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Insights into SO_2 and H_2O co-adsorption on Cu (100) surface with calculations of density functional theory

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Abstract: The co-adsorption behaviors of SO_2 and H_2O on face-centered cubic Cu (100) ideal surface were studied using the GGA-rPBE method of density functional theory (DFT) with slab models. The optimized structures of single H_2O and SO_2 on Cu (100) surface were calculated at the coverage of 0.25 ML (molecular layer) and 0.5 ML. The results show that there was no obvious chemical adsorption of them on Cu (100) surface. The adsorbed structures, adsorption energy and electronic properties including difference charge density, valence charge density, Bader charge analysis and partial density of states (PDOS) of co-adsorbed structures of H_2O and SO_2 were investigated to illustrate the interaction between adsorbates and surface. H_2O and SO_2 can adsorb on surface of Cu atoms chemically via molecule form at the coverage of 0.25 ML, while H_2O dissociated into OH adsorbed on surface and H bonded with SO_2 which keeps away from surface at the coverage of 0.5 ML.
Key words: SO_2; H_2O; Cu; density functional theory; co-adsorption; slab model; adsorption energy; charge transfer

1 Introduction

As a wildly used metal, copper corrodes at negligible rates in unpolluted air, water, and deaerated, nonoxidizing acids. But it appears to show remarkable activity for the sulfur dioxide (SO_2) in atmospheric pollutant [1−3]. From the previous studies, atmospheric corrosion of copper and its alloys is so complex for the process occurring in solid/liquid/gaseous phase and their interfaces [4,5]. Overriding pollution or deposition of aerosol particles, the moisture is the role factor affecting atmospheric corrosion. The importance of atmospheric droplets formation uptake to copper surfaces at the initial stage of atmospheric corrosion is widely recognized [6].

As mentioned by LEYGRAF and GRAEDEL [7], the time scale of surface film formation is about 1 μs, which means that it happens too fast to be observed or detected by experiments. Some researchers have studied the corrosion behaviors at the atomic scale [8−13]. There are also recent reports on the adsorption and transformation of SO_2 [14−19]. However, usually, it is desirable to build structures that do not rely on the real co-adsorption state. The co-adsorption is not equal to the sum of each molecule adsorption, however, monomolecular adsorption can provide a theoretical basis for it. There are various calculations of adsorption geometries of SO_2 on the metal and metallicoxide surface with DFT study [14,15,18,19]. Present structural measurements of SO_2 adsorption on copper surface show one consistent result: on copper surface, the molecular plane of SO_2 lies perpendicularly to the surface through two O atoms or through one O and one S atom [18,19]. Is there chemical adsorption on the copper surface with SO_2? The calculation results of SO_2 adsorption on Cu (111) are different when various exchange-correlation functions are used [20−23]. The calculation results whose exchange-correlation functions are GGA-PBE, GGA-PW91 and LDA yield reasonable adsorption energy and bond lengths are consistent with the experiment results. Moreover, the calculated geometries with the molecular plane parallel to the surface give the lowest energy instead of that with the molecular plane perpendicular to the surface from the previous

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experimental measurements at 0.25 ML coverage. Similar calculation of CASTEP DFT was conducted on Cu (100) surface to investigate the geometry of the adsorption of SO_2 at different coverages. Large coverage may not lead to the perpendicular adsorption. The bonding mechanism of SO_2 on copper involves electron transfer from Cu to SO_2.

The adsorption of H_2O molecular on copper surface has been investigated with VASP code [24]. The adsorption geometry of single H_2O molecule trends to weakly bind to a top position with the molecular plane basically parallel to the Cu surface. Many experimental techniques have been used to regard the adsorption on Cu surfaces [25−34], including infrared reflection adsorption spectroscopy [26], scanning tunneling microscope [27] and electron energy loss spectroscopy [31,32]. However, most of the theoretical studies mainly aimed at monomer H_2O adsorption [33−35] on Cu surface, and there are still some debates between theoretical studies and experimental techniques. The most stable geometry of H_2O adsorption is dimer structure which comprises two water molecules at atop position with tiled H-parallel configuration (one titled up and the other titled down), which is in excellent agreement with the experimental techniques.

There are few existing researches on the adsorption of SO_2 in the presence of H_2O at the atomic scale. The exact mechanism for this process of initial surface film formation is still obscure and leads to numerous debates. The purpose of this work is to report a DFT study of the co-adsorption of SO_2 and H_2O on Cu (100) surface. In this work, the structural evolutions and adsorption energy and electronic properties after the full optimization were analyzed, which may show a depiction of surface co-adsorption groups on copper surface.

2 Computational details

The first-principles calculations based on the DFT were performed with the GGA-rPBE exchange-correlation function in the MedeA-VASP 5.3 [36]. The electronic iterations convergence is 1.00×10^{-5} eV using the normal algorithm and reciprocal space projection operators. The calculations were conducted on 4-layer-slabs of the Cu (100) surface with a 15 Å vacuum gap. A (2×1) mesh and a (2×2) mesh were used for the adsorption calculation, corresponding to a high adsorbate coverages of 0.5 ML and 0.25 ML. The adsorbates and the two free moving uppermost surface layers were allowed and the two bottom layers were fixed. The slab models were calculated with the (6×6×1) and (6×12×1) Monkorst−Pack grid [37] for a coverage of 0.25 ML and 0.5 ML, respectively. All calculations were performed with a cut off energy of 400 eV.

The definition of adsorption energy is as follows:

$$E_{ad}=E_{ads}+E_{sub}-E_{ads/sub} \quad (1)$$

where E_{ads}, E_{sub} and $E_{ads/sub}$ are the total energies of isolated adsorbates, the relaxed clean slab and the slab covered with adsorbates, respectively. According to this definition, the higher the adsorption energy is, the stronger the interaction between adsorbates and the substrate is. The property of PDOS was calculated to investigate the interaction among different atoms. From PDOS diagram, the peak shifting indicates that the electronic number of the atom within a certain energy interval has changed. The interaction between different atoms may relate with overlapping of peaks. The difference in the charge density can be defined as

$$\Delta\rho=\rho_{ads/slab}-\rho_{slab}-\rho_{ads} \quad (2)$$

where $\rho_{ads/slab}$ stands for the charge density of the adsorbed system, ρ_{slab} stands for the charge density of the clean surface, and ρ_{ads} stands for the charge density of adsorbed molecules.

The difference in charge density and Bader charge analysis can characterize the charge transfer among atoms. The charges trend to move towards the middle of two bonding atoms, which can be shown in the figure of valence charge density.

3 Results and discussion

3.1 Single H_2O adsorption on Cu (100) surface

Table 1 lists the optimized structures of single H_2O molecule adsorption on Cu (100) surface at the coverages of 0.25 ML and 0.5 ML, and the related geometric parameters and adsorption energies are listed in Table 2. With respect to the coverage of 0.25 ML, a series of previous calculation results proved that the most stable configuration is similar with our result shown in Table 1 with the parallel molecular plane of H_2O tilt to the surface at top site of surface. The distance of Cu—O is 2.732 Å, which is longer than that of common copper oxide (1.840−2.429Å), according to ICSD database and Pearson's database of MedeA. The H—O bond length and the H—O—H angle are basically in accordance with the experimental values [38] of 0.96 Å and 104.5°, respectively. The most stable configuration whose coverage is 0.5 ML is not similar to that at the coverage of 0.25 ML, which is possibly due to the intermolecular repulsion of H_2O. The distance of Cu—O is 3.301 Å and those of two H—O bonds are 0.974 Å and 0.994 Å. As the copper surface mainly interacts with O atoms in H_2O molecule, our approach employs the distance of Cu—O in the optimized structure (Table 2) to express the strength of interaction between adsorbate and surface. According to our calculation, H_2O prefers to adsorb on Cu (100) surface at the coverage of 0.25 ML more than

0.5 ML. However, in all cases, H_2O binding to Cu (100) surface is very weak.

Table 1 Adsorbed structures of single H_2O and SO_2 molecule adsorption on Cu (100) surface

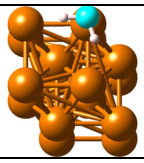
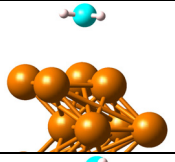
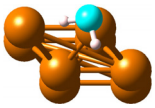
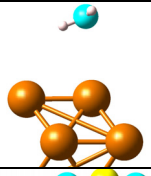
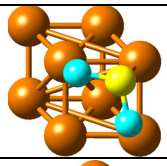
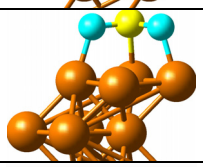
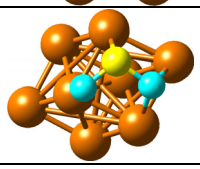
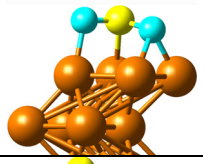
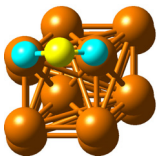
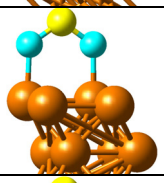
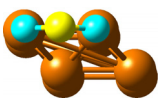
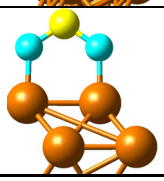
Coverage/ML		Top view	Side view
H_2O	SO_2		
0.25	0		
0.5	0		
0	0.25 (parallel)		
0	0.25 (tilt)		
0	0.25 (perpendicular)		
0	0.5		

Table 2 Geometrical parameters and adsorption energies of single H_2O and SO_2 adsorption on optimized Cu (100) surface at coverages of 0.25 ML and 0.5 ML

Coverage/ ML	Adsorbate	d_{OH}/ Å	d_{CuO}/ Å	d_{SO}/ Å	d_{CuS}/ Å	E_{ads}/ eV
0.25	H_2O	0.977	2.734	–	–	0.084
	SO_2 (parallel)	–	2.064/ 2.068	1.539/ 1.540	2.350	0.411
	SO_2 (tilt)	–	2.062/ 2.078/ 2.287	1.539/ 1.581	2.356	0.385
	SO_2 (perpendicular)	–	2.093/ 2.102	1.509	3.215	0.022
0.5	H_2O	0.974/ 0.994	3.301	–	–	0.043
	SO_2 (parallel)	–	1.992/ 1.997	1.503	3.112	5.655
	SO_2 (perpendicular)	–	1.992/ 1.997	1.503	3.112	5.655

The adsorption energies of H_2O on Cu (100) surface are 0.084 eV and 0.043 eV at the coverages of 0.25 ML and 0.5 ML, respectively. The calculated adsorption energy is not consistent with the experimental value [39], which indicates that the experimental adsorption energy is unlikely derived from the single adsorbed water on the ideal flat surfaces.

3.2 Single SO_2 adsorption on Cu (100) surface

The stable adsorption structures of SO_2 is with the molecular plane parallel to the Cu (111) surface at the coverage of 0.25 ML, which disagrees with the experimental results [40]. In our calculation, the initial structures with SO_2 molecular plane parallel, tilt and perpendicular to Cu (100) surface are calculated at the coverages of 0.25 ML and 0.5 ML. The optimized adsorption structures are also listed in Table 1. The geometric parameters and adsorption energies are also listed in Table 2. The SO_2 molecular plane of optimized structure is parallel to Cu (100) surface when the initial molecular plane of SO_2 is parallel or tilt to the surface at the coverage of 0.25 ML. The Cu atoms interact with S and O atoms. The SO_2 molecular plane keeps perpendicular to the Cu (100) surface when the initial SO_2 molecular plane is perpendicular to the surface at the coverage of 0.25 ML. The Cu atoms only interact with O atoms. The reason for the above condition is that the energy difference (about 0.4 eV) between the two stable structures is very small. For the coverage of 0.5 ML, in all cases, the SO_2 molecular plane of optimized structure keeps perpendicular to the surface and the Cu atoms of the surface interact with O atoms. The molecule plane of SO_2 trends to keep perpendicular to the copper surface with the increasing coverage. The distance of Cu—O is shorter at the coverage of 0.5 ML than that at 0.25 ML, which indicates stronger interaction among each other. However, there is still no interaction between Cu atoms and S atoms at the coverage of 0.5 ML. The distance of S—O is longer than 1.43 Å which is in the SO_2 gas for all cases. The adsorption of SO_2 leads to a rise in the distance of S—O at the coverage of 0.25 ML corresponding to the coverage of 0.5 ML. The loose strength of S—O chemical bond is attributed to electron transfer from copper surface to the SO_2 molecule.

The adsorption energy of SO_2 is much higher at the coverage of 0.5 ML than that at 0.25 ML, which indicates the shorter distance of Cu—O. In terms of the adsorption energy, we may infer that it is mainly contributed by the interaction of Cu—O instead of Cu—S.

3.3 Co-adsorption of SO_2 and H_2O on Cu (100) surface

3.3.1 Adsorption structures

The co-adsorption behavior of SO_2 and H_2O was investigated with the structure of initial SO_2 molecular plane perpendicular to the surface. Corresponding to the fixed SO_2 configuration of initial co-adsorption structure, the optimized H_2O is merged into the slab. The structures of Figs. 1 and 2 present the optimized co-adsorption structures at the coverages of 0.25 ML and 0.5 ML, respectively. For all structures, the lateral movements of the relaxed atoms are negligible and the major variation of the atomic position occurs in the z direction. The H_2O molecular plane is perpendicular to the SO_2 molecular plane with same height relative to the surface. The geometry parameters and adsorption energies of optimized structure are summarized in Table 3.

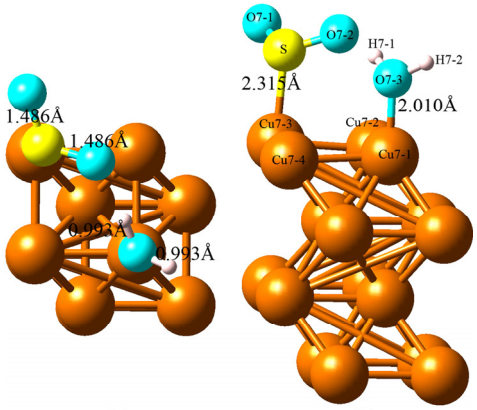


Fig. 1 Optimized top view (a) and side view (b) configurations of co-adsorption of SO_2 and H_2O on Cu (100) surface at coverage of 0.25 ML

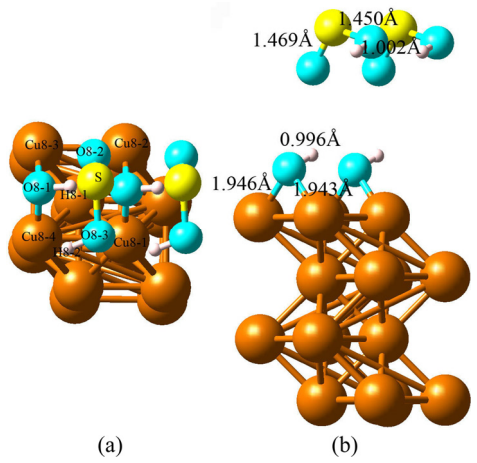


Fig. 2 Optimized top view (a) and side view (b) configurations of co-adsorption of SO_2 and H_2O on Cu(100) at coverage of 0.5 ML (super cell: 2×1×1)

With regard to the optimized structure shown as Fig. 1, the H_2O molecule and SO_2 molecule are adsorbed on different Cu atoms with O and S atoms, respectively. The distances of Cu—O and Cu—S are 2.010 Å and 2.385 Å, respectively. The shorter distance of Cu—O of the single H_2O adsorption geometry illustrates that the existence of SO_2 enhances the adsorption of H_2O. Meanwhile, the existence of H_2O affects the adsorption form of SO_2. The elongated O—H distance and shortened S—O distance of the single adsorption illustrate the redistribution of electrons.

Table 3 Geometric parameters and adsorption energies of H_2O and SO_2 co-adsorption on optimized Cu (100) surface at coverages of 0.25 ML and 0.5 ML

Coverage/ ML	d_{CuO}/Å	d_{CuS}/Å	d_{OH}/Å	d_{SO}/Å	E_{ads}/eV
0.25	2.010	2.385	0.993	1.486	8.619
0.5	1.943/1.946	>4	0.996/1.002	1.469/1.650	5.402

For the optimized structure shown in Fig. 2, one H atom of H—O—H breaks and bonds with SO_2 molecule which keeps away from Cu (100) surface. The adsobates are divided into a first layer containing O—H and a second layer containing O—S—O—H after calculation. The splitting results from displacements in the opposite directions, SO_2 is moving up while H_2O is moving down with respect to the position of the initial mixed layer. Moreover, our calculation results indicate the smallest distance between Cu atom and O atom can be obtained at the level of 1.943 Å which is much smaller than that of single adsorption.

Summarily, all the results of adsorbed structure and the configuration of optimized structure are closely related to the coverages of SO_2 and H_2O. For all structures in this work, the distance of Cu—O illustrates the strength of interaction between adsorbates and surface. According to the distance of Cu—O of single adsorption, it may be inferred that the interaction between SO_2 and surface is stronger than that of H_2O and surface. Considering the co-adsorption optimized structure, the distance of Cu—O is a little smaller than that of single SO_2 adsorption and much smaller than that of single H_2O adsorption.

3.3.2 Adsorption energy

The co-adsorption energy of H_2O and SO_2 (Table 3) is dramatically larger than the sum of the monomolecular adsorption of H_2O and SO_2. It may be inferred that the considerably large co-adsorption energy is caused by the reaction of adsorbates on Cu surface. The co-adsorption energy consists of the energy released in the reaction energy of SO_2 and H_2O and the adsorption energy of their reaction product on the Cu surface.

3.3.3 Electronic properties

To illustrate the electronic interactions between adsorbates and Cu (100) surface, we calculated the partial density of states of Cu and O atoms of co-adsorption configuration at the coverages of 0.25 ML and 0.5 ML, and the results are given in Figs. 3 and 4. As

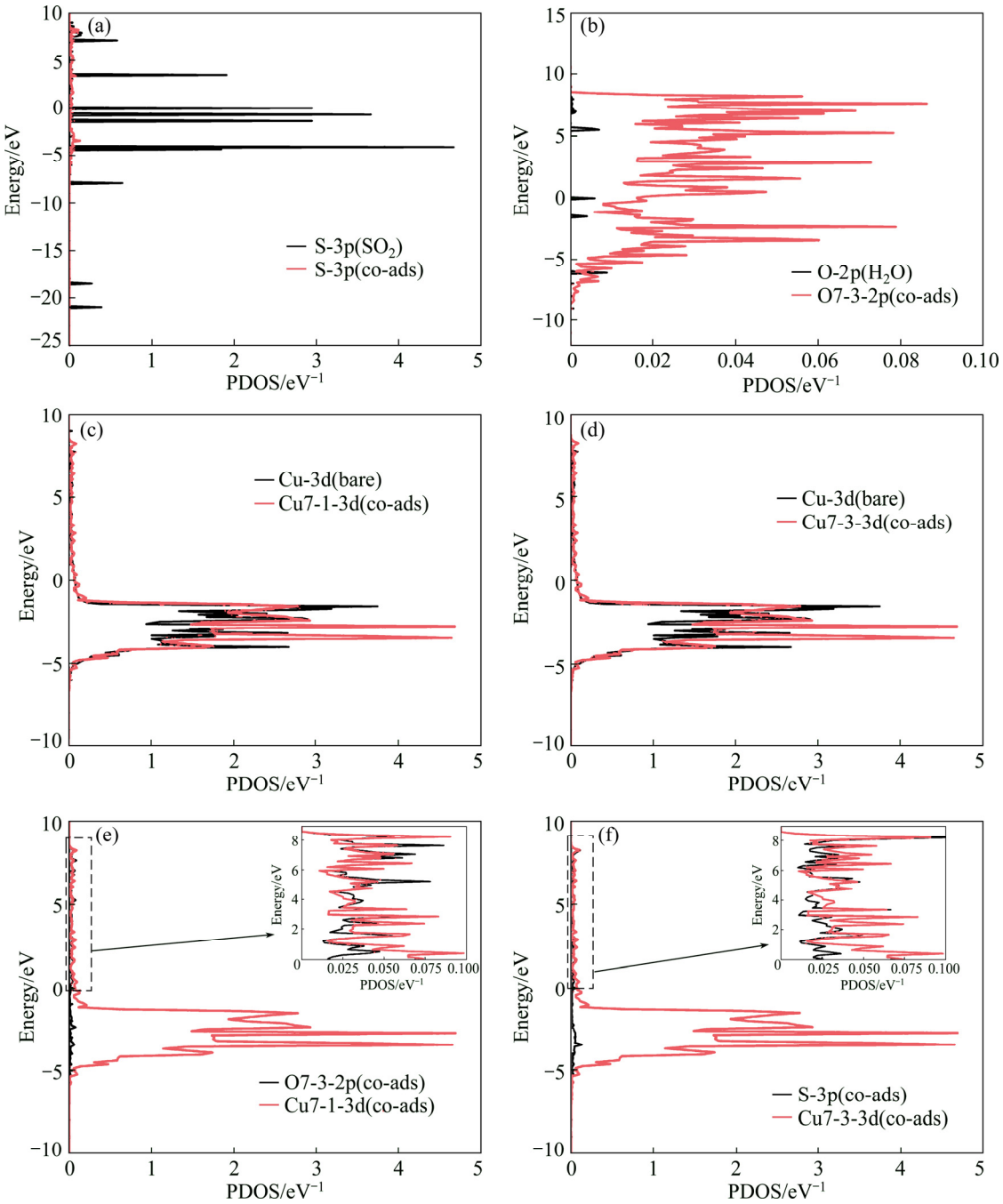


Fig. 3 Partial density of states for co-adsorption of SO_2 and H_2O at coverage of 0.25 ML: (a) S-3p(SO_2) and S-3p(co-ads); (b) O-2p(H_2O) and O7-3-2p(co-ads); (c) Cu-3d(bare) and Cu7-1-3d(co-ads); (d) Cu-3d(bare) and Cu7-3-3d(co-ads); (e) O7-3-2p (co-ads) and Cu7-1-3d(co-ads); (f) S-3p(co-ads) and Cu7-3-3d(co-ads)

shown in Figs. 3(a)−(d) and Figs. 4(a) and (b), the peaks of interacted Cu-3d, O-2p and S-3p shift uptowards in comparison with those of bare Cu atoms, O atoms of H_2O and S atoms of SO_2. This means that the adsorption occurs to adsorbed molecule on Cu (100) surface, which is the same as the geometrical structure. The electronic peaks of Cu-3d, O-2p and S-3p shift uptowards, which implies that the energy increase is due to the interactions between adsorbates and Cu (100) surface. The resonance of the PDOS peaks of O-2p and Cu-3d shown in Figs. 3(e) and (f) and Fig. 4(c) occurs in the entire energy range, indicating that an interaction happens between Cu atom of the surface and O atom.

To show clearly the electronic interactions between adsorbates and Cu (100) surface, we give the difference charge density with co-adsorption at the coverages of 0.25 ML and 0.5 ML. The figures of difference charge density show that the Cu atoms of the surface lose electrons and adsorbed molecules gain electrons (Fig. 5). The Bader charge analysis results (Tables 4 and 5) show

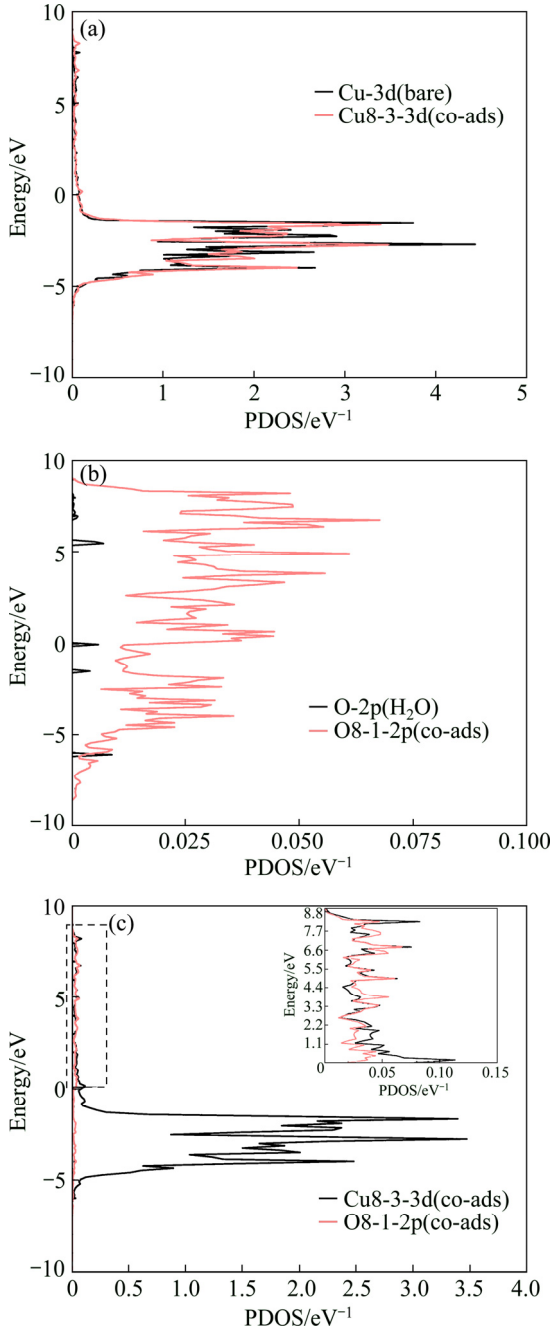


Fig. 4 Partial density of states for co-adsorption of SO_2 and H_2O at coverage of 0.5 ML: (a) Cu-3d(bare) and Cu8-3-3d (co-ads); (b) O-2p(H_2O) and O8-1-2p(co-ads); (c) Cu8-3-3d (co-ads) and O8-1-2p(co-ads)

that Cu atoms, H atom and S atom lose electrons and O atoms get electrons. In order to investigate the bonding of atoms, the valence charge density of co-adsorption at the coverages of 0.25 ML and 0.5 ML is also calculated and shown in Fig. 6. Obviously, the bonding between Cu atom and O may be found at the coverage of 0.5 ML, which indicates a chemical bonding between them. For the coverage of 0.25 ML, the interaction between Cu atoms and O atom or S atom is weaker than that at 0.5 ML.

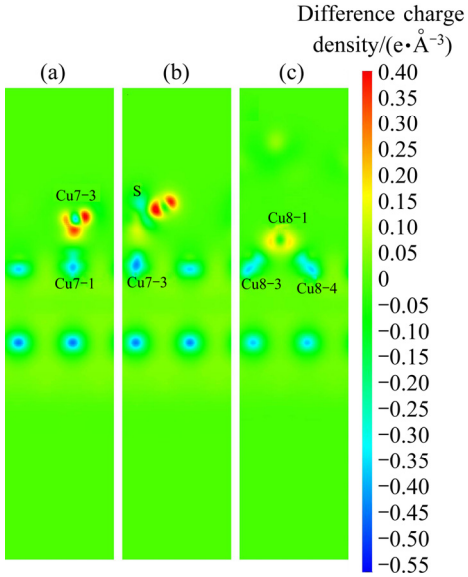


Fig. 5 Difference charge density of Cu atom and O atom (a) and Cu atom and S atom (b) with adsorbates at coverage of 0.25 ML, Cu atom and O atom (c) with adsorbates at coverage of 0.5 ML in co-adsorbed geometry

Table 4 Bader valence electron charges, charge transfer (relative to atoms) of co-adsorption of SO_2 and H_2O on Cu (100) surface at coverage of 0.25 ML

Atom	Valence charge/e	Charge transfer/e
Cu7-1	10.7832	0.2168
Cu7-2	10.9761	0.0239
Cu7-3	10.9406	0.0594
Cu7-4	10.9788	0.0212
S	4.0818	1.9182
O7-1	7.1935	−1.1935
O7-2	7.1981	−1.1981
O7-3	7.2458	−1.2458
H7-1	0.3302	0.6698
H7-2	0.3299	0.6701

Table 5 Bader valence electron charges, charge transfer (relative to atoms) of co-adsorption of SO_2 and H_2O on Cu (100) surface at coverage of 0.5 ML

Atom	Valence charge/e	Charge transfer/e
Cu8-3	10.7559	0.2441
Cu8-4	10.7119	0.2881
S	4.3802	1.6198
O8-3	7.1834	−1.1834
O8-2	7.1465	−1.1465
O8-1	7.1812	−1.1812
H8-1	0.3354	0.6646
H8-2	0.3187	0.6813

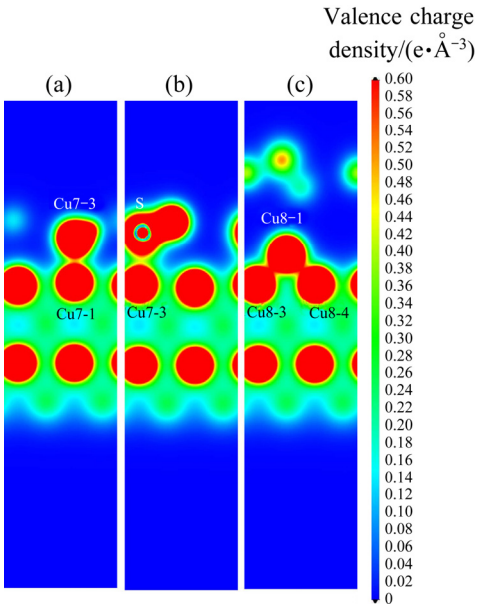


Fig. 6 Valence charge densities of Cu atom and O atom (a) and Cu atom and S atom (b) with adsorbates at coverage of 0.25 ML, Cu atom and O atom (c) with adsorbates at coverage of 0.5 ML in co-adsorbed geometry

4 Conclusions

1) With respect to the co-adsorption, H_2O molecule is dissociated and O—H is adsorbed on Cu atom of the surface with O atom, while another H atom of H_2O is bonded with O atom of SO_2, keeping away from the surface at the coverage of 0.5 ML. The SO_2 and H_2O are adsorbed on different Cu atoms with S and O atoms at the coverage of 0.25ML, respectively.

2) The co-adsorption energy is not equal to the sum of single adsorption energy of SO_2 and H_2O, which contains the interaction energy among the adsorbates.

3) The calculation of PDOS, difference charge density, valence charge density and Bader charge analysis illustrate that there are obviously chemical adsorption between Cu (100) surface and adsorbates at the coverage of 0.5 ML. The bonding of SO_2 and H_2O at 0.5 ML is not as strong as that at 0.25 ML.

4) The adsorption of gases by clean and fresh metal surface is a primary step in atmospheric corrosion, but the detailed mechanisms that drive co-adsorption of H_2O and SO_2 more easily than individual gas are obscure. The co-adsorption behavior of gases may shed light on further investigation of atmospheric corrosion mechanism.

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SO_2 和 H_2O 在 Cu (100)表面共吸附行为的密度泛函计算

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摘 要：利用基于密度泛函 GGA-rPBE 方法的平板模型研究 SO_2 和 H_2O 在面心立方金属 Cu (100)表面的共吸附行为。SO_2 和 H_2O 在 Cu (100)表面单分子吸附的计算结果表明，在覆盖度为 0.25 分子层和 0.5 分子层的情况，二者均不能以化学键的形式吸附在 Cu (100)表面上。针对 SO_2 和 H_2O 在 Cu (100)表面的共吸附行为，计算弛豫后的吸附结构、吸附能和电子性质(包括差分电荷密度、价电荷密度、Bader 电荷分析和分态密度分析)。结果表明，覆盖度为 0.25 分子层时，H_2O 和 SO_2 以化学吸附的形式各自吸附在表面不同 Cu 原子上；覆盖度为 0.5 分子层时，H_2O 分子解离成 OH 和 H，OH 吸附在表面 Cu 原子上，而 H 与 SO_2 键合后共同远离表面。

关键词：SO_2；H_2O；Cu；密度泛函；共吸附；平板模型；吸附能；电荷转移

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