Exploring the Evolution Mechanism of Sulfur Vacancies by Investigating the Role of Vacancy Defects in the Interaction between H$_2$S and the FeS(001) Surface

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ABSTRACT: Vacancy defects are inherent point defects in materials. In this study, we investigate the role of Fe vacancy (V$_{Fe}$) and S vacancy (V$_S$) in the interaction (adsorption, dissociation, and diffusion) between H$_2$S and the FeS(001) surface using the dispersion-corrected density functional theory (DFT-D2) method. V$_{Fe}$ promotes the dissociation of H$_2$S but slightly hinders the dissociation of HS. Compared with the perfect surface (2.08 and 1.15 eV), the dissociation energy barrier of H$_2$S is reduced to 1.56 eV, and HS is increased to 1.25 eV. Meanwhile, S vacancy (V$_S$) significantly facilitates the adsorption and dissociation of H$_2$S, which not only reduces the dissociation energy barriers of H$_2$S and HS to 0.07 and 0.11 eV, respectively, but also changes the dissociation process of H$_2$S from an endothermic process to a spontaneous exothermic one. Furthermore, V$_{Fe}$ can promote the hydrogen (H) diffusion process from the surface into the matrix and reduce the energy barrier of the rate-limiting step from 1.12 to 0.26 eV. But it is very hard for H atoms gathered around V$_S$ to diffuse into the matrix, especially the energy barrier of the rate-limiting step increases to 1.89 eV. Finally, we propose that V$_S$ on the FeS(001) surface is intensely difficult to form and exist in the actual environment through the calculation results.

1. INTRODUCTION

H$_2$S corrosion is the most dangerous factor in the corrosion of equipment in oil and gas fields with high sulfur content. As a highly toxic gas, H$_2$S not only seriously threatens the routine use of equipment and pipeline steel but also directly threatens the safety of human life.$^{1,2}$ When steel is used in the H$_2$S environment, pitting corrosion, local corrosion, uniform corrosion, linear corrosion, stress corrosion cracking, and hydrogen-induced cracking occur easily.$^{3}$ In the 1980s, Canadian scholars found that corrosion products in H$_2$S environments were more complex than other corrosion environments. Especially, when iron-base alloys contacted the wet H$_2$S environment, pitting corrosion, local corrosion, uniform corrosion, linear corrosion, stress corrosion cracking, and hydrogen-induced cracking occur easily.$^{3}$

In a wet H$_2$S environment, the reaction at the iron sulfide compounds/H$_2$S interface has a vast influence on the formation of subsequent corrosion products and the transition between corrosion products.$^{10-13}$ A prior study discovered that in the Fe−H$_2$S−H$_2$O environment at a high temperature, the crystal evolution sequence of iron sulfide compounds is as follows: mackinawite → pyrrhotite → pyrite; trolite → pyrrhotite → pyrite.$^{14}$ In addition, FeS gradually transforms into pyrrhotite converted into other more stable iron sulfide compounds.$^{7}$ Consequently, FeS is regarded as the forerunner of other iron sulfide compounds formed in deposition and hydrothermal systems, including pyrite (FeS$_2$), pyrrhotite (Fe$_7$S$_8$), and greigite (Fe$_3$S$_4$).$^{8}$ Besides, recent studies have shown that FeS exhibits typical metallic characteristics.$^{9}$

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Figure 1. Top and front views (a−c) of the surface structures of perfect and vacancy-defective FeS(001) surfaces. Red dotted lines represent V_{Fe} and V_{S}, respectively. The charge density of perfect (d), vacancy-defective-Fe (e), and vacancy-defective-S (f) FeS(001) surfaces.

as the temperatures increase.\textsuperscript{15} The H atoms generated by H$_2$S dissociation further diffuse from the surface to the interior of the matrix and gather at H traps such as defects and inclusions to form H$_2$, thus generating hydrogen bubbling or cracking.\textsuperscript{16} Bai et al. studied the hydrogen escape behavior of FeS under different hydrogen charging conditions through the pyrolysis adsorption test, and the results showed that H diffused from grain boundary/dislocation to vacancies in the metal and that FeS had no obstruction to hydrogen permeation.\textsuperscript{7}

The formation and transformation of FeS and its hydrogen resistance properties in the H$_2$S environment have been studied in detail experimentally. However, it is difficult to determine the interaction between H$_2$S and the low-dimensional surface of FeS from a microscopic point of view through the existing experimental techniques. Density functional theory (DFT) can provide an understanding of the interactions between small molecules and surfaces at the molecular level. In recent years, DFT has been widely used to study the adsorption/dissociation processes of molecules and charge transfer between molecules and substrates. An FeS crystal has a tetragonal structure. Fe atoms are connected to four equidistant S atoms in a tetragonal lattice by tetrahedral coordination to form an equilateral tetrahedral layered structure stacked along the z-axis and stabilized by vdW force.\textsuperscript{18} FeS is usually layered, so FeS is characterized by surface activity and high specific surface area like other two-dimensional layered materials.\textsuperscript{19} In the past, some scholars have studied the interaction between some small molecules and diverse low-dimensional surfaces of FeS by the DFT method. Dzade et al. systematically studied the adsorption/dissociation of various small molecules on diverse low-dimensional surfaces of FeS.\textsuperscript{20−24} The adsorption energy of small molecules at different adsorption sites on diverse low-dimensional surfaces was investigated, and the dissociation of small molecules was analyzed. The calculation results reported that NO$_x$, CO$_2$, H$_2$O, C$_3$H$_6$NO$_2$S, and C$_6$H$_4$S are more likely to dissociate on the most unstable FeS(111) surface. Meanwhile, the dissociation energy barrier of these molecules is the largest on the FeS(001) surface. Whereafter, further studies found that preadsorption of O$_2$/O atoms on diverse low-dimensional surfaces would promote the subsequent adsorption and dissociation of H$_2$O.\textsuperscript{25} Moreover, Krishna-moorthy of MIT suggested the effect of the insertion of H$_2$ and H atoms in the gap between the FeS layers and the insertion of H atoms in the Fe vacancy on the tensile strength and elastic modulus of the matrix.\textsuperscript{26} Recently, Wen et al. calculated the adsorption and dissociation processes of H$_2$S on diverse low-dimensional surfaces of FeS in corrosive environments.\textsuperscript{27} The results demonstrated that H$_2$S had the lowest dissociation energy barrier on the FeS(011) surface and the highest on the FeS(001) surface.

It is widely known that crystal defects exist in any material.\textsuperscript{28} Vacancy is an inherent point defect in a crystal structure. The existence of vacancy defects has a considerable effect on the reactivity of a surface.\textsuperscript{29} For instance, the presence of S vacancies on the pyrite(100) surface not only promoted the adsorption of formamide but also facilitated the transition of amino acid from a zwitterionic species to an anionic species.\textsuperscript{30,31} Sahraei et al. found that the vacancy defects on the ZnS(110) surface can change the hydrophilicity of the surface and also prompt the conversion of amino acid from neutral to zwitterionic.\textsuperscript{32,33} Ward et al. revealed that pure FeS could be described by FeS$_{0.94}$.\textsuperscript{34} Furthermore, crystallographic evidence found by Taylor and Finger et al. confirmed that FeS was sulfur-deficient (FeS$_{1−x}$, typically $0 \leq x \leq 0.07$).\textsuperscript{35} This may be caused by the existence of V$_{S}$ or the incorporation of interstitial metal atoms. In most calculations, a perfect FeS surface has been emphasized with attention. However, the influence of vacancy defects on the adsorption, dissociation, and H diffusion behavior of H$_2$S on the FeS surface is rarely reported. In view of the metastable nature of FeS, surface defects are very possible to form in the actual environment. Exploring the adsorption/dissociation and diffusion processes of H$_2$S on the vacancy-defective FeS surface by the DFT method can be used to guide the experiment. Besides, this allows us to further enhance the understanding of the hydrogen barrier properties of FeS and the influence of vacancy defects on the subsequent formation and transformation of iron sulfide compounds from the microscopic perspective.

In this work, we investigated the impact of V_{Fe} and V_{S} on the adsorption and dissociation processes of H$_2$S on the most
stable (001) surface of FeS. Besides, the diffusion energy barrier of the H atom from the surface into the matrix was calculated. In the end, according to the calculation results, we found that V$_r$ on the FeS(001) surface is extremely difficult to form and exist in the actual environment.

2. RESULTS AND DISCUSSION

2.1. Properties of FeS(001) Surfaces. First, according to the vacancy formation energy formula, we calculate the formation energies of V$_{Fe}$ and V$_{S}$ of the FeS(001) surface. The results indicate that the formation energies of V$_{Fe}$ and V$_{S}$ are 1.34 and 3.91 eV, respectively. The top and front views of perfect and vacancy-defective FeS(001) surfaces are shown in Figure 1a–c. The red dotted lines represent V$_{Fe}$ and V$_{S}$. Among them, V$_{Fe}$ is in the second atomic layer and V$_{S}$ is in the first atomic layer. Since vacancy defects are vacant in different layered positions, the charge density distribution is carried out to assess the change of the surface electronic structure. The charge density distribution of perfect and vacancy-defective FeS(001) surfaces is shown in Figure 1d–f. Blue and red represent the areas with lower and higher charge densities, respectively. The red dotted lines in the figure represent the location of vacancy defects. It can be clearly seen that a region with considerably low charge density is formed around the vacancy defects. Besides, the charge density around V$_{S}$ decreases more obviously, which has a greater influence on the charge density distribution of the FeS(001) surface.

Moreover, we also calculated that the formation energy of the V$_{S}$ of the third atomic layer is equal to that of the first atomic layer, but the result shows that V$_{S}$ in the third atomic layer has almost no effect on the surface charge density distribution and the adsorption of H$_2$S. Therefore, our study focused on the V$_{S}$ located in the first atomic layer and the V$_{Fe}$ located in the second atomic layer, which are relatively close to the surface.

2.2. Adsorption of H$_2$S. Figure S1b–d shows the possible adsorption sites of different FeS(001) surfaces and dissolution sites in the matrix. Table S1 lists the related parameters of different adsorbents after they are stably adsorbed on different surfaces. Table 1 lists the structural parameters of the most stable adsorption configurations, where d (Å) expresses the distance between adsorbents and the surface. Figure 2 shows the top view, front view, DCD, and adsorption energy of H$_2$S stably adsorbed on perfect and vacancy-defective FeS(001) surfaces. The yellow and blue areas in the DCD represent the areas of charge increase and loss, respectively.

The stable adsorption site of H$_2$S on perfect and vacancy-defective FeS(001) surfaces are all Fe-B sites. However, on the vacancy-defective-Fe FeS(001) surface, the adsorption energy of H$_2$S decreases slightly, which reveals that the existence of V$_{Fe}$ slightly decreases the adsorption capacity of H$_2$S. Nevertheless, the presence of V$_{Fe}$ does not change the stable adsorption location and configuration of H$_2$S. The bond length, bond angle, and the distance between H$_2$S and the surface are almost identical to those of the perfect surface after H$_2$S was stably adsorbed on the vacancy-defective-Fe FeS(001) surface. Since the adsorption of H$_2$S on the FeS(001) surface itself is weak physical adsorption, and V$_{Fe}$ is in the second atomic layer, so it is arduous to affect the adsorption process of H$_2$S on the surface. Besides, it can also be seen from the DCD that the charge transfer between H$_2$S and the vacancy-defective-Fe FeS(001) surface is basically the same as that between H$_2$S and the perfect FeS(001) surface.

| adsorbate | adsorption spot | d (Å) | $\theta$ (deg) | d (H–S) (Å) | $E_{ads}$ (eV) |
|-----------|-----------------|-------|----------------|-------------|--------------|
| H$_2$S    | Fe-B$^a$        | 2.794 | 91.346         | 1.352; 1.332| −0.23        |
| H$_2$       | S-T$^b$        | 2.157 | −              | 1.357       | −1.27        |
| H + H$^+$ | Fe-B + S-T     | 1.665; 2.191 | − | 1.357 | 1.63 |
| H + S$^+$ | Fe-B + S-T     | 1.681; 1.942 | − | −     | −0.36 |

$^a$: represents the bridge site. $^b$: represents the top site. $^c$: represents the location of the vacancy defect.

On the vacancy-defective-S FeS(001) surface, H$_2$S is stably and vertically adsorbed at the S-V site and has evident hybridization with the surface. The adsorption energy of H$_2$S increases to $\approx 1.21$ eV. As one can see from the DCD, the H atom in H$_2$S takes some electrons from the S atom in H$_2$S, which is different from the charge transfer of H$_2$S after it is stably adsorbed on other surfaces. In addition, part of the charge from the S atom in H$_2$S is also transferred to the Fe atom of FeS. The transfer of charge further proves that there is a strong interaction between H$_2$S and the vacancy-defective-S FeS(001) surface, which may be caused by the reduction of the charge density prompted by V$_{S}$ as mentioned above.

On the other hand, it can be seen from the structural parameters, compared with the perfect and vacancy-defective-Fe FeS(001) surfaces, the bond length of H$_2$S increases and the bond angle decreases on the vacancy-defective-S FeS(001) surface, proposing that these states may be the precursors of H$_2$S dissociation. This also provides some evidence from the side that the existence of V$_{S}$ may promote the dissociation process of H$_2$S.

2.3. Dissociation of H$_2$S. In this work, CI-NEB is applied to calculate the maximum dissociation barrier $E_\Delta$ and the minimum energy paths (MEPs) of H$_2$S and HS. The adsorption energies and related parameters of HS + H and S + H after stable co-adsorption on different surfaces were calculated, as shown in Table 1. The top views of the IS$_r$, FS$_r$, and TS$_r$ configurations of MEPs where H$_2$S and HS dissociate on the vacancy-defective FeS(001) surface are shown in Figures 3 and 4. Meanwhile, Table 2 lists the $E_\Delta$ and $\Delta E$ of the H$_2$S dissociation reaction. The energy barriers $E_{a1}$ and $E_{a2}$ as well as the transition state configurations on the perfect FeS(001) surface in this work are consistent with the previous calculations of our group (2.06 and 1.23 eV), which also proves the validity of our work.

The MEPs of H$_2$S dissociated on the vacancy-defective-Fe FeS(001) surface are shown in Figure 3. The dissociation
process of H$_2$S goes through four steps: (a) H$_2$S is stably adsorbed at the Fe-B site near V$_{Fe}$ by releasing an energy of 0.19 eV. (b) H$_2$S rotates horizontally, breaking an H−S bond away from V$_{Fe}$. Then, the H atom breaks off from H$_2$S, diffusing to the nearest Fe atom and forms a bond with it, while HS diffuses directly to the nearest S-T position. The energy barrier to be overcome for this process is 1.57 eV. (c) The isolated H atom diffuses from V$_{Fe}$ to the interior of the matrix by overcoming an energy barrier of 0.34 eV. Meanwhile, HS does not change and still adsorbs at the original S-T site. (d) HS further overcomes an energy barrier of 1.25 eV and decomposes into S + H. After TS$_3$, the H atom continues to diffuse into the matrix through V$_{Fe}$ and the S atom is still adsorbed at the S-T site. The stable dissolution site is the same as that of the H atom separated by H$_2$S in the first order. It can be seen from Table 2 that compared with the perfect surface, the dissociation energy barriers $E_{a1}$ of H$_2$S decrease and $E_{a2}$ increase to some extent, but the change is not conspicuous. The results imply that V$_{Fe}$ has little influence on the dissociation reaction of H$_2$S. It is worth mentioning that although the energy barrier of H$_2$S dissociation does not change observably, we found that all H atoms dissociated from H$_2$S can diffuse into the matrix through V$_{Fe}$, which provides

$$E_{ads} = -0.23 \text{ eV} \quad E_{ads} = -0.19 \text{ eV} \quad E_{ads} = -1.21 \text{ eV}$$

**Figure 2.** Different views of the stable adsorption texture of H$_2$S on perfect (a), vacancy-defective-Fe (b), and vacancy-defective-S (c) FeS(001) surfaces. (d–f) The corresponding DCD.

**Figure 3.** Most beneficial path for the dissociation of H$_2$S on the vacancy-defective-Fe FeS(001) surface.
some guidance for our subsequent study on the H diffusion process from the surface into the matrix.

The MEPs of H₂S completely dissociated on the vacancy-defective-S FeS(001) surface are shown in Figure 4. In this process, the dissociation of H₂S can be divided into three steps: (a) H₂S is stably adsorbed at the S-V site and the adsorption energy is $-1.21 \text{ eV}$. (b) H₂S directly rotates 45° in the horizontal direction at S-V, and then a H-S bond breaks. The liberated H atom diffuses to the nearest Fe-B site and gets adsorbed stably, while HS continues to be adsorbed stably at the original S-V site. The energy barrier to be overcome for this process is 0.07 eV. (c) HS further overcomes an energy barrier of 0.11 eV and decomposes into S + H. Similar to the first H atom, the H atom split from HS also diffuses to the nearest Fe-B site for stable adsorption, while the S atom continues to be adsorbed stably at the S-V site.

Compared with the perfect surface, the dissociation energy barriers $E_{a1}$ and $E_{a2}$ of H₂S on the vacancy-defective-S FeS(001) surface are intensely reduced, and the whole dissociation process changes from endothermic to exothermic. The existence of V₅ greatly promotes the dissociation process of H₂S. Also, H₂S can be dissociated directly through two dehydrogenation processes at the original adsorption site, making the dissociation process more concise. The calculations demonstrate that V₅ has a strong adsorption capacity for H₂S, which is also caused by the extreme decrease of charge density around V₅. The decrease of charge density may also cause the dissociation of H₂S to change into an exothermic process that can occur spontaneously. In addition, we found that after H₂S is completely disintegrated, the S atom fills the previous V₅, thus forming the perfect surface. According to this characteristic, we later put forward an evolution mechanism of sulfur vacancies on the FeS(001) surface.

2.4. Diffusion of H Atoms. H atoms generated by H₂S dissociation adsorb on the FeS(001) surface. By studying the diffusion mechanism of H atoms from the surface into the matrix by the DFT method, we can not only explore the hydrogen resistance performance of FeS but also further examine the influence mechanism of vacancy defects on H diffusion from the microscopic perspective.

Tables S2 and S3 list the $E_{ads}$ and $E_{dis}$ of H atoms on vacancy-defective FeS(001) surfaces and the matrix. Except for the S-V site, the $E_{ads}$ and $E_{dis}$ of H atoms on the perfect and

Table 2. Reaction Heat ($\Delta E$) and Dissociation Energy ($E_a$) of the Dissociation Steps of H₂S on the Perfect and Vacancy-Defective FeS(001) Surfaces

| reaction coordinate | perform ZPE | no ZPE |
|---------------------|-------------|--------|
|                     | $E_{a,ZPE}$ (eV) | $\Delta E_{a,ZPE}$ (eV) | $E_a$ (eV) | $\Delta E$ (eV) |
| Perfect FeS(001)    |             |        |        |        |
| P₁: I S₁ $\rightarrow$ TS₁ $\rightarrow$ FS₁ | 2.08 | 1.77 | 2.19 | 1.86 |
| P₂: I S₂ $\rightarrow$ TS₂ $\rightarrow$ FS₂ | 1.15 | 0.83 | 1.19 | 0.91 |
| Vacancy-Defective-Fe FeS(001) | | | | |
| P₁: I S₁ $\rightarrow$ TS₁ $\rightarrow$ FS₁ | 1.56 | 1.49 | 1.90 | 1.56 |
| P₂: I S₂ $\rightarrow$ TS₂ $\rightarrow$ FS₂ | 0.34 | $-0.06$ | 0.29 | $-0.05$ |
| P₃: I S₃ $\rightarrow$ TS₃ $\rightarrow$ FS₃ | 1.25 | 0.90 | 1.32 | 0.95 |
| Vacancy-Defective-S FeS(001) | | | | |
| P₁: I S₁ $\rightarrow$ TS₁ $\rightarrow$ FS₁ | 0.07 | $-0.69$ | 0.13 | $-0.63$ |
| P₂: I S₂ $\rightarrow$ TS₂ $\rightarrow$ FS₂ | 0.11 | $-0.19$ | 0.18 | $-0.13$ |

Table 3. Adsorption Energy of the H Atom at Different Adsorption and Dissolution Sites on the Vacancy-Defective FeS(001) Surfaces

| surfaces           | adsorption site | $E_{ads}$ (eV) |
|--------------------|-----------------|----------------|
| vacancy-defective-Fe FeS(001) | S-T | 0.69 |
|                    | Fe-B            | 0.71 |
|                    | Fe-L            | 0.68 |
|                    | S-L             | 0.59 |
|                    | S-V             | 0.94 |
|                    | S-L             | 0.84 |
| vacnency-defective-S FeS(001) | | |
|                    | S-T             | 0.73 |

Figure 4. Most beneficial path for the dissociation of H₂S on the vacancy-defective-S FeS(001) surface.
vacancy-defective surfaces are both positive, which indicates that the adsorption/dissolution process of H atoms is not stable. At the S-V site, the adsorption energy of the H atom reaches −0.84 eV, which indicates that VS has a great adsorption capacity for H atoms. As mentioned above, this is also caused by the decrease of the charge density around VS.

Subsequently, we calculate all possible diffusion paths for H atoms on vacancy-defective FeS(001) surfaces. Figures S2, 5, and 6 show the MEPs of individual H atoms diffusing from the surface to the matrix on vacancy-defective FeS(001) surfaces. The illustration shows top and front views of the corresponding adsorption/dissolution locations and the configuration of the transition state. Table 4 lists $E_a$ and $\Delta E$ with and without ZPE correction for all possible diffusion paths of H atoms on the FeS(001) surface. The bold fonts in Table 4 are $E_a$ and $\Delta E$ of the rate-limiting steps for the H diffusion process into the matrix.

On the perfect FeS(001) surface, the MEPs of H diffusion are S-T to Fe-B to Fe-L to S-L. The diffusion energy barrier $E_a$ of the rate-limiting step of H diffusing into the matrix is 1.12 eV, which is not very large, thus H atoms can diffuse from the perfect FeS(001) surface into the matrix under certain conditions. The diffusion process of H atoms on the vacancy-defective-Fe FeS(001) surface is shown in Figure 5. According to the diffusion barrier, the MEPs of H diffusion are S-T to Fe-B to Fe-L to S-L, which is the same as H diffusion on the perfect surface. However, the energy barrier $E_a$ of the rate-limiting step of diffusion is only 0.26 eV, which is overwhelmingly lower than that of the perfect surface (1.12 eV). It can be clearly seen from Figure 5 that the existence of VFe provides an expedited path for H atoms in the diffusion process. Thus, the diffusion process of H atoms is smoother and the diffusion energy barrier is lower. This is consistent with the steps of H diffusion in the H$_2$S dissociation process on the vacancy-defective-Fe FeS(001) surface calculated above, which further proves the rationality of this theory.

The H diffusion process on the vacancy-defective-S FeS(001) surface is shown in Figure 6. The adsorption sites of H atoms on the vacancy-defective-S FeS(001) surface are S-T and S-V. After calculation, we found that the diffusion of H atoms from S-T to S-V only needs to overcome a very small energy barrier of 0.12 eV, and unlike the S-T site, the adsorption of H atoms at the S-V site is an exothermic process. Therefore, it can be inferred that H atoms are very easy to

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**Table 4. Reaction Heat ($\Delta E$) and Dissolution Energy Barrier ($E_{diss}$) for All Possible H Diffusion Paths on Vacancy-Defective FeS(001) Surfaces**

| diffusion pathway steps | perform ZPE | no ZPE |
|-------------------------|-------------|--------|
|                         | $E_{diss}$ (eV) | $\Delta E_{diss}$ (eV) | $E_{diss}$ (eV) | $\Delta E$ (eV) |
| **Vacancy-Defective-Fe FeS(001)** | | | | |
| P1: S-T $\rightarrow$ Fe-B | 0.45 | −0.05 | 0.51 | 0.02 |
| P2: S-T $\rightarrow$ Fe-L | 0.49 | −0.07 | 0.55 | −0.01 |
| P3: Fe-B $\rightarrow$ Fe-L | 0.26 | −0.03 | 0.27 | −0.03 |
| P4: Fe-L $\rightarrow$ S-L | 0.24 | −0.03 | 0.22 | −0.09 |
| **Vacancy-Defective-S FeS(001)** | | | | |
| P1: S-T $\rightarrow$ S-V | 0.12 | −1.82 | 0.14 | −1.78 |
| P2: S-V $\rightarrow$ S-L | 1.89 | 1.61 | 1.96 | 1.57 |
aggregate near $V_S$ on the vacancy-defective-S FeS(001) surface. The energy barrier of H atom diffusion from S-V into the matrix is 1.89 eV, which is higher than that of the rate-limiting step on the perfect FeS(001) surface (1.12 eV). Different from $V_{Fe}$, the existence of $V_S$ does not provide a smoother path for H diffusion. $V_S$ binds the H atom to the vacancy defect, thus making the diffusion behavior of H atoms into the matrix more difficult, which is also caused by the decrease of charge density around $V_S$.

In summary, compared with the perfect FeS(001) surface, $V_{Fe}$ and $V_S$ have different influence mechanisms on the H atom diffusion process. $V_{Fe}$ provides a smoother path for H atoms and considerably reduces the energy barrier of H diffusion into the matrix. On the other hand, the presence of $V_S$ binds H atoms to $V_S$ and hinders the diffusion of H atoms from the surface to the matrix.

2.5. Energy Barrier Split. The influence of vacancy defects on the H$_2$S dissociation and H diffusion process is shown in Figure 7. Compared with the perfect surface, $V_{Fe}$ can promote the dissociation process of H$_2$S but hinder the dissociation of HS, while $V_S$ has an extremely significant promoting effect on both H$_2$S and HS. In particular, $V_S$ can also change the dissociation process of H$_2$S from an endothermic reaction, which is difficult to occur, to an exothermic reaction, which can proceed spontaneously. Furthermore, both $V_{Fe}$ and $V_S$ can promote the H diffusion process into the matrix, and the promotion effect of $V_{Fe}$ is particularly significant.

According to the energy barrier splitting formula, each part contributes to the dissociation barrier $E_a$ of H$_2$S, as shown in Table 5. Compared with the perfect surface, the change of $\Delta E_{slab}$, $E_{TS1}^{3H5}$, $E_{TS1}^{3H5}$, and $E_{int-HS}$ on the vacancy-defective-Fe FeS(001) surface is small, but the change of $\Delta E_{def-HS}$ is obvious, which decreases by 0.46 eV. This is the main reason for the decrease of the dissociation barrier $E_a$ of H$_2$S. On the vacancy-defective-S FeS(001) surface, the changes of $E_{TS1}^{3H5}$, $E_{TS1}^{3H5}$, $E_{TS1}^{3H5}$, and $E_{int-HS}$ are all significant, and their contribution together reduces the dissociation barrier $E_a$ of H$_2$S. It is worth mentioning that compared with the perfect and vacancy-defective-Fe FeS(001) surfaces, the contribution of $\Delta E_{slab}$ and $\Delta E_{def-HS}$ to dissociation barrier $E_a$ is very small, which indicates that the slab model and H$_2$S can move from the initial state to the transition state with little energy absorption. This also proves from the side that the configuration of H$_2$S after stable adsorption at the S vacancy defect mentioned above may be the precursor of H$_2$S dissociation. For the dissociation of HS, on the vacancy-defective-Fe surface, $\Delta E_{int-HS}$ decreases by 1.48 eV, which contributes the most to the dissociation barrier $E_a$. However, the interaction energy between H and S has a great positive contribution to the dissociation barrier $E_a$, which can almost cancel out the negative contribution of $\Delta E_{def-HS}$ so that the change of $E_a$ is not very obvious. On the vacancy-defective-S surface, the changes of each part are manifested, which together lead to the decrease of the dissociation barrier $E_a$.

Based on the research results, we proposed an evolution mechanism of sulfur vacancies on the FeS(001) surface, as shown in Figure 8. In our opinion, $V_S$ is very difficult to exist on the FeS(001) surface due to the following reasons: (a) The formation energy of $V_S$ is very large and reaches 3.91 eV, which indicates that in the actual environment, it is difficult to form $V_S$ on the FeS(001) surface under external conditions such as temperature and pressure. (b) Even if $V_S$ was formed on the surface, H$_2$S in the environment would continue to spontaneously adsorb and dissociate at $V_S$, so as to fill $V_S$ and form the perfect surface. Therefore, according to the calculation results, we propose that there is almost no $V_S$ on the FeS(001) surface in a corrosive environment and the vast majority of $V_S$ may exist within the matrix.

### Table 5. Contribution of Each Part to the Dissociation $E_a$ of H$_2$S and HS

|                    | $\Delta E_{slab}$ (eV) | $\Delta E_{def-HS}$ (eV) | $E_{TS1}^{3H5}$ (eV) | $E_{TS1}^{3H5}$ (eV) | $E_{int-HS}$ (eV) | $E_{int-HS}$ (eV) |
|--------------------|------------------------|--------------------------|----------------------|----------------------|------------------|------------------|
| Perfect FeS(001)   |                        |                          |                      |                      |                  |                  |
| $E_a$              | 0.24                   | 3.44                     | -0.76                | 0.66                 | -0.23            | 1.73             |
| Vacancy-Defective-Fe FeS(001) |             |                          |                      |                      |                  |                  |
| $E_a$              | 0.22                   | 2.98                     | -0.95                | 0.57                 | -0.19            | 1.45             |
| Vacancy-Defective-S FeS(001) |            |                          |                      |                      |                  |                  |
| $E_a$              | -0.02                  | 0.02                     | -4.47                | 2.16                 | -1.21            | -1.17            |

$E_{int-HS}$ are all significant, and their contribution together reduces the dissociation barrier $E_a$ of H$_2$S. It is worth mentioning that compared with the perfect and vacancy-defective-Fe FeS(001) surfaces, the contribution of $\Delta E_{slab}$ and $\Delta E_{def-HS}$ to dissociation barrier $E_a$ is very small, which indicates that the slab model and H$_2$S can move from the initial state to the transition state with little energy absorption. This also proves from the side that the configuration of H$_2$S after stable adsorption at the S vacancy defect mentioned above may be the precursor of H$_2$S dissociation. For the dissociation of HS, on the vacancy-defective-Fe surface, $\Delta E_{int-HS}$ decreases by 1.48 eV, which contributes the most to the dissociation barrier $E_a$. However, the interaction energy between H and S has a great positive contribution to the dissociation barrier $E_a$, which can almost cancel out the negative contribution of $\Delta E_{def-HS}$ so that the change of $E_a$ is not very obvious. On the vacancy-defective-S surface, the changes of each part are manifested, which together lead to the decrease of the dissociation barrier $E_a$.

Based on the research results, we proposed an evolution mechanism of sulfur vacancies on the FeS(001) surface, as shown in Figure 8. In our opinion, $V_S$ is very difficult to exist on the FeS(001) surface due to the following reasons: (a) The formation energy of $V_S$ is very large and reaches 3.91 eV, which indicates that in the actual environment, it is difficult to form $V_S$ on the FeS(001) surface under external conditions such as temperature and pressure. (b) Even if $V_S$ was formed on the surface, H$_2$S in the environment would continue to spontaneously adsorb and dissociate at $V_S$, so as to fill $V_S$ and form the perfect surface. Therefore, according to the calculation results, we propose that there is almost no $V_S$ on the FeS(001) surface in a corrosive environment and the vast majority of $V_S$ may exist within the matrix.

### 3. COMPUTATIONAL DETAILS

3.1. Models. The perfect and vacancy-defective FeS(001) surfaces are created through an utterly relaxed volume structure using Materials Studio (MS). As shown in Figure S1a, the slab model of the FeS(001) surface adopts a $2 \times 2$ supercell structure and is equipped with nine atomic layers to adapt to the relaxation expansion of the first layer. An additional 15 Å vacuum layer is placed to ensure separation. Zero-point energy (ZPE) correction is performed for the adsorption energy and dissociation energy.
In all calculations involving the interaction of H$_2$S and the dissociated atoms with the FeS(001) surface, the adsorbate and top three layers of atoms are totally allowed to relax, while the remaining atomic layers are fixed.

3.2. Methods. All of the calculations are executed using the Vienna Ab-initio Simulation Package (VASP).41−45 The Perdew−Burke−Ernzerhof (PBE) generalized gradient approximation (GGA) exchange−correlation functional using the projector augmented wave method is applied.46−47 We added the spin polarization parameters in the calculation process, which had little effect on the calculation of the perfect and vacancy-defective-Fe FeS(001) surfaces but had a great influence on the calculation of the vacancy-defective-S FeS(001) surface. Since the conventional DFT method cannot accurately describe the weak vdW force between atoms separated by vacuum, the DFT-D2 method is used to correct the weak vdW force between FeS layers in this study, which has been confirmed in other research studies.47 When a cut-off energy of 400 eV is used, the total energy of FeS(001) converges. The K-points are set to be 11 × 11 × 11 for H$_2$S in vacuum and bulk FeS optimizations, while 5 × 5 × 1 is applied for FeS(001) surface calculations. The convergence standards of energy and force are 10$^{-5}$ eV and 0.05 eV−Å$^{-1}$, respectively. The formation energy of vacancy defects is defined by the following formula48

$$E_V = E_{V^0} - E_{FeS} + \mu$$

Here, $E_{V^0}$ is the total energy of the FeS(001) model containing $V_{Fe}/V_{S}$ and the perfect surface, respectively. The $\mu$ represents the atomic chemical potential introduced by the formation of $V_{Fe}/V_{S}$.

The transition state of the dissociation process of H$_2$S/HS and the H diffusion process is probed by a climbing image nudged elastic band (CI-NEB) method,49 and the frequency of the transition state is checked to make sure there is only one virtual frequency. The formulas for adsorption/dissolution energy ($E_{ads/diss}$), ZPE correction, differential charge density (DCD), activation energy barrier ($E_a$), reaction heat ($\Delta E$), and energy barrier splitting are all described in our published papers.50

4. CONCLUSIONS

Vacancy defects are inherent point defects of materials. Two kinds of vacancy defects on the FeS(001) surface can affect the adsorption/dissociation of H$_2$S and the H diffusion process. In our work, the impact of $V_{Fe}$ and $V_{S}$ on the adsorption/ dissociation and diffusion of H$_2$S was calculated using the DFT-D2 method. In our calculation, $V_{Fe}$ did not change the stable adsorption site and adsorption configuration of H$_2$S but promoted the dissociation process of H$_2$S. Compared with the perfect surface (2.08 eV), the dissociation energy barrier of H$_2$S was reduced to 1.56 eV. Meanwhile, $V_{Fe}$ also slightly hindered the dissociation process of HS. $V_{S}$ significantly promotes the adsorption and dissociation process of H$_2$S, which not only reduces the dissociation energy barriers of H$_2$S and HS to 0.07 and 0.11 eV, respectively, but also changes the dissociation process of H$_2$S from an endothermic process to a spontaneous exothermic one. In addition, $V_{Fe}$ and $V_{S}$ have different influence mechanisms on the H atom diffusion process. $V_{Fe}$ provides a barrier-free diffusion channel for the diffusion process of H atoms, so the H diffusion process is more accessible. But the presence of $V_{S}$ binds H atoms to $V_{S}$ and hinders the diffusion of H atoms from the surface to the matrix. Compared with the perfect FeS(001) surface, the energy barriers of the rate-limiting step of H diffusion from the surface into the matrix on the vacancy-defective-Fe and vacancy-defective-S FeS(001) surfaces are 0.26 and 1.89 eV, respectively. In the end, according to the calculation results, we propose that there is almost no S vacancy defect existing on the FeS(001) surface in a corrosive environment. Our research provides a theoretical basis for understanding the influence of vacancy defects on the adsorption, dissociation, and diffusion processes of H$_2$S in FeS. Meanwhile, it can also provide a theoretical basis for the formation, transformation, and further corrosion of iron sulfide compounds. This may encourage scholars to conduct further experimental research and verification.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02639.

Model of layered FeS and different adsorption sites of vacancy-defective-Fe and vacancy-defective-S FeS(001) surfaces; adsorption energy, adsorption sites, and structural parameters of H$_2$S, HS, S, and H stably adsorbed on different FeS(001) surfaces; adsorption energy of the H atom at different adsorption and dissolution sites on the perfect FeS(001) surface; dissolution energy barrier ($E_{diss}$) and reaction heat ($\Delta E$) for all possible diffusion paths of the H atom; and MEPs of the H atom diffusing on the perfect FeS(001) surface (PDF)

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Figure 8. Evolution mechanism of S vacancies on the FeS(001) surface.
Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c02639

Notes
The authors declare no competing financial interest.

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■ REFERENCES
(1) Wang, Z.; Feng, Z.; Zhang. Effect of high temperature on the corrosion behavior and passive film composition of 316L stainless steel in high H2S-containing environments. Corros. Sci. 2020, 174, No. 108844.
(2) Xie, C.; Wang, B.; Li, S.; Wen, X.; Wei, S.; Zhang, S.; Feng, M.; Chen, L.; Zheng, S. The dependence of anti-corrosion behaviors of iron sulfide films on different reactants. Int. J. Hydrogen Energy 2020, 45, 17548–17556.
(3) Wei, S.; Zhang, S.; Xie, C.; Liang, J. Ab initio molecular dynamics study of wet H2S adsorption and dissociation on Fe(100) surface. J. Mol. Liq. 2020, 319, No. 114135.
(4) Abd El Haleem, H.; Abd El Aal, E. E. Electrochemical behaviour of iron in alkaline sulphide solutions. Corros. Eng., Sci. Technol. 2008, 43, 173–178.
(5) Pound, B. G.; Wright, G. A.; Sharp, R. M. The anodic behavior of iron in hydrogen sulfide solutions. Corrosion 1989, 45, 386–392.
(6) Kick, D.; Luther, G. W. Chemistry of iron sulfides. Chem. Rev. 2007, 107, 514–562.
(7) Bollinger, C. L.; Wilkin, R. T.; Barnes, H. L. Reaction pathways in the Fe-S system below 100 °C. Chem. Geol. 2005, 167, 25–51.
(8) Luyten, F. R.; Jones, M. J.; Hynes, A. J.; Charnock, J. M.; Moseleman, J. F.; Hennig, C.; Steele, H.; Collison, D.; Vaughan, D. J.; Patricks, R. A.; Reed, W. A.; Moyes, L. N. X-ray absorption spectroscopy studies of reactions of technetium, uranium and neptunium with mackinawite. J. Environ. Radioact. 2004, 74, 211–219.
(9) Wen, X.; Liang, Y.; Bai, P.; Luo, B.; Fang, T.; Yue, L.; An, T.; Song, W.; Zheng, S. First-principles calculations of the structural, elastic and thermodynamic properties of mackinawite (FeS) and pyrite (FeS2). Phys. B 2017, 525, 119–126.
(10) Bai, P.; Zheng, S.; Chen, C.; Zhao, H. Investigation of the Iron—Sulfide Phase Transformation in Nanoscale. Cryst. Growth Des. 2014, 14, 4295–4302.
(11) Bai, P.; Zheng, S.; Chen, C. Electrochemical characteristics of the early corrosion stages of API X52 steel exposed to H2S environments. Mater. Chem. Phys. 2015, 149–150, 295–301.
Glycine under Inert Conditions: Experimental and Theoretical Approaches. Phys. Chem. Chem. Phys. 2019, 21, 24535–24542.
(32) Sahraei, A. A.; Faïcal, L. How Do Surface Defects Change Local Wettability of the Hydrophilic Zns Surface? Insights into Sphalerite Flotation from Density Functional Theory Calculations. J. Phys. Chem. C 2021, 125, 998–1009.
(33) Sahraei, A. A.; Faïcal, L. Chemical Transformation and Dissociation of Amino Acids on Metal Sulfide Surface: Insights from DFT into the Effect of Surface Vacancies on Alanine-Sphalerite System. Appl. Surf. Sci. 2021, 540, No. 148304.
(34) Ward, J. C. The structure and properties of some iron sulphides Rev. Pure Appl. Chem. 1970, 175–206.
(35) Taylor, L. A.; Finger, L. W. Structural Refinement and Composition of Mackinawite; Carnegie Instution of Washington, Geophysical Laboratory Annual Report, 1970; Vol. 69, pp 318–322.
(36) Pilot, P. version 7.0; Accelrys Inc.: San Diego, CA, 2013.
(37) Han, Z.; Yu, H.; Li, C.; Zhou, S. Mulch-assisted ambient-air synthesis of oxygen-rich activated carbon for hydrogen storage: A combined experimental and theoretical case study. Appl. Surf. Sci. 2021, 544, No. 148963.
(38) Han, Z.; Wu, Y.; Yu, H.; Zhou, S. Location-dependent effect of nickel on hydrogen dissociation and diffusion on Mg (0001) surface: Insights into hydrogen storage material design. J. Magnesium Alloys 2021, DOI: 10.1016/j.jma.2021.03.002.
(39) Cahyanto, W. T.; Zulaehah, S.; Widanarto, W.; Abdullatif, F.; Effendi, M.; Kasai, H. Theoretical Study of an almost Barrier-Free Water Dissociation on a Platinum (111) Surface Alloyed with Ruthenium and Molybdenum. ACS Omega 2021, 6, 10770–10775.
(40) Vakili, M.; Gholizadeh, R.; Ghadi, A.; Salmasi, E.; Sinnokrot, M. Computational investigation of N2O adsorption and dissociation on the silicon-embedded graphene catalyst: A density functional theory perspective. J. Mol. Graphics Modell. 2020, 101, No. 107752.
(41) Kresse, G.; Hafner, J. Ab initio molecular dynamics for open-shell transition metals. Phys. Rev. B 1993, 48, 13115–13118.
(42) Kresse, G.; Hafner, J. Norm-conserving and ultrasoft pseudopotentials for first-row and transition elements. J. Phys.: Condens. Matter 1994, 6, 8245–8257.
(43) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput. Mater. Sci. 1996, 6, 15–50.
(44) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B 1996, 54, 11169–11186.
(45) Wei, S.; Zheng, S.; Wen, X.; Xie, C.; Liang, J. A novel antiferromagnetic semiconductor hidden in pyrite. Comput. Mater. Sci. 2020, 183, No. 109852.
(46) Blochl, P. E. Projector augmented-wave method. Phys. Rev. B 1994, 50, 17953–17979.
(47) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B 1999, 59, 1758–1775.
(48) Chen, D.; Zhang, X.; Tang, J.; Cui, H.; Pi, S.; Cui, Z. Adsorption of SF6 Decomposed Products over ZnO(1010): Effects of O and Zn Vacancies. ACS Omega 2018, 3, 18739–18752.
(49) Peng, M.; Wang, Y.; Han, Y.; Ye, C.; Zou, J.-J.; Li, W.; Zhang, J. Cu-Si bond and Cl defect synergistical catalysis for SiCl4 dissociation on CuCl2(100): A DFT study. Appl. Surf. Sci. 2021, 543, No. 148777.
(50) Wen, X.; Bai, P.; Han, Z.; Zheng, S.; Luo, B.; Fang, T.; Song, W. Effect of vacancy on adsorption/dissociation and diffusion of H2S on Fe(100) surfaces: A density functional theory study. Appl. Surf. Sci. 2019, 465, 833–845.