First principles study of H₂S adsorption and dissociation on Fe(110)

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Abstract

We report first principles density functional theory (DFT) results of H₂S and HS adsorption and dissociation on the Fe(110) surface. We investigate the site preference of H₂S, HS, and S on Fe(110). H₂S is found to weakly adsorb on either the short bridge (SB) or long bridge (LB) site of Fe(110), with a binding energy of no more than 0.50 eV. The diffusion barrier from the LB site to the SB site is found to be small (<0.10 eV). By contrast to H₂S, HS is predicted to be strongly chemisorbed on Fe(110), with the S atom in the LB site and the HS bond oriented perpendicular to the surface. Isolated S atoms also are predicted to bind strongly to the LB sites of Fe(110), where the SB is found to be a transition state for S surface hopping between neighboring LB sites. The minimum energy paths for H₂S and HS dehydrogenation involve rotating an H atom towards a nearby surface Fe atom, with the S–H bonds breaking on the top of one Fe atom. The barrier to break the first S–H bond in H₂S is low at 0.10 eV, and breaking the second S–H bond is barrierless, suggesting deposition of S on Fe(110) via H₂S is kinetically and thermodynamically facile.

Keywords: Density functional calculations; Adsorption; Iron; Hydrogen sulfide; Dissociation

1. Introduction

The reaction of hydrogen sulfide with iron is of great importance in many different fields. For example, in cosmology, the formation of iron sulfide in solar nebula via reaction of H₂S with surfaces of bulk Fe greatly affected the nature of the planets and other bodies formed later [1]. In metal
corrosion, H₂S in the gas or solution phase can attack structural metals aggressively; sulfur itself can embrittle transition metals such as Fe [2]. Although some research has been devoted to understanding the sulfidation of Fe [3,4], little is known about the adsorption geometries and dissociation pathways of H₂S on Fe surfaces, which characterize the initial stage of S deposition. This is likely caused by the fast kinetics of H₂S dissociation on transition metals, which prohibits detailed mechanistic and structural characterization experimentally. In this work, we use first principles theory to examine the adsorption and dissociation of H₂S on Fe surfaces.

We summarize experimental findings briefly here. Polycrystalline iron films [3–7] have been used in most experimental studies of H₂S interaction with iron. Narayan et al. studied iron sulfidation by H₂S from 110 to 773 K [4] with X-ray photoelectron spectroscopy (XPS). Based on binding energy shifts of the S 2p level, they concluded that H₂S adsorption is molecular at 110 K, but dissociative from 190 K up to ambient temperatures. At T > 423 K, they found formation of FeS, where an initial nonstoichiometric form converts to the stoichiometric form with increased H₂S dosing. No direct evidence (such as high-resolution electron energy loss spectroscopy) was presented to confirm the molecular adsorption of H₂S at 110 K. Most other H₂S adsorption experiments on iron surfaces were performed at room temperature or above, where no molecular H₂S or HS were observed, indicating the ease of H₂S dissociation. For example, Kelemen and Kaldor studied [8] S deposition on Fe(110) by dissociative adsorption of H₂S at 150 °C, using low energy electron diffraction (LEED). They found that S first forms a p(2 × 2) pattern (0.25 monolayer, ML) and then a p(3 × 1) pattern (1/3 ML, saturation coverage). The S–Fe(110)-p(2 × 2) structure was also observed in another LEED experiment [9].

In our earlier work [10], we studied H₂S adsorption and dissociation on Fe(100), one of the low-Miller-index surfaces of Fe. We found that H₂S is weakly adsorbed on Fe(100) and that the first and second dehydrogenation steps have a similar barrier of ~0.25 eV. Fe(110), the closest-packed surface of Fe. Convention wisdom suggests that the dissociation barriers of H₂S on Fe(110) will be higher than those on Fe(100), which motivates the present study. In this work, we characterize the H₂S and HS adsorption sites and dissociation pathways on Fe(110) with periodic density functional theory (DFT). In fact, we show that the convention wisdom regarding the decreased activity of closed-packed surfaces is wrong in this case. Overall, our work elucidates the initial kinetics of H₂S attack. This may be helpful for designing sulfur-tolerant steels.

The rest of the paper is organized as follows. Calculational details are given in Section 2. Predictions of H₂S, HS, and S adsorption structures and binding energies are presented in Sections 3.1, 3.2 and 3.3, respectively. Predicted pathways for H₂S dissociation are given in Section 3.4 and for HS dissociation in Section 3.5. We summarize and conclude in Section 4.

2. Calculational details

We perform first-principles calculations based on spin-polarized density functional theory (DFT) [11,12]. The Vienna Ab Initio Simulation Package (VASP) [13,14] is used to solve the Kohn–Sham equations with periodic boundary conditions and a plane-wave basis set. Here we employ Blöchl's all-electron projector augmented wave (PAW) method [15] as implemented by Kresse and Joubert [16]. For the treatment of electron exchange and correlation, we use the generalized gradient approximation (GGA) of PBE [17].

We use a kinetic energy cutoff of 400 eV for all the calculations, which converges the total energy to ~1 meV/atom for the primitive cell of bulk Fe. The Monkhorst–Pack scheme [18] is used for the k-point sampling. The first order Methfessel–Paxton method [19] is used for the Fermi surface smearing, with a width of 0.1 eV in order to obtain accurate forces. Using a 15 × 15 × 15 k-mesh, we obtain an equilibrium lattice constant (a₀ = 2.83 Å), bulk modulus (B = 174 GPa), and local magnetic moment (M = 2.20 μB) for ferromagnetic bcc Fe. The results agree very well with previous
PAW-GGA calculations and experiment ($d_0 = 2.86\,\text{Å}, B = 168\,\text{GPa}, M = 2.22\,\mu_B$) [20].

To model gaseous $\text{H}_2\text{S}$, $\text{HS}$, and $\text{S}$ atom, we place a molecule or atom in a 10 Å cubic box. We perform a non-spin-polarized calculation for $\text{H}_2\text{S}$, but spin-polarized calculations for open-shell $\text{HS}$ and $\text{S}$, where the valence electron configuration used for $\text{S}$ atom is ground state triplet (3p)$^4$, approximately $^3P$ (spin-polarized DFT open-shell states are all slightly spin-contaminated). The molecular geometry, vibrational frequencies, and bond dissociation energies from our work are in good agreement with experiment, as reported earlier [10].

Fe(110) is the closest-packed surface of bcc Fe and is basically bulk-terminated, with very little relaxation and no reconstruction. To model the Fe(110) surface, we use a five-layer slab and a 12-Å vacuum layer, which we showed previously are sufficiently thick [21]. We put adsorbates on one side of the slab; this produces a small dipole due to the dipole of the molecular adsorbate itself, as well as charge transfer between the adsorbate and the metal surface, so an a posteriori dipole correction to the total energy was included (the magnitude of the correction is <0.08 eV/cell). Only the top two layers of the five substrate layers are allowed to relax, together with the adsorbate layer. The bottom three layers are kept fixed in bulk positions to represent the semi-infinite bulk crystal beneath the surface (allowing the middle layer of the substrate to relax only changes the total energy of the slab by ~5 meV.) When the maximum force acting on each of the relaxed atoms drops below 0.01 eV/Å, the structural relaxation is stopped.

In this work, we study only 0.25 ML adsorbate coverages. Experiments show that 1/3 ML is the saturation coverage for $\text{S}$ on Fe(110) as a p(3 × 1) superstructure. However, no direct observation of $\text{H}_2\text{S}$ or $\text{HS}$ on Fe(110) are available. We chose 0.25 ML as a compromise between minimizing adsorbate-adsorbate interactions and being close to the coverage of the stable overlayer structure of $\text{S}$ on Fe(110) from experiment. Coverage effects on adsorption, diffusion, and dissociation of $\text{H}_2\text{S}$ on Fe(110) are left to future work. High-symmetry sites on Fe(110) are displayed in Fig. 1. We use a $k$-mesh of $4 \times 4 \times 1$ for the p(2 × 2) Fe(110) cell, which converges the adsorption energy of $\text{H}_2\text{S}$ to within 0.02 eV.

The climbing image nudged elastic band (CI-NEB) method [22,23] is used to locate the minimum energy paths (MEPs) and the transition states for $\text{H}_2\text{S}$ diffusion, as well as $\text{H}_2\text{S}$ and $\text{HS}$ dissociation on Fe(110). An interpolated chain of configurations (images) between the initial and final positions are connected by springs and relaxed simultaneously to the MEP. With the climbing image scheme, the highest-energy image climbs uphill to the saddle point. We use the same force tolerance for the transition state search as that used for structural relaxations.

Vibrational frequencies of $\text{H}_2\text{S}$ and $\text{HS}$ on Fe(110) are determined by diagonalizing a finite difference construction of the Hessian matrix with displacements of 0.02 Å (only allowing H and S atoms to move). The natures of the relaxed adsorbate configurations and the saddle points found by the CI-NEB method are also checked in the same way we do vibrational frequency calculations.

3. Results and discussion

3.1. $\text{H}_2\text{S}$ adsorption on Fe(110)

Previous experimental work of the sulfidation of Fe focused on thin films. No knowledge of $\text{H}_2\text{S}$ geometry on Fe has been inferred, perhaps due to it fast dissociation kinetics above 190 K.
[4]. To our knowledge, no low temperature characterization of the adsorbate structure has been attempted experimentally. H$_2$S can adopt many adsorption geometries on Fe(110), however we only explored the high-symmetry sites shown in Fig. 1. We started with four initial structures for the on-top (OT) site and two for each of the other sites. In two of the four structures for the OT site, the molecular plane of H$_2$S is parallel to the surface and the symmetry axis of H$_2$S is either parallel or perpendicular to [001] (see Fig. 1). In the other two initial structures for the OT site, the symmetry axis of H$_2$S is perpendicular to the surface and the H$_2$S plane is either parallel or perpendicular to [001]. In the initial structures for the other sites, the symmetry axis of H$_2$S is perpendicular to the surface. The lowest energy structures from the initial guesses for each of the sites are shown in Fig. 2 and their corresponding H$_2$S adsorption energies, geometries, and vibrational frequencies are displayed in Table 1. We see that H$_2$S is quite weakly adsorbed, with the short-bridge (SB) and the long-bridge (LB) sites almost degenerate at about $-0.50 \text{ eV}$. The OT site is neither a local minimum nor a transition state, but a higher-order (rank-2) saddle point. We found that the threefold (TF) site is not stable for H$_2$S, with the adsorbate relaxing to the LB site after initially being placed at the TF site. For both LB and SB adsorption, the molecular plane and the symmetry axis of H$_2$S are perpendicular to the substrate surface, indicating an interaction between the two S lone electron pairs and the substrate Fe atoms. In another orientation we explored for the SB or LB site, the molecular plane is perpendicular to the one shown in Fig. 2(b) or (c), but its energy is 0.60 eV higher for the SB site and 0.20 eV higher for the LB site. Moreover, we found that if H$_2$S is initially oriented parallel to the surface at the LB or SB site, it dissociates.

Because the interaction between H$_2$S and Fe(110) predicted from these DFT-PBE calculations is weak, we also evaluated H$_2$S adsorption on Fe(110) with the RPBE exchange-correlation functional [24] using PBE-optimized geometries. As usual, DFT-RPBE reduces the typical overbinding between adsorbates and the metal surface by DFT-PBE [24]. The resulting adsorption energies are only slightly negative ($\sim -0.15 \text{ eV}$) and very similar for all three sites (OT, LB, and SB), indicating the interaction between H$_2$S and Fe(110) is indeed weak. We caution that such weak interactions are not well described by conventional DFT-GGA theory.

At the SB site, the geometry of H$_2$S changes only slightly upon adsorption (slightly lengthened H–S bonds), but stretching frequencies are significantly softened. At the LB site, the softening of stretching frequencies is even more pronounced, with H–S bonds even longer than for adsorption on the SB site. By contrast, the H–S–H bond angle remains very similar to the gaseous H$_2$S value, with only a slight blue-shifting of the bending frequencies. Moreover, H$_2$S is closer to the Fe(110) surface in the LB site. All of these trends point to stronger interactions between H$_2$S and Fe at the LB site.

3.2. HS adsorption on Fe(110)

We find that the final structure of HS on Fe(110) depends strongly on the initial guess employed. Many initial guess structures resulted in dissociation of HS to H and S on Fe(110), indicating that HS is likely to be unstable on Fe(110). Fig. 3 shows the three high symmetry adsorption sites obtained for HS on Fe(110) and Table 2 displays their corresponding binding energies, vibrational frequencies, and geometries. Only the LB

![Fig. 2. Lowest energy structures of H$_2$S adsorbed on high symmetry sites on Fe(110): (a) on-top; (b) short bridge; (c) long bridge. Upper panel is the side view, and lower panel is the top view. Fe atoms are in grey, S in white, and H in black. The same grey scale convention is used in all subsequent figures.](image-url)
site is a local minimum, with HS strongly chemisorbed on Fe(110) and the HS bond pointing along the surface normal. By contrast, both the OT and SB sites are rank-2 saddle points. We observe a softening of the H–S stretching frequency upon adsorption, consistent with the lengthening and likely weakening of the H–S bond.

Fig. 4 displays an electron density difference plot for HS at the LB site. One can see that the rearrangement of electron density reflects the $C_{2v}$ symmetry of the adsorbate structure. Electron density is depleted from under the S atom, from the two sides of the S atom facing the two closer Fe atoms (B-type Fe atom in Fig. 4, $d_{\text{Fe-S}} = 2.21 \, \text{Å}$, and also from those two Fe atoms, while electron density accumulates on the other two sides of the S atom facing the two farther Fe atoms (A-type Fe in Fig. 4, $d_{\text{Fe-S}} = 2.46 \, \text{Å}$). The accumulated electron density appears to be in an S p-orbital, suggesting charge rearrangement to render the S p-orbitals in HS equally populated. In the extreme limit, the depletion of charge from Fe would produce HS$_{C_0}$, which has filled p-orbitals that would prefer a perpendicular adsorption structure (as found here) to optimize electron back-donation toward the Fe surface.

### 3.3. S adsorption on Fe(110)

The adsorption of S on Fe(110) at 0.25 ML can cause a mild reconstruction of the metal surface, and S is found to reside on the LB site, as shown by LEED [9]. A recent DFT-USPP-GGA (PW91) study [25] by Spencer et al. reported the structural details of S–Fe(110)-p(2×2) and confirmed the LB site preference by LEED. Our study also shows that S is strongly chemisorbed on the LB site, with the LB site as the only minimum (Table 3). The SB site is a transition state for S diffusion on Fe(110), with a barrier of

0.52 eV. By contrast, the on-top site is a rank-2 saddle point.

Our theoretical predictions of the Fe–S distances and the height of S atoms over Fe(110) (h), tilt angle of H–S bond axis with respect to the surface normal (θ), and HS vibrational frequencies, including the stretch (ωs), the frustrated rotations (ωr), the adsorbate–substrate stretch (ωFe–S), and the two frustrated translations (ωt) are close to the DFT-GGA results by Spencer et al. [9]. Moreover, we also found a buckling of the surface and subsurface substrate layers as Spencer et al. did in their study. However, this degree of freedom was not included in the models of Shih et al.’s LEED study [9]. This may account for the rather large discrepancy between DFT-GGA and experiment regarding the height of S atom above the substrate surface (Table 3).

### 3.4. H2S dissociation on Fe(110)

As mentioned above, we use the nudged elastic band (NEB) method to locate the minimum energy path for H2S dissociation to HS and H. The NEB method requires that the initial and final states of the transition be specified beforehand. We consider first the dehydrogenation of H2S to HS and H. In the initial state H2S will reside either on the LB site or the SB site, since they are almost degenerate. We have examined the diffusion from the LB site to the SB site, and the barrier is small (0.11 eV). In Section 3.1, we showed that the structure of H2S changes more upon adsorption at the LB site than the SB site, so we begin with the LB site since it may be that H2S is more activated at this site. Next we need to know where HS prefers to be in the presence of H (for the final state). Our earlier study of H/Fe(110) [21] showed that H always prefers the TF site for the coverage of 0.11–1.0 ML. We tried several combinations of HS in the LB site and H in the nearby TF site. We found only one stable configuration with these two species close to each other. In all the other cases, HS lost its hydrogen, just as we found for the many initial structures of the isolated HS group on Fe(110). This indicates again that HS is rather unstable on Fe(110).

Fig. 5 shows the minimum energy path of the dehydrogenation of H2S to HS and H starting with...
H$_2$S on the LB site. The structures for the initial and final states, together with several intermediate structures, are also shown in Fig. 5. We predict that H$_2$S breaks one H–S bond by rotating one H atom towards a nearby surface Fe atom and the H–S bond dissociates over that Fe atom. The dissociation barrier is 0.10 eV, indicating the ease of breaking the first H–S bond of H$_2$S on Fe(110). At the transition state, the length of the breaking H–S bond is 1.45 Å, only 0.07 Å longer than the initial state. After the transition state, one H atom breaks away and moves to the TF site with a $\sim$1.40 eV energy drop. Then the system descends through a flat step to reach the final state with an energy drop of 0.20 eV, which corresponds to bending of the HS group towards H. In the final state, the HS group is stabilized by $\sim$0.30 eV by the presence of the nearby H atom, compared to isolated HS$_{(o)}$. Despite this, H–S bond is still significantly lengthened at 1.49 Å. We found that HS will spontaneously dissociate to H and S over the opposite Fe atom if the HS group rotates away from H.

Four Fe atoms coordinate around S when H$_2$S resides at the LB site, with two of them farther away from the S atom than the other two. Fig. 5 shows that H$_2$S breaks its first H–S bond on one of the two more distant Fe atoms, with a barrier of 0.10 eV. We also examined dissociation of H$_2$S on one of the two closer Fe atoms. The barrier is 0.11 eV, almost the same as the former. This indicates that H$_2$S can break its first H–S bond on any of the four Fe atoms coordinated around S with a very low barrier. In our earlier study of

### Table 3

Adsorption energy $[E_{ad} = E_{S/Fe-slab} - E_{Fe-slab} - E_S]$ of S atom on Fe(110), the smallest Fe–S distance ($d_{Fe-S}$), the height of S atom over Fe(110) ($h$), and the S vibrational frequencies, including the adsorbate–substrate stretch ($\omega_{Fe-S}$) and the two frustrated translations ($\omega_t$)

<table>
<thead>
<tr>
<th>Site</th>
<th>OT$^a$</th>
<th>SB$^a$</th>
<th>LB$^a$</th>
<th>LB$^b$</th>
<th>Experiment$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{ad}$ (eV)</td>
<td>−4.408 (hos)</td>
<td>−5.271 (ts)</td>
<td>−5.788 (min)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$d_{Fe-S}$ (Å)</td>
<td>2.038</td>
<td>2.144</td>
<td>2.180</td>
<td>2.19</td>
<td>2.17</td>
</tr>
<tr>
<td>$h$ (Å)</td>
<td>1.971</td>
<td>1.655</td>
<td>1.526</td>
<td>1.567</td>
<td>1.43</td>
</tr>
<tr>
<td>$\omega_{Fe-S}$ (cm$^{-1}$)</td>
<td>396</td>
<td>353</td>
<td>325</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>$\omega_t$ (cm$^{-1}$)</td>
<td>117i, 130i</td>
<td>125i, 231</td>
<td>111, 257</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

The nature of the critical point is given in parentheses (min = minimum, ts = transition state, and hos = higher order saddle point).

$^a$ This work.

$^b$ Ref. [25].

$^c$ Ref. [9].
H₂S dissociation on Fe(100), we also found that H₂S breaks its H–S bonds on top of one Fe atom coordinated to S [10], again with a relatively low barrier of 0.25 eV.

3.5. HS dissociation on Fe(110)

From the above discussion, we already observed that HS is at best metastable on Fe(110). To further confirm this finding, we examine the dehydrogenation of HS on Fe(110) in the absence of H. We found an MEP (Fig. 6), which is similar to the first dehydrogenation step of H₂S. However, the barrier here is much smaller, basically zero (1 meV). At the “transition state”, the HS axis is rotated ~19° toward the surface compared with the initial state and we see that the potential energy surface (PES) is very flat from the initial state to the “transition state”. Such a flat PES indicates that, within the inherent errors of DFT-GGA, we essentially have no barrier, no transition state, and simply a spontaneous exothermic reaction. The large exothermicity provides the driving force for spontaneous dissociation of HS.

In our earlier work, we examined H₂S dissociation on the more open, but similarly stable, Fe(100) surface. Conventional wisdom might suggest that dissociation of H₂S on the less highly coordinated Fe(100) surface would have a lower barrier. Instead, we found that the barriers to break the first and second S–H bonds in H₂S on Fe(100) are about the same, ~0.25 eV, and non-trivially higher than those on Fe(110).

4. Conclusions

Using periodic density functional theory within the all-electron projector augmented wave formalism and the generalized-gradient approximation to electron exchange and correlation, we have studied H₂S, HS, and S adsorption, H₂S and S diffusion, and H₂S and HS dissociation on Fe(110). We find that H₂S is weakly molecularly adsorbed on either the long bridge (LB) or short bridge (SB) site of Fe(110), with the molecular plane oriented along the surface normal. The adsorption of H₂S in a bridge site is exothermic by 0.50 eV. Adsorption at an on-top site is not a local minimum for H₂S on Fe(110), but a higher order saddle point. This is likely due to the interaction of the two H₂S lone pairs, which drive H₂S to higher coordination sites. The diffusion barrier between the LB and the SB sites is predicted to be only ~0.10 eV. By contrast with H₂S, HS is strongly chemisorbed on Fe(110). The only stable configuration of HS on Fe(110) has S in the LB site and the HS bond upright, with a binding energy of 3.47 eV. At this
adsorption configuration, the two S p-orbitals of HS redistribute charge to be equally occupied in order to interact better with Fe(110). Lastly, we find that S atom strongly binds to the LB site of Fe(110). The SB site serves as a transition state with a barrier of 0.52 eV for diffusion between two neighboring LB sites for S/Fe(110).

With the climbing-image nudged elastic band method, we obtained the minimum energy paths for H₂S and HS dehydrogenation on Fe(110). Starting from the LB site, we predict that H₂S loses one H atom by rotating the molecule to orient the H atom towards one of Fe atoms coordinated to the S atom. The dissociation barrier is very small, 0.10 eV, independent of which type of Fe atom is involved. After the transition state, the H atom first moves from the on-top site to the three-fold site, and then the HS group rotates towards the breaking-away H atom and is stabilized in a lying-down configuration. If the HS group rotates away from the H atom, the HS group immediately dehydrogenates further to S and H, due to the larger exothermicity of this reaction. In the absence of H, HS breaks its bond in exactly the same way that H₂S loses its first H, but with essentially no barrier.

Our present work shows that H₂S loses its first H with a barrier of 0.10 eV and its second H effortlessly on Fe(110); our earlier work for H₂S/Fe(100) indicated similarly high reactivity, with only slightly higher dissociation barriers (~0.25 eV [10]). Since the (110) and (100) surfaces are the most stable surfaces of Fe, they tend to be preferentially exposed. Our work therefore implies that H₂S will attack polycrystalline iron (and steel) surfaces in a much faster manner than will other deleterious gases such as CO, where dissociation barriers are considerably higher [26,27].

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References