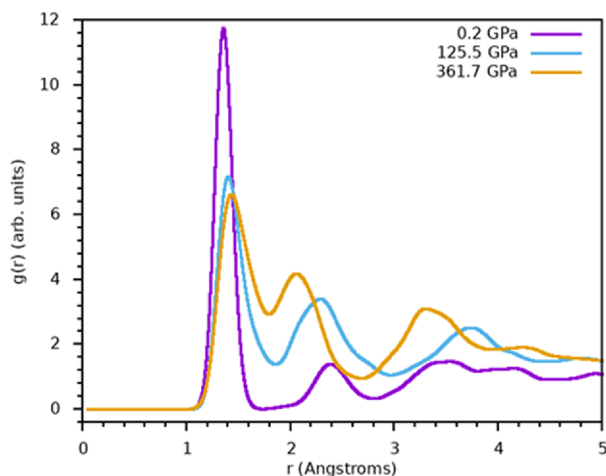

Figure 4. S−H pair distribution function for different pressures.

with pressure. The slight increase observed in these bond lengths at the highest pressure indicates a slight weakening of the S−H interaction.

Changes in the atomic distribution with pressure must surely be associated with changes in the electron distribution in the cluster. Therefore, we performed a Mulliken charge analysis[16] of the cluster for each pressure during the geometry optimizations.

Figure 5 shows the result of a qualitative analysis of the Mulliken charges associated with each atom for different pressures. In this figure, negative charges correspond to red while positive charges correspond to blue; a charge close to zero corresponds to a gray color. For the lowest pressure (Figure 5A), the sulfur atoms have negative Mulliken charges, while all the H atoms have positive charges. At this pressure, the atomic distribution corresponds to a set of H_2S molecules that interact weakly through hydrogen bonds: the observed Mulliken charges reflect the molecular character of the sulfur and hydrogen atoms at this pressure.

At the pressure of 17.5 GPa, some sulfur atoms have charges close to zero, some have positive charges, and some hold negative charges. At this pressure, hydrogen atoms have charges close to zero.

At the pressure of 125.5 GPa, most of the sulfur atoms have positive charges, while the charge of the hydrogen atoms becomes negative. This trend in the charge changes of the sulfur and hydrogen atoms is enhanced when the pressure was 361.7 GPa.

Figures 6 through 9 give a quantitative analysis of the evolution of these charges with pressure. These figures show histograms of the hydrogen and sulfur Mulliken charge in the cluster for different pressures. We used the last 20 frames of the atomic distribution optimization process of the $155H_2S$ cluster to construct the histograms.

For the pressure of 0.2 GPa (Figure 6), the hydrogen atoms have positive Mulliken charges with a distribution that has a
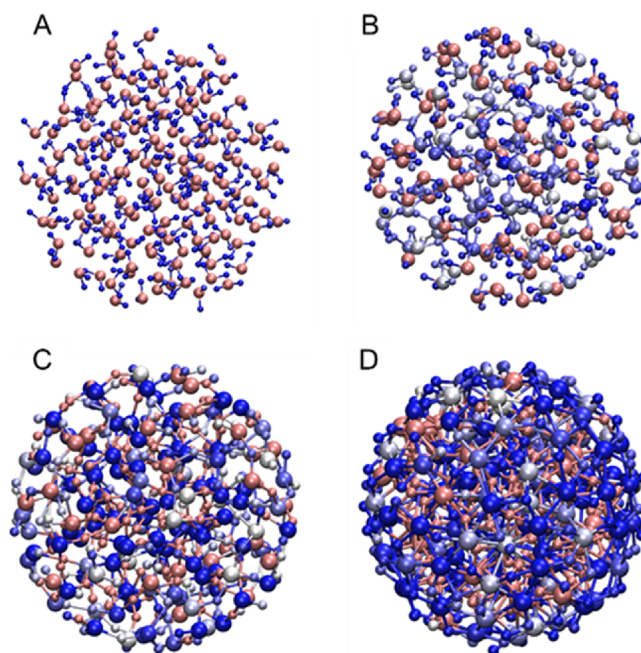

Figure 5. Mulliken charges, the red color corresponds to negative charges, while the blue color corresponds to positive charges; the gray color corresponds to charges close to zero. The large spheres represent sulfur atoms and the small spheres represent hydrogen atoms. (A) 0.2 GPa, (B) 17.5 GPa, (C) 125.5 GPa, (D) 361.7 GPa. Increasing pressure reduces the diameter of the cluster, so to construct the figure, we scaled the diameter of the clusters to be the same size in the figure. As a consequence of this, the apparent size of the spheres representing the S and H atoms increases with pressure.
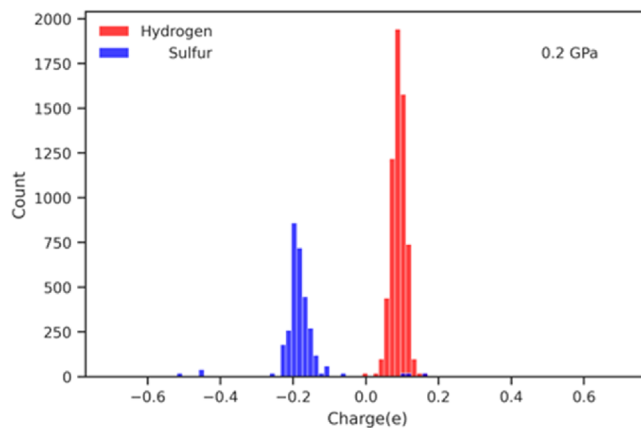

Figure 6. Distribution of the Mulliken charges of the hydrogen and sulfur atoms for the pressure of 0.2 GPa.

mean value of 0.090 e with a standard deviation of 0.019 e (Table 2), while the sulfur atoms have a Mulliken charge distribution that has a mean value of −0.183 e and standard deviation of 0.027 e.

As we increased the pressure to 17.5 GPa (Figure 7), the mean value of the Mulliken charge distribution of the hydrogen atoms moves to 0.045 e with a standard deviation of 0.048 e, while that of sulfur atoms moves to −0.110 e with a standard deviation of 0.072 e (Table 2).

For the pressure of 125.5 GPa (Figure 8), the mean value of the Mulliken charge distribution of hydrogen is negative, −0.123 e, with a standard deviation of 0.096 e, while the distribution of

Table 2. Mean Values and Standard Deviations of the Mulliken Charge Distribution of the Hydrogen and Sulfur Atoms for the Different Pressures

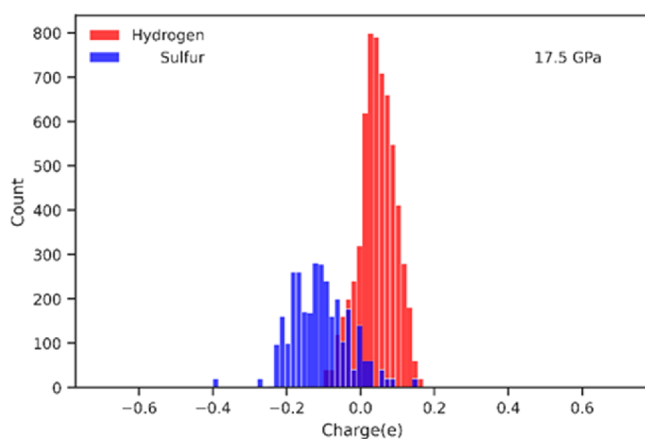| pressure (GPa)	H mean (e)	H std (e)	S mean (e)	S std (e)
0.2	0.090	0.019	−0.183	0.027
1.2	0.085	0.023	−0.178	0.027
5.6	0.071	0.035	−0.158	0.041
17.5	0.045	0.048	−0.110	0.072
47.5	−0.008	0.067	−0.024	0.115
76.0	−0.039	0.077	0.009	0.121
125.5	−0.123	0.096	0.099	0.155
208.3	−0.156	0.100	0.107	0.188
361.7	−0.249	0.124	0.219	0.222

Figure 7. Distribution of the Mulliken charges of the hydrogen and sulfur atoms for the pressure of 17.5 GPa.
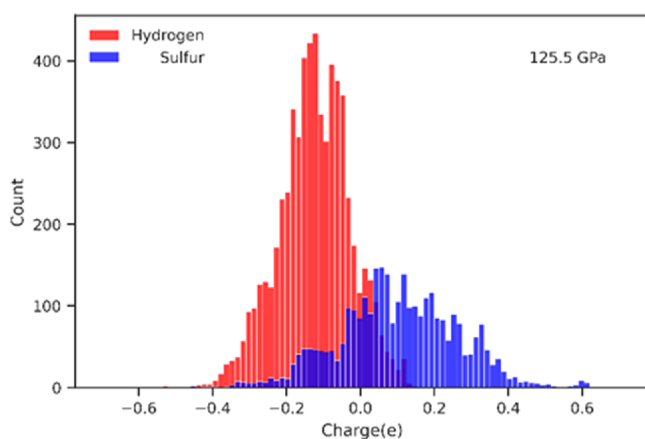

Figure 8. Distribution of the Mulliken charges of the hydrogen and sulfur atoms for the pressure of 125.5 GPa.

sulfur atoms has a positive mean value of 0.099 e, with a standard deviation of 0.115 e (Table 2).

For the highest pressure, 361.7 GPa (Figure 9), the Mulliken charge distribution of hydrogen atoms has a mean value of −0.249 e, with a standard deviation of 0.124 e (Table 2). The corresponding distribution for sulfur atoms has a mean value of 0.219 e, with a broad, standard deviation of 0.222 e.

Figures 6 to 9 clearly show how electrons, under pressure, move from sulfur atoms to hydrogen atoms.

These types of histograms were quantified for all pressures used in the analysis. Table 2 summarizes, for each pressure, the
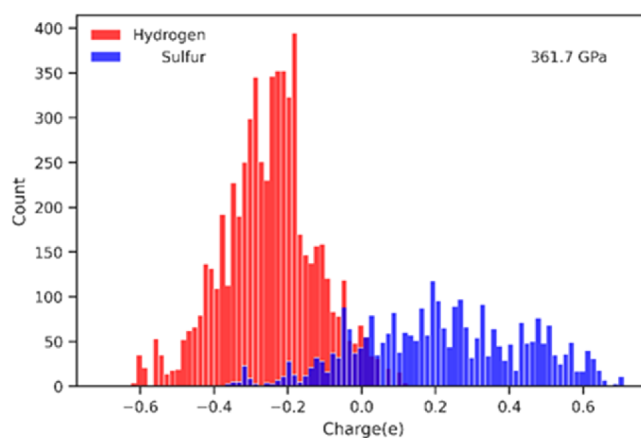

Figure 9. Distribution of the Mulliken charges of the hydrogen and sulfur atoms for the pressure of 361.7 GPa.

mean value of the histogram obtained and the corresponding standard deviation.

To more clearly illustrate the evolution, with pressure, of the Mulliken charges associated with the atoms in the $155H_2S$ cluster, we have chosen a representative H_2S molecule from the cluster and plotted, for each pressure, the Mulliken charges obtained for the last 100 steps of the geometry optimization (Figure 10).
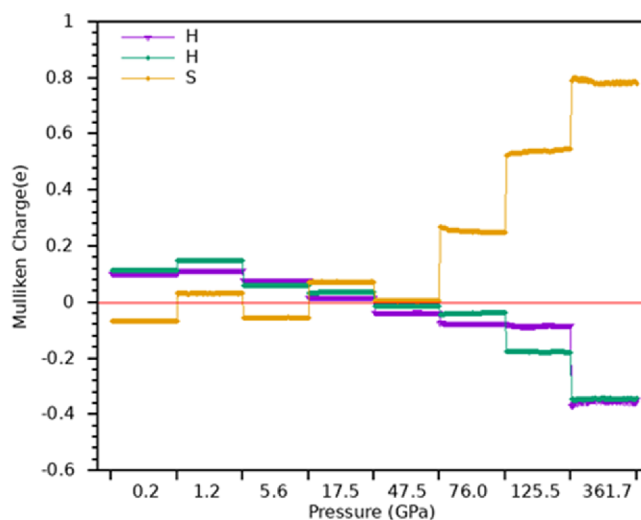

Figure 10. Evolution of Mulliken charges with pressure. The yellow curve corresponds to the S atoms, while the green and purple curves correspond to the H atoms.

Figure 10 shows that the Mulliken charges of S atoms move from negative values to positive values with increasing pressure. This movement from negative to positive values is relatively small for pressures below 76.5 GPa, but the charge increase is noticeably more significant at higher pressures. These changes in the Mulliken charges of the sulfur atoms correlate with the changes in the Mulliken charges of the hydrogen atoms, from positive to negative values. This result indicates that electrons move, with pressure, from the environment surrounding the sulfur atoms to the environment surrounding the hydrogen atoms.

The above observation is fundamental since the analysis of the S−S, S−H, and H−H radial distributions (Figures 2 to 4) shows

that, with pressure, hydrogen atoms move toward spatial regions rich in hydrogen. Consequently, with pressure, the electrons move into these hydrogen-rich regions of space. Therefore, the electrical conductivity, including the superconducting behavior, of the $155H_2S$ cluster should occur in all these spatial regions rich in hydrogen atoms.

CONCLUSIONS

When the $155H_2S$ cluster is under pressure, the H_2S molecules lose their molecular character. For the lowest pressure, the S—H—S angle between two neighboring H_2S molecules has a distribution with a mean value of 167.1°. This angle will be smaller as the pressure increases, reaching a distribution with a mean value of 125.5° at the highest pressure. Changes in this angle result from a strong S—S interaction, displacing H atoms from the line joining the sulfur atoms. This rearrangement of the atomic distribution gives rise to spatial regions rich in hydrogen. Analyzing the evolution of Mulliken charges on S and H atoms with pressure, we conclude that electrons move from S to H atoms, suggesting that the hydrogen-rich spatial regions should be the regions where the electrical conductivity and super-conductivity of the solid H_2S under pressure occur.

METHODS

For optimization of the geometry of the $155H_2S$ cluster, we used DFT,[20] with 6-31g as the basis set, and the generalized gradient functional B3LYP,[21] with dispersion correction to model the exchange-correlation energy.[22]

Molecular dynamics calculations were performed on the system using the canonical ensemble (NVT), with an integration time step of 1.0 fs, and the Bussi−Parrinello velocity rescaling thermostat.[23]

We did some calculations using two basis sets different from the 6-31g basis set: the basis set 6-31g**, which includes polarization functions in the hydrogen and sulfur atoms; and the basis set 6-31+g, which includes diffuse functions. The results obtained with these new basis sets were similar to those obtained with the basis set 6-31g.

TeraChem[24,25] was the code used to perform the molecular calculations. The L-BFGS[26] algorithm generated the atomic distribution of the system with minimum energy, with the following convergence conditions: an energy threshold of 10^{-6} Hartree, maximum step of 10^{-3} Bohr, RMS step of 10^{-3} Bohr, maximum gradient of 10^{-4} Hartree/Bohr, and RMS gradient of 10^{-4} Hartree/Bohr. Two workstations were used for the calculations: one with 4 Nvidia Tesla V100 GPU cards and the other with 4 Nvidia Tesla A100 GPU cards.

For some pressures, the atomic charges associated with the optimized $155H_2S$ cluster were obtained using the Merz−Kollman[27] analysis method, the CHELPG[28] analysis method, and the RESP[29] analysis method. These analysis methods show the same trend of evolution of hydrogen and sulfur charges with pressure as observed with the Mulliken analysis method (Figures 11 and 12).

The Merz−Kollman and the CHELPG analysis methods were performed with the code Gaussian 16 Rev. A.03[30] while the RESP analysis was performed using the TeraChem code.

The VMD[31] code was used to display the images colored with Mulliken charges, to obtain the pairwise distribution functions and to inspect the distribution of atoms in the cluster.
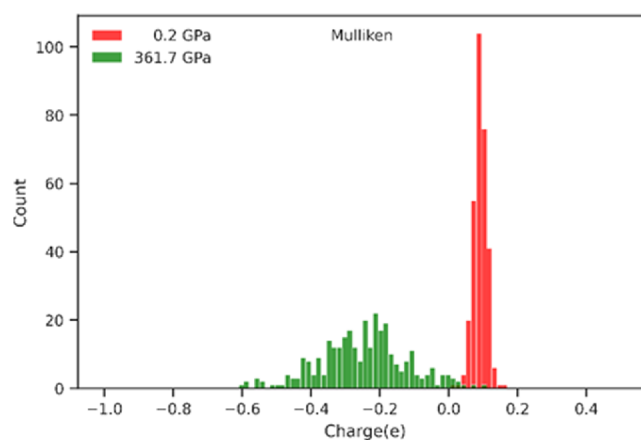

Figure 11. Distribution of the Mulliken charges of the hydrogen atoms for the pressures of 0.2 and 361.7 GPa.
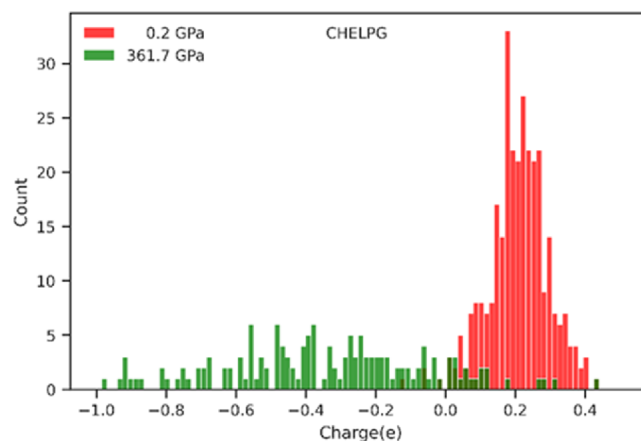

Figure 12. Distribution of the CHELPG charges of the hydrogen atoms for the pressures of 0.2 and 361.7 GPa.

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