

DFT Studies on the Nature of Coadsorbates on $\text{SO}_4^{2-}/\text{Au}(111)$

By Sudha Venkatachalam and Timo Jacob*

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, D-14195 Berlin, Germany

Dedicated to Prof. Dr. Dieter M. Kolb on the occasion of his 65th birthday

(Received May 18, 2007; accepted July 23, 2007)

Density Functional Theory / Au(111) Surface / Sulfate Adsorption / Hydronium / Water / Electrochemistry

Density Functional Theory (DFT) studies were performed on the adsorption of sulfate on Au(111). Focusing on the well-known $(\sqrt{3} \times \sqrt{7})\text{R}19.1^\circ$ structure reported by various surface sensitive techniques, the coadsorption of H_3O^+ and/or H_2O has been considered in different combinations. The calculated binding energies show that the coadsorption of a single H_3O^+ per sulfate is the most stable configuration, which is in agreement with experimental observations. Further, we find that in the case of coadsorption of both H_3O^+ and H_2O along with sulfate, one of the protons of hydronium moves to sulfate, finally leading to bisulfate with two coadsorbed water molecules. Besides the morphology and energetics of the different configurations, we also discuss the nature of the surface bonds by analyzing the charge density distribution.

1. Introduction

Specific adsorption of anions is a topic of interest in interfacial electrochemistry for the past two decades. Since the adsorption of anions, especially (bi)sulfate plays a major role in the structural modification of electrode surfaces, it has been extensively investigated by employing various electrochemical techniques in conjunction with *in-situ* structure sensitive methods [1, 2]. In the case of an Au(111)-electrode in contact with an aqueous electrolyte containing sulfuric acid, the nature of the species adsorbing at positive electrode potentials is still controversial. While the predominantly adsorbed species is

* Corresponding author. E-mail: jacob@fhi-berlin.mpg.de

mostly assumed to be sulfate, the presence of bisulfate cannot fully be excluded, resulting in the expression *(bi)sulfate* often used in literature. Although there is an agreement that the role of coadsorbates is to stabilize the sulfate structure, there is still no clear conclusion on their nature and geometry.

From Infrared Reflection Absorption Spectroscopy (IRAS) [3, 4] it has been observed that in the range of 0.4–1.2 V (*vs.* SCE – Saturated Calomel Electrode) the adsorbed species is sulfate ordered in a $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ structure with coadsorption of hydronium ions. Similar results have been reported from Scanning Tunneling Microscopy (STM) [5], Chronocoulometry, Radiotracer method [6] and Second Harmonic Generation (SHG) [7] studies. However, images obtained by Atomic Force Microscopy (AFM) [8] indicated that the adsorbed sulfate has C_{2v} -symmetry with coadsorption of water molecules in a zigzag-like structure. Using Surface-Enhanced Infrared Reflection Absorption Spectroscopy (SEIRAS) [9] in the range of 0–1.2 V (*vs.* RHE – Reversible Hydrogen Electrode) implies that between 0.75 and 1.0 V water coadsorbs along with sulfate, but below 0.5 V coadsorption of hydronium ions is seen with weak intensity. But from recent SEIRAS studies with an Attenuated Total Reflection (ATR) configuration on 20 nm thick Au(111)-film electrodes, Wandlowski *et al.* [10] proposed a new model, representing the adsorption of ordered $(\sqrt{3} \times \sqrt{7})$ -sulfate in three-fold hollow sites in conjunction with coadsorption of hydrated hydronium ions $H_5O_2^+$ (Zundel-ions). In this configuration one proton is shared between two water molecules, hydrogen-bonded to adjacent sulfate molecules.

While all previous studies agree that sulfate is adsorbed on the Au(111)-surface, using a combination of Fourier Transform Infrared Reflection Absorption Spectroscopy (FTIRS) and Low Energy Electron Diffraction (LEED) under Ultra-High Vacuum (UHV) Shingaya *et al.* [11–13] concluded that the adsorbate is ordered bisulfate with coadsorption of hydronium ions. This model is somehow supported by the increase of mass measured with Quartz Crystal Microbalance (EQCM) [14], which agrees with specific adsorption of hydrated bisulfate anions ($HSO_4^- + 4H_2O$).

While many experimental investigations of (bi)sulfate adsorption on Au-electrodes exist, at present there are only few theoretical simulations on the electronic structure and the interaction between (bi)sulfate and Au(111). Parritro *et al.* [15] have extensively studied the nature of the sulfate–Au(111) surface bond by performing *ab initio* calculations at the second-order Møller-Plesset (MP2) level on Au-clusters ranging from 22 to 64 atoms. Considering a single sulfate molecule only, they found the most stable adsorption site to have C_{3v} -symmetry, with three oxygens of sulfate being bound to three-fold hollow-sites (fcc), giving an overall binding energy of the anion of 143.9 kcal/mol.

Further studies on the electronic structure were performed by Legault *et al.* using Density Functional Theory (DFT) on finite Au-clusters sized between 3 and 13 atoms [16]. They concentrated on the adsorption of bisulfate and found

the most stable orientation to be tripod-like, where sulfur is located above a fcc-position with three oxygens pointing towards the next-nearest gold atoms. These latter interactions stabilize the sulfate orientation, for which they calculated a binding energy of 38.87 kcal/mol. In order to mimic the presence of an electrode potential, they additionally varied the overall charge state of the systems and discussed its behavior on the binding energy and geometry.

Hermse *et al.* [17] performed Kinetic Monte Carlo (KMC) simulations employing a lattice gas model for the substrate in order to study the adsorption of bridge-bonded anions on face-centered cubic (111) surfaces. The simulated voltammograms, which were obtained by determining the anion-coverage as a function of electrode potential, showed similarity to the behavior of (bi)sulfate adsorption on fcc(111) surfaces. In addition, they were able to compare the influence of sweeping rate, presence of surface steps, and the effect of lateral interactions to experiments.

Motivated by these somehow controversial models for the structure and role of the coadsorbates, we performed DFT-calculations studying the nature of coadsorbates on $\text{SO}_4^{2-}/\text{Au}(111)$. Concentrating on the $(\sqrt{3} \times \sqrt{7})\text{R}19.1^\circ$ structure of sulfate various combinations of coadsorbed water and/or hydronium ions have been investigated. After giving a short description of the methods (Sect. 2), we will first discuss each system separately and afterwards draw combining conclusions for the realistic system (Sect. 3). Finally, Sect. 4 will summarize and motivate future directions.

2. Methods

In order to study the nature of adsorbates on the Au(111) surface, we used Seq-Quest [18], a periodic DFT program with localized basis sets represented by a linear combination of Gaussian functions, together with the PBE [19] Generalized Gradient Approximation (GGA) exchange–correlation functional. A standard (non-local) norm-conserving pseudopotential [20] was applied to replace the 69 core electrons of each Au-atom, leaving the 5*d*- and 6*s*-electrons in the valence space and invoking a nonlinear core correction [21]. The basis sets were optimized “double zeta plus polarization” contracted Gaussian functions.

All calculations were performed on a six-layer slab, in which the lowest two layers were fixed to the calculated bulk crystal structure (with a lattice constant of $a_0 = 4.152 \text{ \AA}$), while the remaining four surface layers and the adsorbates were allowed to fully optimize their geometry (to $< 0.01 \text{ eV/\AA}$). Finally, all calculations were done (and tested to be converged), using a Brillouin zone (BZ) sampling of $8 \times 5 k$ -points for the $(\sqrt{3} \times \sqrt{7})$ unitcell.

It should be remarked that although the adsorption of sulfate is usually understood as binding of a negatively charged anion to the surface, after adsorption the electronic structure of the system is determined by the Fermi-energy

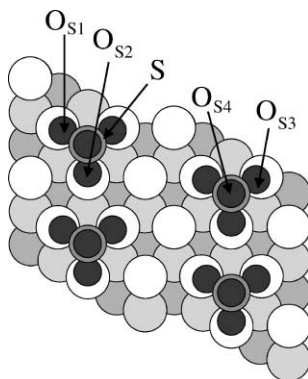


Fig. 1. On-top adsorption of $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ sulfate on Au(111).

of the entire system. Consequently, we allowed the electronic structure of the system to optimize self-consistently without manually manipulating the charge distribution. Future work will aim on investigating the role of an external electrode potential.

3. Results and discussion

In the following sections we first discuss the structural properties of adsorbed sulfate on Au(111) (see Fig. 1). Then the geometries and energetics of different combinations of coadsorbed water and/or hydronium ions are explained (Figs. 2–6). While structural parameters on covalent- and hydrogen-bonds are summarized in Tables 1, 2 and 3, binding energies are given in Table 4. Besides these information we will also compare charge density distributions, giving further insights into the electronic structures.

3.1 Sulfate adsorption

Our calculations on the nature of coadsorbates we began with first considering sulfate only. Besides the well-known $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ structure we also tested a $p(2 \times 2)$ -configuration, but as expected found the latter one to be less stable (*i.e.* higher surface free energy). The binding energies (E_{bind}) of the adsorbates on the slab were calculated as,

$$E_{\text{bind}} = E_{\text{tot}} - E_{\text{slab}}^{\text{clean}} - E_{\text{ads.}}^{\text{gas}} \quad (1)$$

where E_{tot} , $E_{\text{slab}}^{\text{clean}}$ and $E_{\text{ads.}}^{\text{gas}}$ are the total energies of the substrate–adsorbates system, the clean slab and the adsorbate molecules in gas-phase, respectively. The binding energy for top-adsorption of sulfate, where three of the oxygens form single covalent bonds on top of surface Au-atoms (see Fig. 1), is calculated to

Table 1. Distance between Au surface atoms and the adsorbed sulfate, water and hydronium in Å. The structure with initially coadsorbed water and hydronium transformed into bisulfate + 2 waters during the geometry optimization. See figures for atom labeling.

system		sulfate	1 water (Fig. 2a)	2 water (Fig. 3)	hydr. (Fig. 4)	water + hydr. (Fig. 6c)
(bi)sulfate	O_{S1}	2.19	2.26	2.22	2.29	2.54
	O_{S2}	2.19	2.20	2.31	2.35	3.17
	O_{S3}	2.19	2.18	2.22	2.56	2.55
water 1	H_{W1}^1		2.66	2.64		2.80
	H_{W2}^1		2.64	2.66		2.71
	O_{W}^1		2.38	2.42		2.53
water 2	H_{W1}^2			2.69		2.72
	H_{W2}^2			2.65		2.80
	O_{W}^2			2.43		2.54
hydr.	H_{H1}				2.93	
	H_{H2}				3.00	
	H_{H3}				3.00	
	O_{H}				3.28	

Table 2. Bond lengths within the adsorbates in Å. The structure with initially coadsorbed water and hydronium transformed into bisulfate + 2 waters during the geometry optimization. See figures for atom labeling.

system		sulfate	1 water (Fig. 2a)	2 water (Fig. 3)	hydr. (Fig. 4)	water + hydr. (Fig. 6c)
(bi)sulfate	$\text{S}-\text{O}_{\text{S1}}$	1.55	1.55	1.54	1.52	1.49 ($\text{S}-\text{O}_{\text{B1/2/3}}$)
	$\text{S}-\text{O}_{\text{S2}}$	1.55	1.54	1.56	1.53	1.64 ($\text{S}-\text{O}_{\text{B4}}$)
	$\text{S}-\text{O}_{\text{S3}}$	1.55	1.55	1.54	1.60	0.98 ($\text{O}_{\text{B4}}-\text{H}_{\text{B}}$)
	$\text{S}-\text{O}_{\text{S4}}$	1.45	1.45	1.46	1.46	
water 1	$\text{O}_{\text{W}}^1-\text{H}_{\text{W1}}^1$		0.99	0.99		0.98
	$\text{O}_{\text{W}}^1-\text{H}_{\text{W2}}^1$		0.99	0.99		0.99
water 2	$\text{O}_{\text{W}}^2-\text{H}_{\text{W1}}^2$			0.99		0.99
	$\text{O}_{\text{W}}^2-\text{H}_{\text{W2}}^2$			0.99		0.98
hydr.	$\text{O}_{\text{H}}-\text{H}_{\text{H1}}$				1.05	
	$\text{O}_{\text{H}}-\text{H}_{\text{H2}}$				1.02	
	$\text{O}_{\text{H}}-\text{H}_{\text{H3}}$				0.98	

be 2.41 eV. However, few earlier investigations about the adsorption of single sulfate ions on Au(111) proposed a structure in which these three oxygen atoms are adsorbed at surface hollow sites. Thus, in order to compare the stability

Table 3. Length of hydrogen-bonds between adsorbed species. See figures for atom labeling.

system		bond length [\AA]
1 water (Fig. 2a)	$\text{O}_{\text{S3}}-\text{H}_{\text{W2}}^1$	2.01
	$\text{O}_{\text{S1}}-\text{H}_{\text{W1}}^1$	1.99
2 water (Fig. 3)	$\text{O}_{\text{S1}}-\text{H}_{\text{W1}}^1$	2.54
	$\text{O}_{\text{S2}}-\text{H}_{\text{W2}}^2$	2.08
	$\text{O}_{\text{W}}^2-\text{H}_{\text{W2}}^1$	1.94
	$\text{O}_{\text{W}}^1-\text{H}_{\text{W1}}^2$	1.96
hydr. (Fig. 4)	$\text{O}_{\text{S3}}-\text{H}_{\text{H1}}$	1.72
	$\text{O}_{\text{S3}}-\text{H}_{\text{H2}}$	1.91
water + hydr. (Fig. 6c)	$\text{O}_{\text{B1}}-\text{H}_{\text{W1}}^1$	2.66
	$\text{O}_{\text{W}}^2-\text{H}_{\text{W2}}^1$	1.88
	$\text{O}_{\text{W}}^1-\text{H}_{\text{W1}}^2$	1.90
	$\text{O}_{\text{B2}}-\text{H}_{\text{W2}}^2$	2.17
	$\text{O}_{\text{B3}}-\text{H}_{\text{W2}}^2$	2.66

Table 4. Total binding energies of the different systems calculated using Eq. (1).

system		E_{bind} [eV]
sulfate		2.41
1 water	struct. a	3.35
	struct. b	3.32
2 water		4.47
hydr.		7.11
water + hydr.	struct. a	8.51
	struct. b	8.53
	struct. c	8.72

of top and hollow sulfate adsorption structures, we performed similar calculations on C_{3v} -hollow symmetry, but found a 0.58 eV lower binding energy. Therefore, it seems that top-adsorption becomes favorable when establishing an ordered adlayer on Au(111). Motivated by this result, in our further studies we concentrated on the top-adsorbed structure only. In this geometry the three surface-bound O-atoms are 2.19 \AA above the surface plane and their connections with the central sulfur are $\approx 1.55 \text{\AA}$. In contrast, the oxygen, pointing away from the surface, has $d(\text{S}-\text{O}_{\text{S4}}) \approx 1.45 \text{\AA}$.

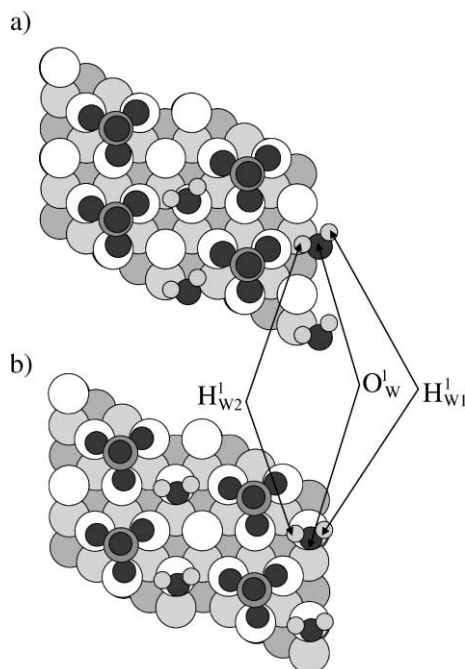


Fig. 2. Coadsorption of a single water on $\text{SO}_4^{2-}/\text{Au}(111)$ at different adsorption sites.

3.2 With coadsorption

Although several experimental methods have hitherto been employed, the composition and role of coadsorbate(s) is still a controversy. Moreover, theoretical investigations so far, have been mainly focused on adsorption of sulfate only without considering coadsorbate(s). Therefore, we performed calculations on different structures of coadsorption of H_3O^+ , H_2O and their mixture along with sulfate.

3.2.1 One water molecule

For this system we considered two possible orientations of water molecules at different adsorption sites, one in which the molecule is oriented parallel and another with perpendicular orientation with respect to the surface. Among these structures, we find the parallel orientation to be more stable by 0.85 eV. Interestingly, both possible adsorption sites shown in Fig. 2 are almost degenerate in binding energy ($\Delta E_{\text{bind}} = 0.03$ eV). This is certainly a result of the water molecules at both binding sites to be able to form the same amount of hydrogen-bonds to neighboring sulfate molecules. For the system shown in Fig. 2a the coadsorbed water molecule forms hydrogen-bonds to

O_{S1} of one sulfate molecule [$d(O_{S1}-H_{W1}^1) = 1.99 \text{ \AA}$] and O_{S3} of the diagonally opposite sulfate, which forms a chain-like structure along the $\sqrt{3}$ -direction [$d(O_{S3}-H_{W2}^1) = 2.01 \text{ \AA}$], whereas in Fig. 2b hydrogen-bonds are established to O_{S1} and O_{S2} of two adjacent sulfates. The overall binding energy of the former structure has been calculated to be 3.35 eV. In order to better understand the surface bond, we analyzed the charge density distribution, which showed a negative charge flow from Au surface atoms to the highly electronegative oxygen atoms of sulfate coordinated to the surface. In addition, there is also a slight charge flow from the surface to the coadsorbed water, indicating that besides the two hydrogen-bonds mentioned before the coadsorbates weakly bind to the surface. This is supported by the behavior of the overall binding. Assuming the same sulfate-surface bond strength as for the system without coadsorbates ($E_{\text{bind}} = 2.41 \text{ eV}$) and no water-surface connection, we would be able to deduce an energy contribution per hydrogen-bond of $\Delta E_{\text{bind}} = 0.47 \text{ eV}$, which is 0.19 eV larger than the typical hydrogen-bond energy obtained for a water-bilayer adsorbed on Pt(111) [22].

Regarding the geometry of the adlayer, the coadsorbed water molecule does not influence the bond distances within the sulfate molecule. Instead it slightly weakens the surface bonds of those oxygen atoms it forms hydrogen-bonds to, resulting in a slight increase in their distance to the surface plane.

3.2.2 Two water molecules

The coadsorption of two water molecules per surface unitcell has been considered with different initial orientations. While the first water has been chosen to be parallel to the surface, the other molecule was calculated either perpendicular (H-up and H-down, see Ref. [22]) or parallel to the surface. In all cases the final relaxed geometry accomplished with both water molecules being oriented parallel to the surface (Fig. 3). In this configuration O_{S2} of sulfate is hydrogen-bonded to the two neighboring water molecules (on different sides), leading to a distance to the surface of 2.31 \AA , which is 0.09 \AA larger compared to the surface distance of O_{S1} and O_{S3} . Furthermore, Fig. 3 reveals that the coadsorption of two water molecules along with sulfate forms a densely packed adsorbate layer with a continuous chain-like water network, connected by hydrogen-bonds (see dashed lines in Fig. 3). This leads to a configuration more stable than coadsorption of a single water, which is also reflected in the overall binding energy. Starting with sulfate only, coadsorption of the first water increases the overall binding energy by 0.94 eV, but with the second water molecule further increases by 1.12 eV to 4.47 eV for the final system. The larger increase coming with the second water can also be seen in the charge density distribution, showing over-proportionally more changes on the surface atoms compared to the coadsorption of a single water molecule.

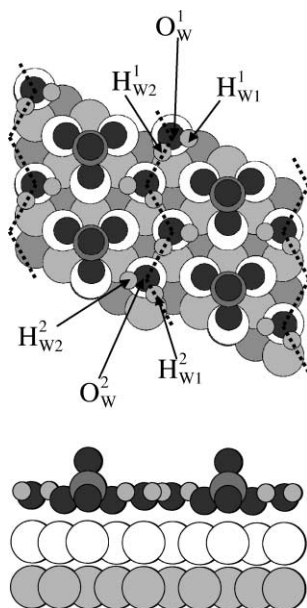


Fig. 3. Top and side view of the coadsorption of two water molecules on $\text{SO}_4^{2-}/\text{Au}(111)$. The hydrogen-bond network is indicated by dashed lines.

3.2.3 Hydronium ion

Since besides sulfate or bisulfate the electrolyte contains hydroniums as positively charged species its coadsorption along with sulfate is of particular interest. Although the specific adsorption of sulfate on Au(111) is observed at positive electrode potentials only, the two negative electron charges connected with each SO_4^{2-} somewhat overcompensate the positive charge distribution at the electrode surface. As a consequence, the electrolyte feels a net negative charge, attracting cations, *i.e.* hydroniums.

Figure 4 shows the top and side view of the most stable structure we obtained for coadsorption of a hydronium ion. In this geometry, each hydronium forms two hydrogen-bonds to $\text{O}_{\text{S}3}$ of adjacent sulfate molecules ($d(\text{O}_{\text{S}3}-\text{H}_{\text{H}1}) = 1.72 \text{ \AA}$ and $d(\text{O}_{\text{S}3}-\text{H}_{\text{H}2}) = 1.91 \text{ \AA}$). This weakens the surface bond of $\text{O}_{\text{S}3}$, leading to a distance to the surface of 2.56 \AA , which is 0.24 \AA longer than the surface distance of $\text{O}_{\text{S}1}$ and $\text{O}_{\text{S}2}$ (2.32 \AA).

In order to study the surface bonds and the electronic structure of the system in more detail, we again analyzed the charge density distribution. Figure 5a represents the side view of the single sulfate molecule coadsorbed with hydronium on Au(111), while Fig. 5b and c give the corresponding positive and negative charge density distribution of this system. For comparison, Figs. 5d–f

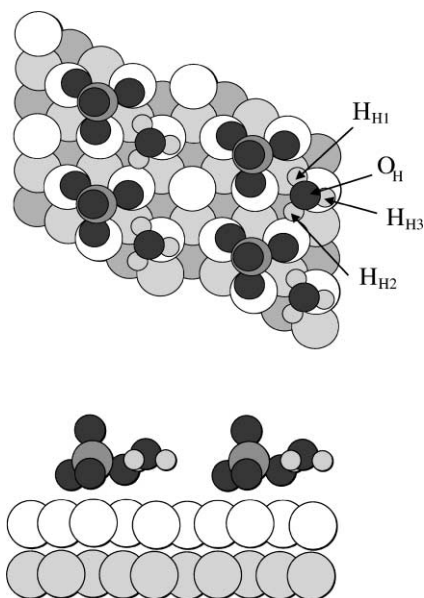


Fig. 4. The coadsorption of hydronium along with sulfate on Au(111). Top and side view of the systems is shown.

are the analogous plots for the system in which besides sulfate no coadsorbate is present on the surface. These plots show that the influence of sulfate on the charge density distribution of the surface is mainly limited to the three Au-atoms it binds to, which can be understood by the high electronegativity of the oxygen atoms. As a consequence, quite some negative partial charge is accumulated at these oxygens (Figs. 5c and f), coming from the three Au-atoms but also from the central sulfur atom (Fig. 5b and e). By comparing the charge density plots with and without coadsorbed hydronium, it turns out that there is no flow of charge from the surface to the coadsorbate, which means that there is no or only minor direct interaction of hydronium with the surface. Instead, due to the rather large positive partial charge located at each H-atom of hydronium, which interacts with and is polarized by the adjacent oxygen atoms of sulfate, hydronium establishes two relatively strong hydrogen-bonds to sulfate. Therefore, it is lucid that the major role of hydronium as coadsorbate is only to stabilize the $(\sqrt{3} \times \sqrt{7})R19.1^\circ$ sulfate structure, giving rise to the large overall binding energy of 7.11 eV.

3.2.4 Mixture of water and hydronium ion

Finally we studied the mixture of water and hydronium as coadsorbates. Interestingly, for all different initial configurations of the coadsorbates we have

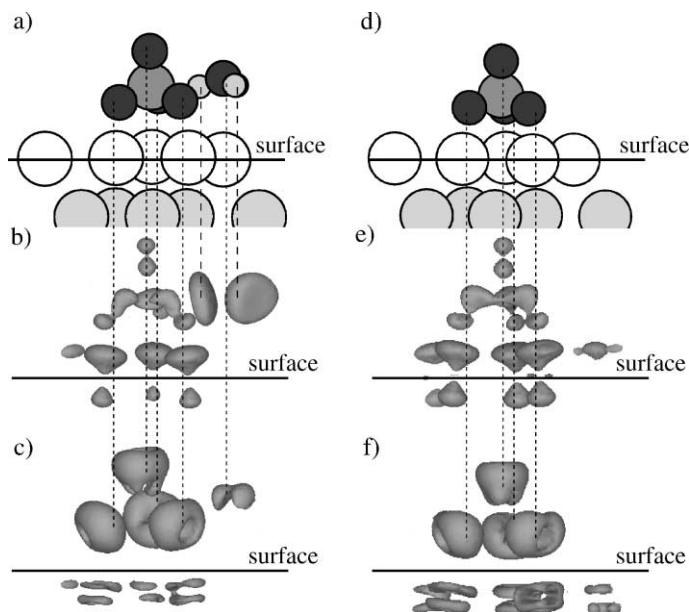
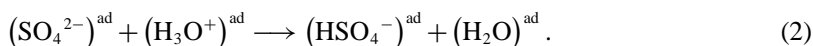


Fig. 5. Side views of the structure of sulfate on Au(111) coadsorbed with hydronium (a) and without (d). The corresponding positive [(b) and (e)] and negative [(c) and (f)] charge density distributions are also shown. In either case the charge density plots represent the distributions within the system part shown by the hard-sphere model above.

studied, it was observed that during the geometry optimization calculation one of the H-atoms of hydronium moves towards sulfate and hence forms bisulfate. Mapping the energy showed that there is no energetic barrier connected with this conversion. So, the final relaxed structure we obtained has one bisulfate and two water molecules (see Fig. 6a) and gives an overall binding energy of 8.51 eV. Here it should be remarked that this binding energy is referenced to the clean surface, sulfate, water, and hydronium, thus includes the formation energy:



For comparison, referencing to the clean surface, bisulfate and two waters would give an overall binding energy of only 3.14 eV, which is 1.33 eV lower than the binding energy obtained for coadsorption of two waters along with sulfate.

Since the bisulfate structure we obtained when starting the optimization with sulfate, water, and hydronium might represent a stable, but higher energy configuration, we also considered systems in which we directly begin the geometry optimization procedure with an adlayer of bisulfate and two water

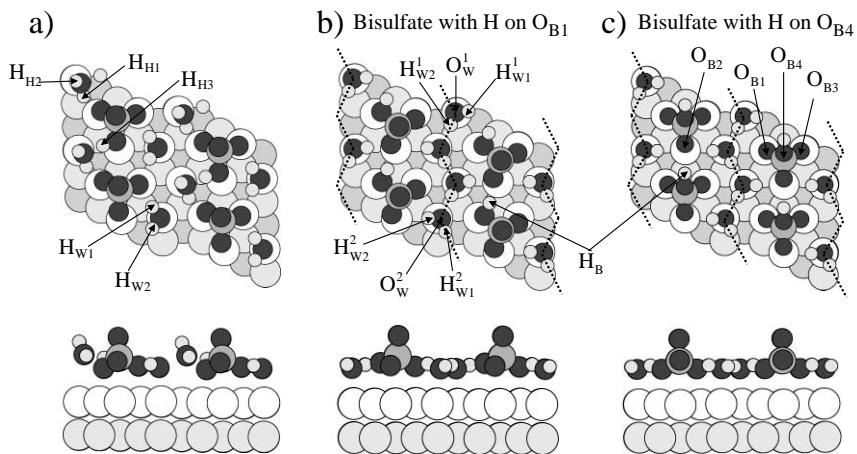


Fig. 6. Top and side views of the coadsorption of one water and one hydronium on Au(111). (a) shows the final geometry obtained from initially adsorbing sulfate + water + hydronium, while (b) and (c) result from the adsorption of bisulfate + 2 waters. H_B represents the hydrogen atom of the bisulfate. Structure (c), in which H_B is bound to the top O-atom of bisulfate (O_{B4}) is most stable. Hydrogen-bonds are indicated by dashed lines.

molecules. Here two different bisulfate conformations, one with the H-atom connected to O_{B1} (Fig. 6b), and another with hydrogen-bound to O_{B4} (Fig. 6c) are considered. Since the former structure, which can be understood as a *lying-down* orientation of bisulfate, shows a comparable binding energy of 8.53 eV, Fig. 6a seems not to be only a local minimum, but one of the degenerate *lying-down* structures. However, both systems are less stable than the *standing-up* orientation of bisulfate, in which the hydrogen is directed away from the surface, giving an overall binding energy of 8.72 eV.

The barrier-less formation of bisulfate observed here might have some implications for experimental studies. In case sulfate adsorbs specifically on the surface together with hydronium *and* water (only water is not sufficient), this results in an unstable adlayer, which transforms into *low-lying* bisulfate and two water molecules, again forming a chain-like hydrogen-bonded network. This transformation will also modify the overall geometric and electronic structure of the electrode/electrolyte-interface. However, if bisulfate is already formed in the bulk-electrolyte and adsorbs as such on the electrode surface, it most probably will adapt a *standing-up* configuration together with the coadsorption of one or two water molecules. In both cases there will most probably be no hydronium be present within the adlayer, is the single negative electron charge of bisulfate not sufficient to compensate the repulsion between the positive charges on the electrode surface and the hydronium molecules.

4. Summary and outlook

Different combinations of water and hydronium as coadsorbates on $(\sqrt{3} \times \sqrt{7})\text{R}19.1^\circ$ -ordered $\text{SO}_4^{2-}/\text{Au}(111)$ have been studied performing *ab initio* DFT-calculations. From the calculated binding energies we find that coadsorption of a single hydronium along with sulfate leads to the most stable structure. By analyzing the corresponding charge density distribution it was found that hydronium has no influence on the surface atoms, but instead stabilizes the ordered sulfate structure by forming connections between adjacent sulfate molecules along the $\sqrt{3}$ -direction via hydrogen-bonds. Interestingly, this connection was found to be even more relevant for the overall stability of the sulfate-structure than analogous connections along the $\sqrt{7}$ -direction. Instead of providing further stability, the combination of both kinds of connections, which could only be realized by the mixture of coadsorbed water and hydronium, led to the formation of bisulfate on the surface in the *low-lying* orientation. However, this structure, which might have some relevance for the experiment, is less stable than an analogous adlayer with *standing-up*-oriented bisulfate.

Acknowledgement

Support by the “Fonds der Chemischen Industrie” (FCI), the “Deutsche Forschungsgemeinschaft” (DFG), and the “Alexander von Humboldt Stiftung” (AvH) is gratefully acknowledged.

References

1. O. M. Magnussen, J. Hageböck, J. Hotlos, and R. J. Behm, *Faraday Discuss.* **94** (1992) 329.
2. O. M. Magnussen, *Chem. Rev.* **102** (2002) 679.
3. G. J. Edens, X. Gao, and M. J. Weaver, *J. Electroanal. Chem.* **375** (1994) 357.
4. I. R. de Moraes and F. C. Nart, *J. Electroanal. Chem.* **461** (1999) 110.
5. A. Cuesta, M. Kleinert, and D. M. Kolb, *Phys. Chem. Chem. Phys.* **2** (2000) 5684.
6. Z. Shi, J. Lipkowski, M. Gamboa, P. Zelenay, and A. Wieckowski, *J. Electroanal. Chem.* **366** (1994) 317.
7. S. Mirwald, B. Pettinger, and J. Lipkowski, *Surf. Sci.* **335** (1995) 264.
8. T. Nishizawa, T. Nakada, Y. Kinoshita, S. Miyashita, G. Sazaki, and H. Komatsu, *Surf. Sci.* **367** (1996) L73.
9. K. Ataka and M. Osawa, *Langmuir* **14** (1998) 951.
10. Th. Wandlowski, K. Ataka, S. Pronkin, and D. Dising, *Electrochim. Acta* **49** (2004) 1233.
11. Y. Shingaya and M. Ito, *Electrochim. Acta* **44** (1998) 745.
12. Y. Shingaya and M. Ito, *J. Electroanal. Chem.* **467** (1999) 299.
13. Y. Shingaya and M. Ito, *Chem. Phys. Lett.* **340** (2001) 425.
14. H. Uchida, M. Hiei, and M. Watanabe, *J. Electroanal. Chem.* **452** (1998) 97.
15. E. M. Patrito, P. Paredes Olivera, and H. Sellers, *Surf. Sci.* **380** (1997) 264.

16. M. D. Legault and D. E. Babelo, *J. Phys. Chem. A* **106** (2002) 9059.
17. C. G. M. Hermse, A. P. van Bavel, M. T. M. Koper, J. J. Lukkien, R. A. van Santen, and A. P. J. Jansen, *Surf. Sci.* **572** (2004) 247.
18. C. Verdozzi, P. A. Schultz, R. Wu, A. H. Edwards, and N. Kioussis, *Phys. Rev. B* **66** (2002) 125408.
19. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **88** (1996) 3865.
20. D. R. Hamann, *Phys. Rev. B* **40** (1989) 2980.
21. S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26** (1982) 1738.
22. T. Jacob and W. A. Goddard III, *J. Am. Chem. Soc.* **126** (2004) 9360.