Adsorption and diffusion of sulfur on the (111), (100), (110), and (211) surfaces of FCC metals: Density functional theory calculations

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We have studied the adsorption and diffusion of sulfur at the low-coverage regime of 0.25 ML on the (111), (100), (110), and (211) surfaces of Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au using density functional theory calculations. Sulfur adsorbed preferentially on three-fold or four-fold high-coordination sites over most of the studied surfaces. On the Ir(110), Pt(110), and Au(110) surfaces, sulfur is more stable on the two-fold sites. Calculations of the minimum energy diffusion pathway show that the energy barrier for the surface diffusion of sulfur depends on the orientation and nature of the metal surfaces. On the (100), sulfur shows the highest diffusion energy, ranging from 0.47 eV in Au(100) to 1.22 eV in Pd(100). In the (110) surface, the diffusion of sulfur is along the channel for Ni, Cu, Rh, Pd, and Ag, and across the channel for Ir, Pt, and Au. In the case of the (211) surfaces, the diffusion is preferentially along the terrace or step-edge sites. Our work provides data for the adsorption of sulfur on many surfaces not previously reported. The present work is a reference point for future computational studies of sulfur and sulfur-containing molecules absorbed on face center cubic metal surfaces. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5063464>

I. INTRODUCTION

The adsorption of sulfur on metal surfaces has been extensively studied,^{1–37} in part, to understand the poisonous impact that sulfur has on metal surfaces.^{22,38,39} Many technologically relevant processes are affected by sulfur poisoning, including methanation, alkane hydrogenolysis, olefin hydrogenation, and water-gas-shift reactions.³⁹ The Fischer-Tropsch synthesis, steam reforming, fuel cell power production,³⁸ metal-based membranes,¹⁷ and solid oxide fuel cells³⁰ (SOFC) are also sensitive to sulfur poisoning. More recently, sulfur adsorption on metal surfaces has been studied in connection to Li–S batteries.^{40–43} Introducing Ni or Pt nanoparticles enhances the lithium polysulfide conversion reactions, improving the performance of Li–S batteries.⁴³ The metal nanoparticles seem to anchor the Li_yS_x intermediates, reducing the so-called shuttling effect.⁴² The details of the anchoring mechanism and the adsorption state of the Li_yS_x intermediated species are still unknown.

Density Functional Theory (DFT) calculations have been performed to study the adsorption of sulfur on the low-index surfaces of multiple Face Center Cubic (FCC) metals.^{3–5,7,9,10,12–17,21,22,25,26,28–30,33–37} We surveyed the DFT calculations of sulfur on FCC metal surfaces reported since the year 2000; see Ref. 39 for an account of earlier calculations. DFT calculations are typically performed with (2×2) to (10×10) slab surface models consisting of three to six atomic layers. Most of the calculations were performed with either the Perdew–Wang (PW91),^{2–4,7,13,15,21,22,25,26,29,31,33–37}

Perdew–Burke–Ernzerhof (PBE),^{5,9,10,12,14,16,17,28,30} or Revised PBE (RPBE)^{2,12,34} functional. Previous studies normally report the preferred sulfur adsorption binding site, the binding (adsorption) energy, the sulfur-surface interatomic distances, and the diffusion energy of sulfur. The preferred adsorption site and the binding energy have been reported for sulfur on Ni(111),^{3,9,17,28,30,31} Cu(111),^{9,13–15,17,25,26,31,35} Rh(111),¹⁷ Pd(111),^{4,15,22,26,35} Ag(111),^{2,15,17,25,35} Ir(111),³⁴ Pt(111),^{4,17,37} Au(111),^{15,16,22,26} Ni(110),⁹ Cu(110),^{5,9,13} Au(110),²¹ Ni(100),^{9,12,30} Cu(100),^{9,12,14} Ir(100),²⁹ Au(100),^{7,16} Pd(211),³⁶ and Au(211).¹⁶ The surface diffusion energy of sulfur has been calculated for Ni(111),^{3,33} Cu(111),^{33,35} Pd(111),³⁵ Ag(111),^{2,35} Ir(111),³⁴ Pt(111),³³ Au(111),¹⁶ Au(100),¹⁶ and Au(211).¹⁶ The surfaces of Ni^{3,9,12,17,28,30,31,33} and Cu^{5,9,12–15,17,25,26,31,33,35} have been studied more extensively than the other FCC metals. The reason is because Ni has a high melting temperature and it is extensively used as the anode in SOFC. Cu has a low cost and good tolerance⁴⁴ to sulfur poisoning, making it an attractive alternative catalyst for many reactions. The (111) surface has been the most extensively studied because of its stability.⁴⁵ Adsorption of sulfur on the low-index (110) and (100) surfaces has been studied to a lesser extent. DFT calculations of sulfur adsorption on high-index surfaces like (211) are very uncommon. We did not find reports for sulfur on the following surfaces: Rh(110), Pd(110), Ag(110), Ir(110), Pt(110), Rh(100), Pd(100), Ag(100), Ni(211), Cu(211), Rh(211), Ag(211), Ir(211), and Pt(211). Further calculations of the adsorption geometry, binding, and diffusion energies are required to have a more complete understanding of the adsorption of sulfur on FCC metal surfaces.

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The general picture that emerges from previous calculations of the adsorption of sulfur on FCC metals is as follows. At a coverage of 0.50 monolayer (ML) or higher, adsorbed disulfur (S_2)³⁷ can be present and different structural phases are possible because of surface reconstruction.¹² At a coverage of 0.25 ML or lower, the adsorbed species is atomic sulfur.²⁵ Sulfur is more stable when adsorbed on high coordination sites, like the three-fold FCC site on the (111)^{4,9,16,17,22,31,26,25,34–36} surface and the four-fold site on the (110)⁹ and (100)^{9,29,30} surfaces. Sulfur is strongly bound to surfaces of FCC metals; the calculated binding energy ranges from 6.0 eV in Ni³⁰ and Ir²⁹ to 3.5 eV in Au.¹⁶ The surface diffusion energy of sulfur ranges from 0.2 eV in Cu³⁵ and Ag³⁵ to 0.6 eV in Ir.³⁴ The interatomic distance between sulfur and the surface is in the range of 2.2⁹–2.6⁷ Å. The bonding between sulfur and the metal surface arises from the overlap of *p*-states of sulfur with the *d*-band of the metal surfaces. The bonding shows covalent character for sulfur on some metals, like Pt and Rh, where charge transfers¹⁷ from the surface to the sulfur adsorbate; the charge transfer ranges from 0 to 0.2*e*. For the other FCC metals, like Cu,²⁵ Ni,¹⁷ and Ag,¹⁷ the bonding seems more ionic with a charge transfer close to 0.5*e*.

In the present work, we have performed DFT calculations to study the adsorption and the diffusion of sulfur on the (111), (100), (110), and (211) surfaces of Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. This work is a systematic evaluation of the adsorption energies, adsorption geometries, and diffusion energies of sulfur on these surfaces. Cross-comparison of the adsorption properties of sulfur on multiple metal surfaces can bring insights that are not accessible when each surface is studied individually and with dissimilar computational methods. We expect our work to be a reference point for future studies of the adsorption of sulfur and sulfur-containing molecules on FCC metal surfaces. For instance, our results can be used with the so-called surface mixing method⁶ to study sulfur on alloyed FCC metal surfaces. The present results can also be employed as a starting point to further studies on the sulfur-induced reconstruction of FCC metal surfaces,¹² sulfur penetration into the subsurface, and the phase diagram of sulfur-metal systems.^{14,30} The rest of the paper is organized as follows. In Sec. II, we describe the computational details of the DFT calculations, including the possible errors and limitations of the models. In Sec. III, we discuss our results for the adsorption energy, geometry, and diffusion energy of sulfur on FCC metals. We summarize our findings in Sec. IV.

II. COMPUTATIONAL METHODS

DFT calculations were employed to study the adsorption and diffusion of sulfur on the low-index and (211) surfaces of the FCC metals Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. Calculations were performed with the Atomic Simulation Environment (ASE)⁴⁶ and the Vienna *Ab initio* Simulation Package (VASP).^{47–49} The ionic cores were described by projector augmented wave method (PAW)^{50,51} potentials. We used the standard PAW potentials available in the VASP distribution; see Table S1 of the [supplementary material](#) for a list

of the PAW potentials employed. The transition states (TSs) for the diffusion of sulfur on the (111) and (100) surfaces were determined by applying the Nudged-Elastic-Band (NEB) method,^{52,53} where the components of the forces on the various images perpendicular to the path were converged to 0.02 eV/Å. In the case of the more open (110) and (211) surfaces, we evaluated the potential energy surface (PES) to determine the minimum energy diffusion pathway (see Sec. III B 2 for further details). In Secs. II A and II B, we include further details of electronic structure calculations and the surface models employed and discuss the possible errors and limitations of the employed methods.

A. Electronic structure calculations and surface models

The electronic structure was evaluated with spin-polarized calculations with the RPBE⁵⁴ exchange-correlation functionals. A 550 eV wavefunction energy cutoff was employed in all calculations; see Sec. II B for details. The fractional number occupation technique (Methfessel-Paxton scheme)⁵⁵ was used with a level width of 0.01 eV; total energies were extrapolated to $k_B T = 0$ eV.

The low-index (111), (110), and (100) surfaces were simulated with a (2×2) supercell separated by a vacuum region of 12 Å. The (111) and (100) surfaces were simulated with six atomic layers, and the (110) surface was simulated with eight layers; see Sec. II B for details. Geometry optimizations were performed with the four bottom atomic layers of the surface models kept fixed at the calculated lattice constants: Ni: 3.553 Å, Cu: 3.677 Å, Rh: 3.846 Å, Pd: 3.982 Å, Ag: 4.207 Å, Ir: 3.888 Å, Pt: 3.989 Å, and Au: 4.196 Å. The two top atomic layers were allowed to relax until all residual forces were less than 0.02 eV/Å. Calculations were performed with a *k*-point mesh of $12 \times 12 \times 1$. Calculations for the (211) surface were performed with a (3×3) supercell of six atomic layers. For this surface, the three top atomic layers were allowed to relax. The geometry optimizations in these cases were performed with a $6 \times 6 \times 1$ *k*-point mesh and final calculations were performed with an $8 \times 8 \times 1$ mesh; see Sec. II B for details.

B. Possible errors and limitations of the models

There are several possible sources of error in our calculations: (i) errors from the DFT approximations, (ii) errors coming from the slab surface model approximation (e.g., effect of surface coverage, use of a limited number of atomic layers, and omission of surface reconstruction), and (iii) numerical errors coming from the use of a finite wavefunction energy cutoff and *k*-point mesh.

Errors of type (i) have been well documented for surface adsorption.^{54,56,57} In general, the errors come because DFT does not provide the form of the exchange-correlation functional and instead DFT calculations are performed with exchange-correlation functionals that are based on approximations, like the Local Density Approximation (LDA)⁵⁸ and the Generalized Gradient Approximation (GGA).⁵⁹ These approximations introduce errors, commonly attributed to the self-interaction energy and the electron density

overdelocalization.⁶⁰ Multiple methods have been developed to overcome the inherent errors in the DFT approximations. Some methods simply go beyond the DFT approximations; see Refs. 57, 61, and 62 for methods already at the application stage and Ref. 63 for methods currently under development. Methods that go beyond the DFT approximations are more accurate and reliable; however, it has higher computational cost when compared to DFT-based methods. As a result, the application of these types of methods to surface processes has been limited to the selected systems.^{64,57,65} In other methods, with a manageable computational cost, GGA-based functionals have been designed particularly for surface reactions and adsorption processes.^{54,66} One of these methods is RPBE,⁵⁴ which yields chemisorption energies with deviations from the experiment of the order of 0.3 eV, an improvement over LDA, PW91, and PBE.^{54,56} Another method developed more recently with machine learning techniques is the Bayesian error estimation functional with van der Waals correlation (BEEF-vdW).⁶⁶ This method is like RPBE but includes Langreth–Lundqvist⁶⁷ non-local corrections. BEEF-vdW and RPBE perform equally well for surface processes involving strong surface-adsorbate interactions.⁵⁶ In the surface process where dispersion interactions are dominant, BEEF-vdW is superior to RPBE. In the present study, we employed the RPBE functional. For the adsorption energy of sulfur on surfaces of FCC metals, we expect errors from the DFT approximations to be of the order of 0.3 eV.

Errors of type (ii), coming from the use of a limited number of atomic layers and surface coverage effects, are more difficult to assess and control. We have performed test calculations of the sulfur adsorption energy with a (2×2) surface model of an increasing number of atomic layers, from 2 to 14 layers. For the FCC(111), FCC(100), and FCC(211) surfaces, the adsorption energies evaluated with six atomic layers are within 50 meV of results with 14 layers; see Fig. S2 of the [supplementary material](#). For FCC(110), the adsorption energies need to be evaluated with eight atomic layers to reach a 50 meV uncertainty with respect to 14 layers. The fact that the adsorption energy of sulfur changes with an increasing number of atomic layers indicating that the sulfur-surface bonding is modulated by the third- and fourth-layer. In the case of surface coverage effects, we employed (2×2) and (3×3) models of the low-index and stepped surfaces, respectively, with a single sulfur atom on one side of the surface. Previous computational studies have explored a coverage effect for sulfur on the (111) surface of Ni,³⁰ Cu,²⁵ Pd,³⁵ Ag,²⁵ and Pt³⁷ as well as on the (100) surface of Ni³⁰ and Ir.²⁹ The previous calculations show that the adsorption energy gets lower with increasing sulfur coverage, reflecting the repulsive adsorbate-adsorbate interaction of adsorbed sulfur. For a coverage of 0.25 ML or lower, the adsorbed species is atomic sulfur and the adsorption energy only changes slightly when lowering the coverage.²⁵ A different scenario takes place at a coverage of 0.50 ML or higher, where the strong adsorbate-adsorbate repulsion can lead to the formation of adsorbed disulfur (S_2) instead of atomic sulfur.³⁷ At such a high coverage, different structural phases are also possible because of surface reconstruction.¹² Therefore, our models are representative of

sulfur adsorption at the low-coverage regime, 0.25 ML or lower, where adsorbate-adsorbate repulsion can be expected³⁰ to be less significant.

Finally, errors of type (iii), coming from the use of a finite wavefunction energy cutoff and k-point mesh, are easily assessed and controlled by increasing these parameters until the property of interest is converged. We performed test calculations for the total energy of the FCC metals in the bulk state increasing the energy cutoff from 200 eV to 1500 eV. The total energies calculated with a 550 eV energy cutoff are within 1 meV/atom of results with 1500 eV; see Fig. S1a of the [supplementary material](#). For the k-point mesh, calculations were performed from a $4 \times 4 \times 4$ mesh to a $44 \times 44 \times 44$ mesh. Calculations with a $24 \times 24 \times 24$ mesh yield total energies within 1 meV/atom of results with a $44 \times 44 \times 44$ mesh; see Fig. S1b of the [supplementary material](#). Thus, we used a 550 eV wavefunction energy cutoff and $12 \times 12 \times 1$ and $8 \times 8 \times 1$ k-point meshes for the (2×2) and (3×3) surface models.

III. RESULTS AND DISCUSSION

In this section, we discuss our results for the adsorption and diffusion of adsorbed sulfur on FCC metal surfaces. The adsorption energy E_{ads} is defined as $E_{ads} = E_{S-Surf} - E_{Surf} - E_S^{atom}$, where E_{S-Surf} , E_{Surf} , and E_S^{atom} are, respectively, the total energies of the sulfur-surface system, the clean surface, and the sulfur atom. Note that there are several choices for the reference sulfur atom (or sulfur chemical potential), including atomic sulfur, molecular disulfur (S_2) or octasulfur (S_8), and solid orthorhombic sulfur. We used atomic sulfur (in the 3P ground state) as references unless otherwise specified. For reference, the calculated total energy (per atom) of atomic sulfur, disulfur, octasulfur, and solid orthorhombic sulfur is -1.117 , -3.482 , -3.921 , and -3.914 eV, respectively. The diffusion energy E_{diff} is defined as $E_{diff} = E_{TS} - E_{S-Surf}$, where E_{TS} and E_{S-Surf} are, respectively, the total energy of the diffusion transition state (TS) and the total energies of the initial sulfur-surface state. The frequency of the stretching mode and the frustrated translational mode of sulfur adsorbed on FCC metals is below 500 cm^{-1} and 200 cm^{-1} , respectively.^{29,31} Our results for E_{ads} and E_{diff} of sulfur on FCC metal surfaces do not include zero-point energy corrections because they are expected to be below 0.05 eV. In what follows, we will first discuss the energetic and geometric aspects of the sulfur adsorption. Afterward, we will discuss the energetic aspects of the surface diffusion of sulfur.

A. Energetic and geometric properties of sulfur adsorbed on FCC metal surfaces

We studied the adsorption of sulfur on multiple sites of the (111), (100), (110), and (211) surfaces. The initial positions of adsorbed sulfur are shown in Figs. 1 and 2. Not all initial conformations were stable (i.e., local minimum) after geometrical optimization. The adsorption energies of stable sites are summarized in Fig. 3; see Table S2 of the [supplementary material](#) for numerical values. On the (111) surface, the stability order for the sulfur adsorption sites is

FIG. 1. Initial adsorption sites on the (a) (111) and (b) (100). The FCC, HCP, Ontop, and Bridge adsorption sites on the (111) surface are labeled 1, 2, 3, and 4, respectively. For the (100) surface, the labels are 1: Hollow, 2: Bridge, and 3: Ontop.

FCC $\approx$ HCP $\gg$ Ontop; the Ontop site is over 1 eV less stable than the HCP site. These results are in line with previous calculations of the (111) surface.^{2,4,9,16,17,22,25,26,34–36} In the case of the (100) and (110) surfaces, the Hollow site is in general the most stable site. Similar results were previously reported^{9,29,30} for the (110) and (100) surfaces. We found three exceptions where the Hollow site is not the preferred adsorption site. These are the Pt(110), Ir(110), and Au(110) surfaces, where the Short Bridge sites are 0.31, 0.13, and 0.08 eV, respectively, more stable than the Hollow site. The Short Bridge sites were also found to be the most stable site in a previous calculation²¹ of sulfur on missing-row reconstructed Au{110}-(1 $\times$ 2). For the (211) surfaces, the adsorption of sulfur in the various stable sites is very close in energy. On average, the various sites are within 0.3 eV. The most stable site for Ni, Cu, Rh, Pd, and Ag is the site labeled number 6. Site number 6 is a Hollow site located at the (100) atomic high step (the so-called A-type step). For Ir(211), Pt(211), and Au(211), the preferred adsorption site is the site labeled number 3, a HCP site on

FIG. 2. Initial adsorption sites on the (a) (110) and (b) (211). For the (110) surface, they are 1: Hollow, 2: Short Bridge (S-Bridge), 3: Ontop, and 4: Long Bridge (L-Bridge). The adsorption sites on the (211) surface are labeled 1, 2, 3, 4, 5, 6, 7, 8, and 9. The dashed lines indicate the area that was explored to determine the PES.

FIG. 3. Adsorption energy E_{ads} of sulfur on stable sites of the (a) (111), (b) (100), (c) (110), and (d) (211) surfaces of the FCC metals Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au.

the (111) terrace. A previous study¹⁶ found similar results for sulfur on the Au(211) surface, showing the HCP site on the (111) terrace as the most stable, within ~ 0.4 eV of other stable sites. In another work, Makkonen *et al.* also reported³⁶ that sulfur binds to the step site of stepped surfaces of Pd and pointed out the possible formation of sulfur stripes along the step edges. Our results for the (211) stepped surface point out the possibility of similar formation of sulfur stripes along the steps of Ni, Cu, Rh, and Ag. Excluding the (110) and (211) surfaces of Ir, Pt, and Au, the relative adsorption energy for sulfur on Hollow, Bridge, and Ontop can be explained with bond-counting arguments, a lowering in the number of sulfur-surface bonds results in a lower adsorption energy. A similar argument can be used to explain the activation energy for the diffusion of sulfur over the various surfaces (see Sec. III B) because the transition states have a lower number of bonds than the initial state.⁶⁸ In the cases of the (110) and (211) surfaces of Ir, Pt, and Au, the relativistic effects present in these heavy atoms are likely influencing^{69,70} the bonding with sulfur. Further detailed studies are required to better understand the adoption of sulfur on the (110) and (211) surfaces of Ir, Pt, and Au.

The calculated adsorption properties of the preferred adsorption sites of sulfur on the various surfaces of the FCC metals are summarized in Table I. In Fig. 4(a), we show the adsorption energy of the preferred adsorption sites for

TABLE I. Adsorption properties of the most stable adsorption site for sulfur on surfaces of FCC metals.^a

Surface	Site ^b	E_{ads}	$\langle S-M_1 \rangle$	$\langle \Delta z(S-M_1) \rangle$	$\langle M_1-M_2 \rangle$	$q(S)$	$\epsilon_d(M)$	E_{diff}
Ni(111)	FCC	-4.69	2.158	1.569	2.508	-0.466	-1.148	0.275
Cu(111)	FCC	-3.99	2.232	1.613	2.600	-0.561	-2.028	0.168
Rh(111)	FCC	-4.90	2.270	1.606	2.710	-0.235	-1.573	0.446
Pd(111)	FCC	-4.54	2.255	1.521	2.808	-0.182	-1.318	0.381
Ag(111)	FCC	-3.25	2.453	1.692	2.970	-0.516	-3.674	0.184
Ir(111)	FCC	-4.83	2.318	1.655	2.741	-0.241	-1.915	0.589
Pt(111)	FCC	-4.63	2.276	1.525	2.809	-0.084	-1.751	0.703
Au(111)	FCC	-3.15	2.392	1.569	2.960	-0.240	-2.893	0.439
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Ni(100)	Hollow	-5.32	2.207	1.282	2.508	-0.641	-1.135	1.038
Cu(100)	Hollow	-4.47	2.302	1.357	2.586	-0.768	-1.945	0.881
Rh(100)	Hollow	-5.49	2.352	1.339	2.716	-0.317	-1.536	0.994
Pd(100)	Hollow	-5.15	2.312	1.146	2.807	-0.356	-1.295	1.217
Ag(100)	Hollow	-3.60	2.553	1.400	2.960	-0.699	-3.658	0.766
Ir(100)	Hollow	-5.43	2.420	1.441	2.753	-0.263	-1.843	0.890
Pt(100)	Hollow	-5.16	2.364	1.239	2.801	-0.319	-1.713	0.980
Au(100)	Hollow	-3.31	2.521	1.326	2.933	-0.420	-2.840	0.474
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Ni(110)	Hollow	-4.99	2.246	0.941	2.467	-0.602	-1.220	0.371
Cu(110)	Hollow	-4.27	2.417	1.036	2.545	-0.712	-1.967	0.350
Rh(110)	Hollow	-4.93	2.324	0.960	2.670	-0.420	-1.599	0.312
Pd(110)	Hollow	-4.86	2.276	0.704	2.677	-0.245	-1.400	0.316
Ag(110)	Hollow	-3.44	2.633	1.018	2.879	-0.647	-3.696	0.294
Ir(110)	S-bridge	-4.88	2.234	1.733	2.624	-0.289	-1.933	0.406
Pt(110)	S-bridge	-4.37	2.210	1.681	2.669	-0.118	-1.818	0.227
Au(110)	S-bridge	-2.95	2.317	1.725	2.834	-0.289	-2.882	0.251
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Ni(211)	Site 6	-5.06	2.252	0.478	2.509	-0.626	-1.182	0.546
Cu(211)	Site 6	-4.28	2.309	0.548	2.602	-0.735	-2.020	0.458
Rh(211)	Site 6	-5.18	2.365	0.457	2.703	-0.334	-1.640	0.701
Pd(211)	Site 6	-4.92	2.561	0.226	2.812	-0.283	-1.374	0.549
Ag(211)	Site 6	-3.50	2.350	0.462	2.976	-0.676	-3.692	0.386
Ir(211)	Site 3	-5.11	2.296	1.397	2.741	-0.311	-2.011	0.700
Pt(211)	Site 3	-4.66	2.263	1.369	2.789	-0.098	-1.896	0.428
Au(211)	Site 3	-3.32	2.373	1.411	2.895	-0.258	-2.952	0.238

^aAdsorption site, adsorption energy (E_{ads}), average distance $\langle S-M_1 \rangle$ between sulfur and the nearest surface metal (M) atoms, S-M outermost layer average spacings $\langle \Delta z(S-M_1) \rangle$, average distance $\langle M_1-M_2 \rangle$ between the first and second surface metal layers, charge $q(S)$ of absorbed sulfur from a Bader charge analysis, d -band center $\epsilon_d(M_1)$ (relative to the Fermi energy) of the first layer of the surface without absorbed sulfur, and the energy, E_{diff} , for the diffusion of sulfur on the metal surface. All energies are given in eV and distances in Å.

^bSee Figs. 1 and 2.

each surface. A quick inspection of Fig. 4(a) reveals the following trends for the adsorption of sulfur on FCC metals. First, $|E_{ads}|$ follows the general trend (100) $\approx$ (211) $\approx$ (110) $>$ (111). An exception to this trend is Pt, where $|E_{ads}|$ of sulfur is slightly higher on the (111) than that of the (110) surface. As mentioned previously, the sulfur-surface bonding arises primarily from the overlap of p -states in sulfur with the d -band in the metal surfaces and partial charge transfer from the surface to the sulfur adsorbate. Taking into consideration such a bonding mechanism, the trend for E_{ads} with respect to surface orientation is easily understood by analyzing the charge $q(S)$ of absorbed sulfur and the d -band center $\epsilon_d(M_1)$ of the first surface layer (see Table I). In general, $\epsilon_d(M_1)$ changes slightly from one surface orientation to another for a given FCC metal. However, $q(S)$ is generally 0.1e–0.2e more negative for sulfur on the (100) surface, partially explaining the stronger binding of sulfur on this surface. A second general trend for the adsorption of sulfur on FCC metals is that the adsorption energy $|E_{ads}|$

follows the general trend (Rh: 5.5–4.9 eV) $\approx$ (Ir: 5.4–4.9 eV) $\approx$ (Ni: 5.3–4.7 eV) $\approx$ (Pd: 5.2–4.5 eV) $\approx$ (Pt: 5.2–4.4 eV) $>$ (Cu: 4.5–4.0 eV) $>$ (Ag: 3.6–3.2 eV) $>$ (Au: 3.3–3.0 eV). This general trend for $|E_{ads}|$ is expected from the so-called d -band model of Hammer and Nørskov,⁷¹ which show a general linear correlation between E_{ads} and the d -band center ϵ_d of the metal surfaces. In general, the adsorption gets stronger as the d -band center approaches the Fermi energy. Figure 4(b) shows the expected general linear correlation between E_{ads} and the d -band center ϵ_d .

The RPBE functional has been previously employed to calculate E_{ads} of sulfur on Ni(100),¹² Cu(100),¹² Ag(111),² and Ir(111)³⁴ with a surface coverage of 1/(2 × 2) ML. In the case of Ni(100)¹² and Cu(100),¹² E_{ads} of sulfur was calculated using disulfur (S_2) as a reference (sulfur chemical potential). The reported values in Ref. 12 for E_{ads} are –3.282 and 2.475 eV for Ni(100) and Cu(100), respectively. We evaluated E_{ads} for sulfur using S_2 as a reference and found values

FIG. 4. (a) Adsorption energy E_{ads} of the most stable adsorption site for sulfur on the FCC metals Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. (b) E_{ads} as a function of the d-band center $\epsilon_d(M)$ of the first layer of the clean surface.

of -2.95 and -2.11 eV for Ni(100) and Cu(100), respectively. There is a clear discrepancy between the two set of results. However, we believe that the results disagree because S_2 was in the singlet state in Ref. 12, instead of the triplet group state. We evaluated E_{ads} with S_2 in the singlet state and found values of -3.29 and -2.44 eV for sulfur on Ni(100) and Cu(100), respectively, which are practically the same as in Ref. 12. In the case of sulfur on Ag(111)² and Ir(111),³⁴ E_{ads} was calculated using atomic sulfur in the ground state as a reference and can be directly compared with our results. The reported values for E_{ads} evaluated with RPBE are -3.16 and -4.67 eV for Ag(111)² and Ir(111),³⁴ respectively. Our results are -3.25 and -4.69 eV for Ag(111) and Ir(111), respectively. The small deviation for Ag(111) may come from differences in the computational methods.

We also determined the average distance $\langle S-M \rangle$ between sulfur and the nearest surface metal (M) atoms, the S-M outermost layer average spacings $\langle \Delta z(S-M_1) \rangle$, and the average distance $\langle M_1-M_2 \rangle$ between metal atoms in the first and second surface layers. Our results for the average distances $\langle S-M \rangle$ show good agreement with previous calculations. For Ni(111), (100), and (110), our values are 2.158, 2.207, and 2.246 Å, respectively. Previous studies reported the values of 2.15,^{3,9} 2.19,⁹ and 2.29⁹ Å for the Ni(111), (100), and (110) surfaces, respectively. The experimental S-Ni distance ranges from 2.02(6) to 2.35(4) Å.⁷²⁻⁷⁴ The S-M outermost layer average spacings $\langle \Delta z(S-M_1) \rangle$ in Ni(100) and Cu(100) are 1.282 and 1.357 Å, respectively. Our results are in line with experimental values of 1.3(1) Å for Ni(100)⁷⁵ and 1.30(5) Å for Cu(100).⁷⁶

B. Diffusion of adsorbed sulfur on FCC metal surfaces

1. Diffusion of adsorbed sulfur on FCC(111) and FCC(100) surfaces

The most stable site for sulfur on the (111) surfaces is the FCC site. To move across the (111) surfaces, sulfur likely

hops from one FCC site to the next via the FCC $\rightarrow$ HCP $\rightarrow$ FCC and/or FCC $\rightarrow$ Ontop $\rightarrow$ FCC pathways. Figure 5(a) shows the change in energy for the diffusion of adsorbed sulfur via the FCC $\rightarrow$ HCP $\rightarrow$ FCC pathway on the (111) surface of Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. The diffusion energy for such pathway ranges from 0.17 eV in Cu(111) to 0.70 eV in Pt(111). The diffusion energies for each surface are summarized in Table I. The FCC $\rightarrow$ Ontop $\rightarrow$ FCC pathway was not explored because the diffusion energy via the Ontop state is at least 1 eV higher in energy than by the HCP state.

Previous calculations have evaluated the diffusion of sulfur on Cu(111),^{33,35} Ni(111),^{3,33} Pd(111),³⁵ Ag(111),³⁵ Ir(111),³⁴ Pt(111),³³ and Au(111).¹⁶ Our results agree within 0.06 eV with previous calculations. We found slightly large disagreements in the case of Ni(111) and Pt(111). For Ni(111), our calculations yield a value of 0.27 eV for the diffusion of adsorbed sulfur while previous studies^{3,33} reported values of 0.40 and 0.37 eV for the FCC $\rightarrow$ HCP $\rightarrow$ FCC pathway. Our result of 0.27 eV for the diffusion of adsorbed sulfur on Ni(111) agrees well with the experimental value of 0.29–0.30 eV from field-ion-microscopy (FIM) at temperature above 107 K.⁷⁷ An earlier investigation of sulfur diffusion on the Ni surface by the field-electron-emission-microscopy (FEM) reported diffusion energy barriers ranging from 0.65 to 1.21 eV. The higher barrier in the FEM experiments is likely because in such experiments the sulfur diffusion was over a defected and corrugated Ni surface.^{78,79} In the case of Pt(111), we calculated a diffusion energy of 0.70 eV, while in a previous calculation³³ a value of 0.54 eV was reported, which agrees with the experimental value of 0.55 eV for the sulfur diffusion on Pt(111) from scanning tunneling microscopy (STM).⁸⁰ It is unclear why our calculations and those in Refs. 3 and 33 yield different surface diffusion energies for sulfur on Ni(111)^{3,33} and Pt(111).³³ To corroborate our results, we employed dimer calculations⁸¹ (starting from the NEB results)

FIG. 5. Energy change (ΔE) during the diffusion of sulfur from (a) FCC to HCP sites on (111) surfaces and (b) from Hollow to Bridge sites on (100) surfaces of the FCC metals Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au.

to converge upon the diffusion transition saddle point for sulfur on Pt(111). The dimer calculations yield an energy barrier of 0.72 eV.

In the case of the (100) surfaces, the Hollow site is the most stable sulfur adsorption site. The diffusion of sulfur is via the Hollow $\rightarrow$ Bridge $\rightarrow$ Hollow and/or Hollow $\rightarrow$ Ontop $\rightarrow$ Hollow pathways. Figure 5(b) shows the change in energy for the diffusion of adsorbed sulfur via the Hollow $\rightarrow$ Bridge $\rightarrow$ Hollow pathway on the (100) surface of Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. The diffusion energy is the energy difference between the Bridge and Hollow sites, ranging from 0.47 eV in Au(100) to 1.22 eV in Pd(100). The diffusion energies for each surface are summarized in Table I. The Hollow $\rightarrow$ Ontop $\rightarrow$ Hollow pathway was not explored because the diffusion energy via the Ontop state is at least 1.5 eV higher in energy than by the Bridge state. Diffusion of sulfur on (100) surfaces is unlikely at normal temperatures. We only found one previous calculation¹⁶ for the surface diffusion of sulfur on the (100) surface of the studied FCC metals. They found a value of 0.45 eV for the diffusion energy of sulfur on the Au(100) surface via the Hollow $\rightarrow$ Bridge $\rightarrow$ Hollow pathway.

2. Diffusion of adsorbed sulfur on FCC(110) and FCC(211) surfaces

In the case of the (110) and (211) surfaces, the minimum energy diffusion pathway was determined from the PES of the system comprising adsorbed sulfur and the metal surface. The PESs were estimated placing sulfur on a (20×10) grid over the (110)- (2×2) surfaces and a (60×6) grid over the (211)- (3×3) surface. For each point, sulfur was constrained on the x and y coordinates, while the top two layers of the surface and the z coordinate of sulfur could fully relax. The calculations to determine the PES were performed with a wavefunction energy cutoff of 260 eV and k -point meshes of $6 \times 6 \times 1$ and $4 \times 4 \times 1$ for the (110) and (211) surfaces, respectively. We performed calculations for the PES of the S–Pt(110) systems with a finer energy cut-off and k -point mesh (see Sec. II A), and the PESs were similar within 0.05 eV.

Figure 6 shows the contour maps of the PES for sulfur on the Ni(110), Pt(110), and Au(110) surfaces. PES for sulfur on the other surfaces is shown in Fig. S4 of the [supplementary material](#). Sulfur is preferentially located on the Hollow sites over Ni(110), Cu(110), Rh(110), Pd(110), and Ag(110). For these metals, the diffusion of sulfur is via the Hollow $\rightarrow$ Long Bridge $\rightarrow$ Hollow pathways. The diffusion energies range from 0.30 eV in Ag(110) to 0.37 eV in Ni(110). The diffusion energies are summarized in Table I. In the case of the Ir(110) surface, sulfur is preferentially absorbed on the Short Bridge site. The diffusion is via the Short Bridge $\rightarrow$ Hollow $\rightarrow$ Short Bridge, with a diffusion energy of 0.41 eV. On the Pt(110) surface, sulfur shows a more complex PES, with two energetically closed adsorption sites; the diffusion energy is 0.23 eV. The surface diffusion of sulfur is in-channel for the (110) surface of Ni, Cu, Rh, Pd, and Ag and cross-channel for Ir, Pt, and Au.

Figure 7 shows the contour maps of the PES for sulfur on the Ni(211), Ir(211), and Au(211) surfaces. PES for

FIG. 6. Contour maps of the PES for sulfur on the (a) Ni(110), (b) Pt(110), and (c) Au(110) surfaces. The labels 1, 2, 3, and 4 on panel (a) are intended as a guide and indicate the high symmetry adsorption sites [see Fig. 2(a)].

sulfur on the other surfaces is shown in Fig. S5 of the [supplementary material](#). As expected, the PESs of (211) surfaces are more complex than those of (110) surfaces, with

FIG. 7. Contour maps of the PES for sulfur on the (a) Ni(211), (b) Ir(211), and (c) Au(211) surfaces. The labels 1–9 are intended as a guide and indicate the high symmetry adsorption sites [see Fig. 2(b)].

FIG. 8. Diffusion energy E_{diff} for sulfur on the FCC metals Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au.

many more possible adsorption sites. The diffusion of sulfur is also more complex, with multiple possible pathways. For (211) surfaces of Ni, Cu, Rh, Pd, and Ag, sulfur binds preferentially to the Hollow site located at the (100) atomic high step (site 6). For these metals, the diffusion of sulfur is preferentially via the site 6 $\rightarrow$ site 7 $\rightarrow$ site 6 pathway. The diffusion energies range from 0.46 eV in Cu(211) to 0.70 eV in Rh(211). For the Ir(211), Pt(211), and Au(211) surfaces, the preferred adsorption site is a HCP site on the (111) terrace (site 3). In these cases, the diffusion is via the site 3 $\rightarrow$ site 1 $\rightarrow$ site 3 pathway. The diffusion energies range from 0.24 eV in Au(211) to 0.70 eV in Ir(211). For Au(211), our calculated diffusion energy is close to a previous calculated value¹⁶ of 0.3 eV. Sulfur can hop from site 3 to the region of site 6, going across the step, with an energy barrier of 0.23 eV. In the region of site 6 over Au(211), sulfur is confined and needs to hop back to site 3 for diffusion via the site 3 $\rightarrow$ site 1 $\rightarrow$ site 3 pathway. The surface diffusion of sulfur is along the step on the (211) surface of Ni, Cu, Rh, Pd, and Ag and along the terrace site for Ir, Pt, and Au. The diffusion across the step is unlikely due to the higher energy barrier for such pathways.

Figure 8 shows the diffusion energy for sulfur on the surfaces (111), (100), (110), and (211) of the FCC metals Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. Overall, the diffusion of sulfur varies between surface orientations as well as between metals. Sulfur has higher diffusion energy on the (100) surfaces, with some variation from one metal to another. As mentioned above, the surface diffusion of sulfur on the (110) surfaces is cross-channel for Ir, Pt, and Au but in-channel for the other metals. However, the diffusion energy is almost very similar for all metals, close to 0.3 eV.

IV. SUMMARY

In summary, we have performed DFT calculations to study the adsorption and the diffusion of sulfur on the (111), (100), (110), and (211) surfaces of Ni, Cu, Rh, Pd, Ag, Ir, Pt, and Au. Calculations were performed with the RPBE functional, and the error in the calculated adsorption energies is expected to be of the order of 0.3 eV. Our results agree with previous calculations showing that sulfur binds preferentially on high coordination sites on most FCC metal surfaces. On the (211)

stepped surfaces, sulfur adsorbed preferentially on stepped sites of Ni, Cu, Rh, Pd, and Ag, showing the possible formation of sulfur stripes along the step edges on these metals. The adsorption energy of sulfur by surface orientation follows the general trend (100) $\approx$ (211) $\approx$ (110) $>$ (111). The overall trend for the adsorption energy of sulfur by metal is (Rh: 5.5–4.9 eV) $\approx$ (Ir: 5.4–4.9 eV) $\approx$ (Ni: 5.3–4.7 eV) $\approx$ (Pd: 5.2–4.5 eV) $\approx$ (Pt: 5.2–4.4 eV) $>$ (Cu: 4.5–4.0 eV) $>$ (Ag: 3.6–3.2 eV) $>$ (Au: 3.3–3.0 eV). Calculations of the surface diffusion pathway for sulfur on the various surfaces show that the diffusion can be along multiple directions on the (111) and (100) surfaces but along one preferred direction on the (110) and (211) surfaces.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for PAW potentials employed, figures with energies calculated with various k-points, wavefunction energy cutoff and number of atomic layers, adsorption energy of sulfur on difference sites of FCC metal surfaces, and figures with the contour maps of the PES for sulfur on FCC metal surfaces.

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