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The determination of the local adsorption structure of SO₂/Ni(111): multiple-scattering cluster studies

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Abstract

The multiple-scattering cluster (MSC) method has been used to calculate the sulphur 1s near-edge x-ray absorption fine structure of SO₂ adsorbed on Ni(111). Our investigation confirms the flat-lying adsorption structure of SO₂/Ni(111) and shows for the first time that the fcc threefold hollow site is the most preferable adsorption site. It has been shown that the O–S intramolecular bond length is elongated by 0.07 Å, the ∠OSO bond angle is reduced by 10° after adsorption and the adsorption height is 2.0 ± 0.2 Å. Furthermore, *R*-factor analysis exhibits a local minimum in the vicinity of the fcc threefold hollow site, which is partly in agreement with the experimental result.

1. Introduction

In recent years, the interaction between sulphur dioxide (SO₂) and transition metal surfaces has become an attractive subject because of its important role in environmental protection [1–5]. Since the SO₂ molecule is a stronger π acceptor than carbon monoxide (CO), it reveals many different properties when adsorbed on metal surfaces. The flat-lying molecular orientation was elucidated through surface-extended and near-edge x-ray absorption fine-structure (SEXAFS and NEXAFS) studies of the molecule on all three low-index faces of nickel performed by Yokoyama *et al* [1]. They attributed the adsorption structure to the strong π acceptor, and suggested that the SO₂ molecule is adsorbed at the bridge site according to their SEXAFS analysis. Recently, Jackson *et al* repeated the NEXAFS experiment on the SO₂/Ni(111) adsorption system, and performed a normal incidence x-ray standing wavefield (NIXSW) study for the same system [2]. Their S K-edge NEXAFS spectra are in excellent agreement with those previously published by Yokoyama *et al* [1], and supported the flat-lying orientation of SO₂ on Ni(111), but NIXSW results indicate that both O and S atoms are found to be in the vicinity of atop sites, which are different from the bridge-site. They point out that the detailed sites can only be reconciled with a model in which the SO₂ molecules are centred close to hollow sites (with equal occupation of both types of hollow) and the bond angle is reduced to no more than 100°.

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NEXAFS has been shown to be a ‘fingerprint’ of the local structure near an absorbing atom [6], which contains a lot of adsorption geometry information, but the information obtained directly from the NEXAFS data is very limited. To obtain enough information about an adsorption system from NEXAFS, it is necessary to perform a theoretical analysis of the NEXAFS spectra. The multiple-scattering cluster (MSC) method is a powerful tool in studying NEXAFS processes. Our group has successfully employed the MSC method to analyse some adsorption systems [7–12], and obtained their adsorption information. Up to date there are very few NEXAFS theoretical reports of SO₂ adsorption systems, the main exception being our investigations of SO₂ adsorbed on Ag(110) and Cu(100) surfaces [11, 12]. It is urgent to perform a theoretical NEXAFS analysis of the SO₂/Ni(111) adsorption system which is helpful to clarify the conflicts between two previous studies [1, 2], and clearly obtain the local adsorption structure of SO₂/Ni(111). In this paper, we will use the MSC method to study the atomic structure as well as unoccupied electronic states of SO₂/Ni(111), and elucidate the physical origin of these resonances in the NEXAFS spectra.

2. The physics of NEXAFS and the MSC theoretical method

In the NEXAFS process, the core level electrons of a centre atom are excited by incident x-rays. The excited photoelectrons are scattered by atoms surrounding the centre and then transit into the unoccupied antibonding states or the shape resonance states, or directly leave the system if the x-ray energy is high enough (photoemission). As described above, the physical origin of NEXAFS and photoemission is similar, and this property allows us to utilize the dynamic theory of photoelectron diffraction to calculate the wavefunction of an intermediate photoelectron in NEXAFS [13, 14], then we can obtain the absorption cross section by the MSC method.

The multiple-scattering process of the excited photoelectrons in NEXAFS shows strong localization because of their low energy, so we can choose an adsorbed molecule and a few neighbouring atoms (about 30) in the substrate to construct a cluster which simulates the adsorption system. In the MSC calculation, we consider all multiple-scattering effects in the cluster, which are taken into account by the application of a Green function formalism. A detailed derivation of the formalism can be found elsewhere [7, 8]. Inputs to the calculation of NEXAFS spectra include the position of atoms in the chosen cluster, the incident x-ray polarization and the atomic scattering phase shifts (corresponding to s, p, d waves), which are calculated by the self-consistent field (SCF) X α method. For the calculation of the phase shifts a cluster muffin-tin (MT) potential with touching MT spheres has been used. The muffin-tin radii for the atoms is obtained according to the rule that the touching MT space is about 10% of the MT sphere. In the SCF X α calculation, the excited atom with one core hole has been considered, so the whole potential reflects the core hole effect on photoelectron scattering. This technique is in agreement with the so called ($Z + 1$) rule of phase shift calculation. The super-position and spherical averaging are done according to the scheme of Mattheiss in which the coulombic and exchange contributions to the muffin-tin potential are treated separately. We have obtained satisfactory NEXAFS results for a series of adsorption systems, such as SO₂/Ag(110), (SO + 2O)/Cu(100) by MSC calculation [7–12].

3. Results and discussion

3.1. The character of the experimental NEXAFS spectra of SO₂/Ni(111)

The S K-shell NEXAFS spectrum of SO₂/Ni(111) has been measured by Yokoyama *et al* [1], and is plotted in both figures 1(a) and 1(b). According to [1], The first and the second peak were

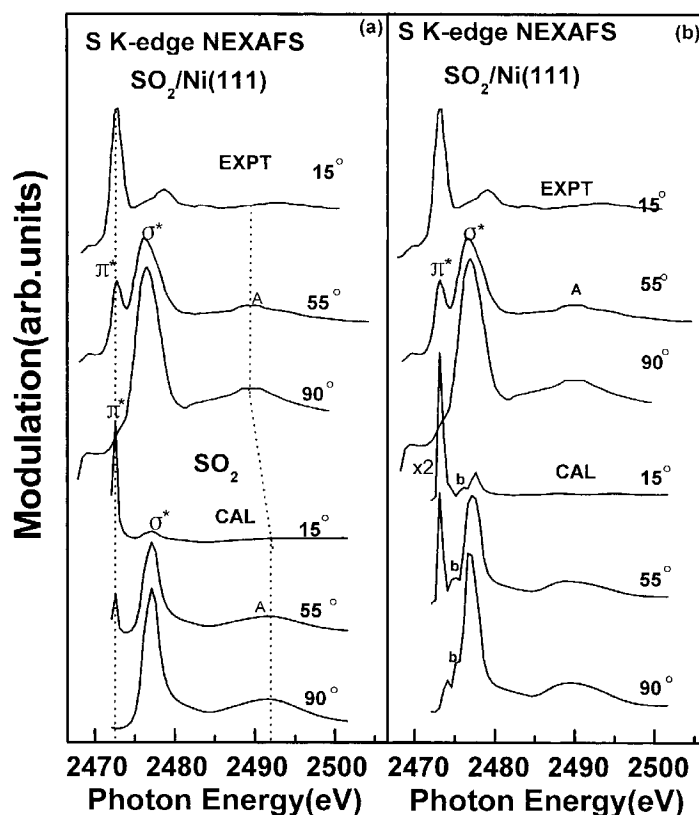


Figure 1. (a) Comparison between the experimental spectra of SO₂/Ni(111) and the calculated S 1s NEXAFS spectra of a flat-lying SO₂ molecule. (b) Comparison between the calculated S 1s NEXAFS spectra and the experimental data of SO₂/Ni(111). The experimental spectra are quoted from [1].

assigned the π^* and the σ^* resonances respectively, but there is no any assignment for the third broad structure in figure 1(a) or 1(b), which we labelled as the resonance 'A'. It is shown that the π^* resonance is strongly excited and the σ^* resonance is very weak at grazing incidence of x-rays, while the π^* resonance almost vanishes and the σ^* resonance is strongly excited at normal incidence. The strong dependence of the spectra on x-ray polarization is consistent with an orientation such that the molecular plane lies essentially parallel to the surface if the symmetry of the hybrid orbital of SO₂ is not reduced on adsorption as suggested in [1] and [2]; moreover, the broad structure 'A' reveals itself to be a shape resonance (discussed later). In order to inspect the contribution of a flat-lying SO₂ molecule to the experimental NEXAFS spectra and achieve a better understanding of the experimental ones, we have performed an MSC calculation for S 1s NEXAFS of the flat-lying molecule SO₂. The calculated S K-edge NEXAFS curves were also plotted in figure 1(a). Because the calculation of a flat-lying SO₂ is different from that of a free molecule, we do not compare it with the experimental result of the free SO₂ molecule. In our calculation, the S–O intramolecular bond length is taken as 1.43 Å, a commonly accepted bond length value for the gas-phase sulphur dioxide, and the OSO bond angle as 120°. We set the molecular plane perpendicular to the x-ray incident plane, and the incident angle (θ) of the x-rays with respect to the molecular plane changes from 15° to 90° according to the experimental conditions. The profile similarity between the calculated

spectra of the SO_2 molecule and the experimental ones of the $\text{SO}_2/\text{Ni}(111)$ adsorption system indicates that the main contribution of the experimental NEXAFS spectra comes from the flat-lying SO_2 molecule. Lower energy shifts of the A resonances for $\text{SO}_2/\text{Ni}(111)$ are observed as compared with the calculated spectra of the flat-lying SO_2 molecule. It is well known that for NEXAFS spectra of molecules constituted of low- Z elements, the energy position of the shape resonances is strongly correlated to the corresponding bond length; as the bond length increases, the energy position decreases [6]. The present results indicate elongation of the S–O bond after the SO_2 molecule is adsorbed on the Ni(111) surface.

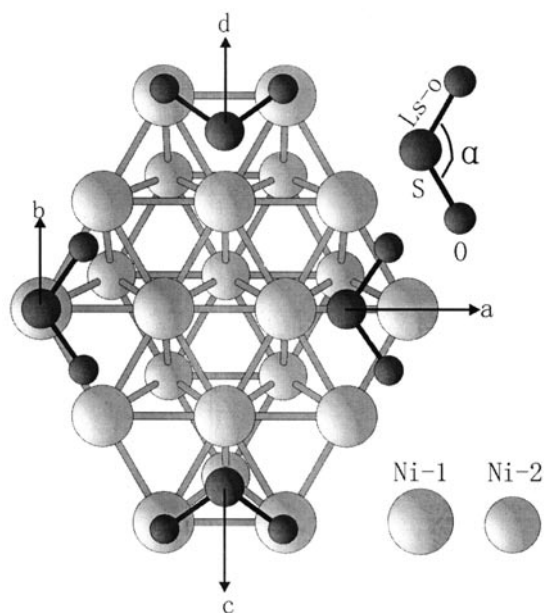


Figure 2. Top view of $\text{SO}_2/\text{Ni}(111)$ with four SO_2 molecules located at different adsorption sites: (a) bridge site; (b) top site; (c) hcp threefold hollow site; (d) fcc threefold hollow site.

3.2. Structure determination of SO_2 on Ni(111)

3.2.1. Comparison between different adsorption sites. Based on the flat-lying adsorption structure suggested by the experiments, we have constructed four high symmetry models shown in figure 2, and calculated the S K-shell NEXAFS spectra for these adsorption models. In our calculation, every parameter of each model has been optimized. Figure 3 shows the comparison between the calculated spectra and the experimental data of SO_2 adsorbed on different adsorption sites. The bold letters **a**, **b**, **c** and **d** in figure 3 represent the bridge site, the atop site, the hcp hollow site and the fcc hollow site respectively. By a direct inspection, one can find that many peaks appear in the calculated curves corresponding to models **a** and **b**; this character disagrees with the experimental result: we have to rule out the bridge-site and the atop-site adsorption models. For the hcp model, the calculated π^* resonances are too weak to fit the experiment, and we also have to get rid of this result. Fortunately, the calculated NEXAFS spectra of SO_2 adsorbed on the fcc threefold hollow site are perfectly in accord with the experimental ones on the whole. We judge that the fcc threefold hollow site is the preferable adsorption site.

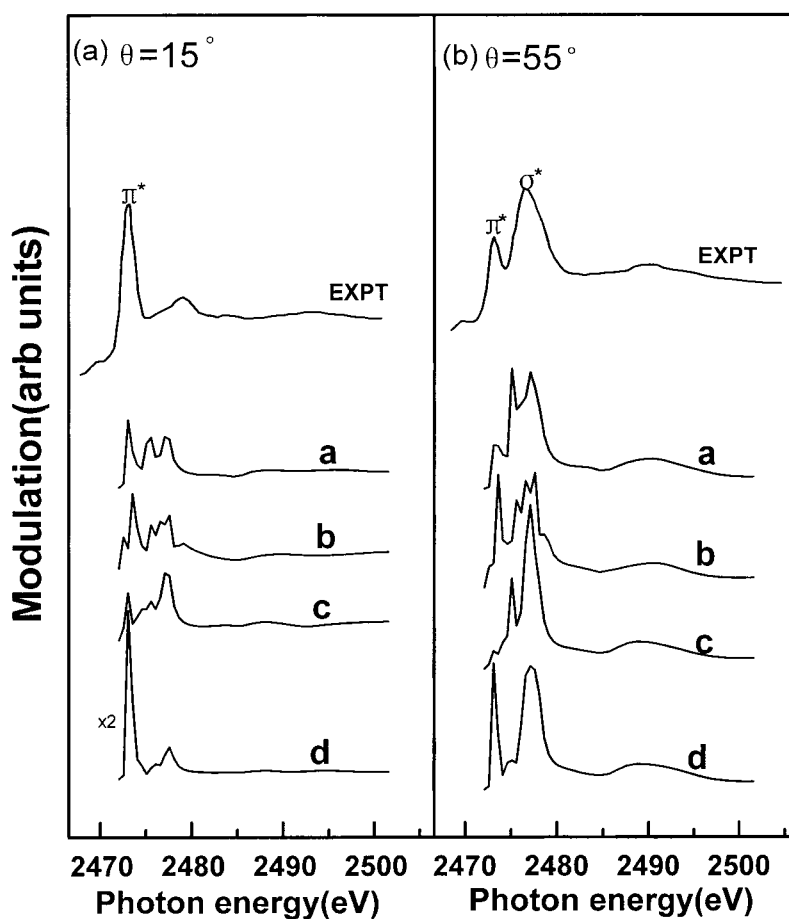


Figure 3. Comparison of the calculated S 1s NEXAFS curves in different models with the experimental spectrum: incident angle (θ) is (a) 15° and (b) 55° .

Incidentally, we exhibit the comparison between the experimental spectra and the calculated S 1s NEXAFS curves of SO₂/Ni(111) based on fcc threefold hollow model as well as those calculated for the flat-lying molecule SO₂ in figures 1(b) and (a). In our calculation, the adsorption height h (the distance between the S atom and the topmost layer of the substrate) is 2.0 Å, the S–O intramolecular bond length L_{S-O} is 1.5 Å and the OSO bond angle α is 110° . Because there are three equivalent orientations for the SO₂ adsorbed on Ni(111), we have to take the average over them. Obviously the calculated spectra are in good agreement with the experimental data as well. By a direct observation of the calculated spectra, we find that the intensity of the σ^* resonance is noticeably enhanced compared to the flat-lying sulphur dioxide spectrum at grazing incidence ($\theta = 15^\circ$). Meanwhile, there is a weak structure labelled as ‘b’ appearing between the π^* and the σ^* . The σ^* enhancement and the peak b appearance must originate from the charge transfer from the Ni substrate to the SO₂ molecule i.e. the effect of charge back-donation. Charge transfer from transition metals to adsorbed molecules has happened in many adsorption systems [9–11].

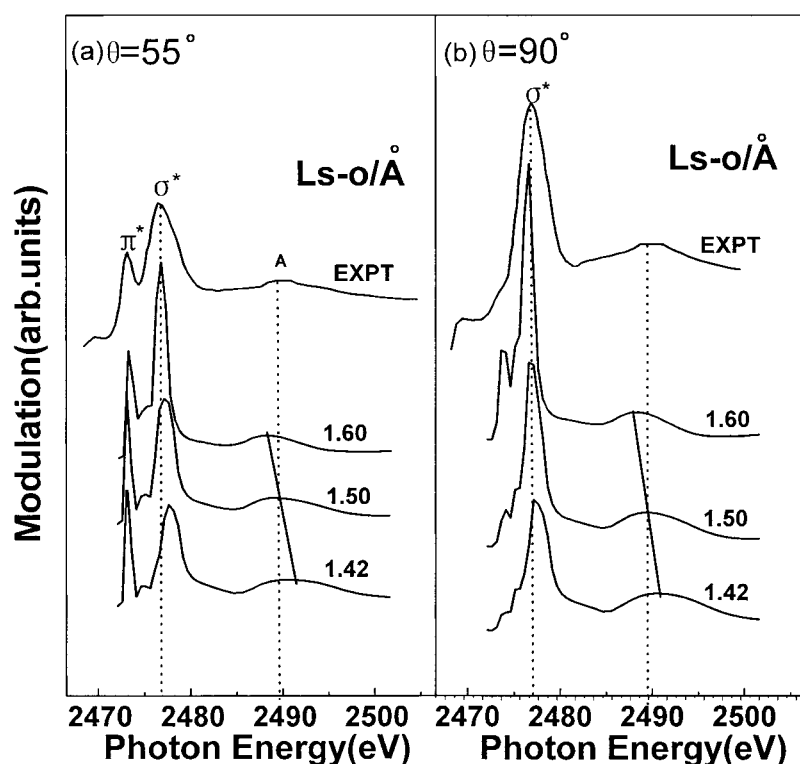


Figure 4. The calculated S 1s NEXAFS spectra of $\text{SO}_2/\text{Ni}(111)$ against the intramolecular bond lengths. The intramolecular bond length changes from 1.42 Å to 1.60 Å. The incident angle (θ) is (a) 55° and (b) 90° .

3.2.2. Determination of the internal conformation of the molecule SO_2 . Figure 4 is the comparison between the calculated NEXAFS spectra with different S–O intramolecular bond lengths of SO_2 and the experimental spectra. The other parameters in the calculation are kept the same as in figure 1(b). It is observed in figure 4 that the resonance A shifts towards the lower energy direction as the bond length $L_{\text{S-O}}$ increases, which is in agreement with the statement in [11]. By a direct observation of the peak A, we can find that it obviously moves to lower energy when the bond length $L_{\text{S-O}}$ increases, which is the character of the shape resonance. The strong dependence of peak A on S–O intramolecular bond length makes it possible to determine $L_{\text{S-O}}$ based on the energy position of peak A. From the comparison of calculation and experiment, the intramolecular bond length of SO_2 is estimated to be 1.50 ± 0.02 Å, which is in agreement with the experimental results [1, 2]. This S–O bond length is longer than that of the gas-phase SO_2 ; the elongation of $L_{\text{S-O}}$ originates from the interaction between the SO_2 and the Ni substrate.

Now we determine the last geometrical parameter of the adsorbed SO_2 , i.e. the bond angle $\angle\text{OSO}$. The σ^* resonance of gas-phase SO_2 corresponds to the electrons in the 1s state of the S atom excited to two nearby antibonding states a1 and b2 [15]. In figure 5, we have calculated the spectra for different OSO bond angles with other parameters taken the same as in figure 1(b). The experimental spectrum is also plotted in figure 5. One finds that the energy deviation between the states a1 and b2 is very sensitive to the bond angle; the smaller the bond angle α , the wider the deviation between a1 and b2. When α equals 100° , the σ^*

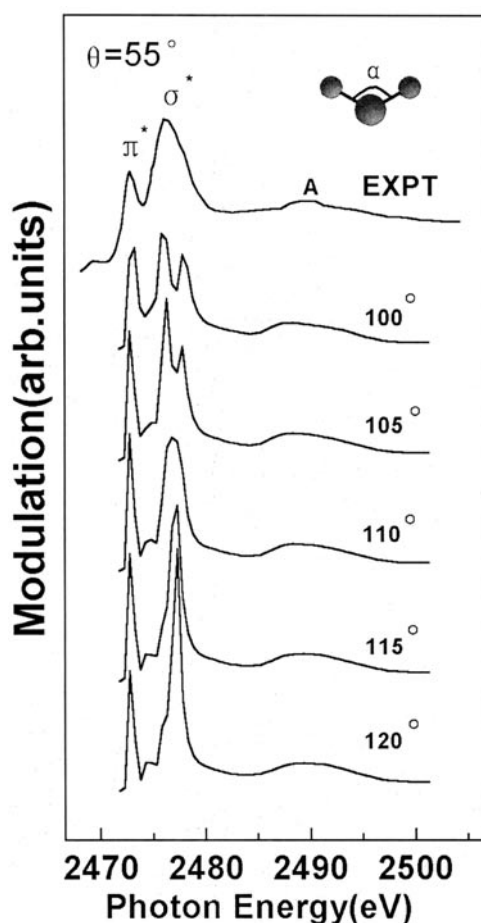


Figure 5. Plot of the calculated S 1s NEXAFS spectra of SO₂/Ni(111) against the OSO bond angles (α); in the calculation α changes from 100° to 120°. The incident angle (θ) is 55°.

resonance splits due to the separation of the states a1 and b2, which is not in agreement with the experiment. The calculated curve, corresponding to $\alpha = 120^\circ$, is also not in agreement with the experiment spectrum because the σ^* resonance is too narrow to conform to the experimental one. We conclude that the OSO bond angle is equal to $110^\circ \pm 5^\circ$. Our conclusion supports the statement about the reduction of the bond angle α due to the interaction between SO₂ and Ni(111) suggested by Jackson *et al* [2].

3.2.3. Is the fcc threefold hollow site the preferable adsorption site? The NIXSW experiment indicated that the S atoms are displaced significantly further from the atop site by about 1.0 Å [2]. In order to check up this result, we have constructed a different model in which the S atom is displaced from the atop site by a parameter X which is the distance taken from the atop site to the S atom. Both figures 6 and 7 exhibit the comparison between the experimental NEXAFS spectrum and the calculated curves in which the parameter X changes from 0.7 to 1.7 Å. In figure 6, the calculation was made according to setting the S atom at the hcp site and its vicinity, and none of the calculated curves are in agreement with the experimental spectrum.

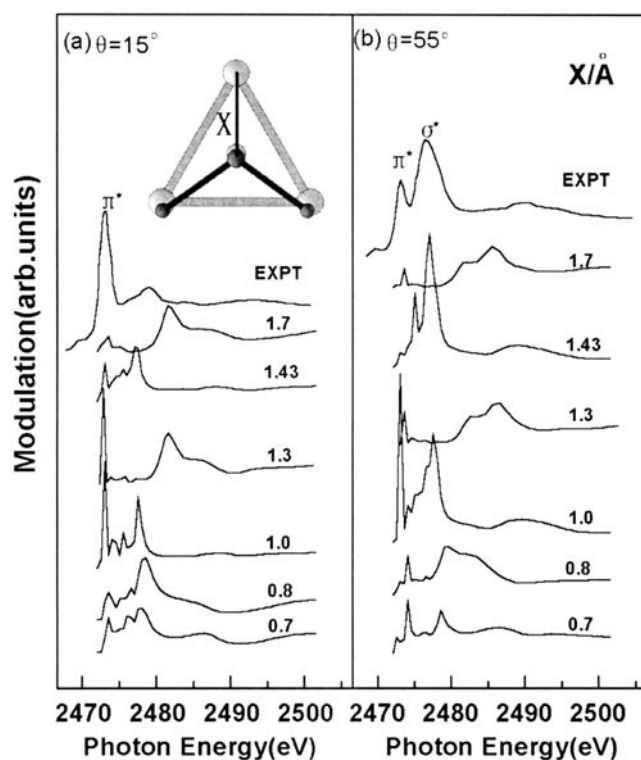


Figure 6. Plot of the calculated S 1s NEXAFS spectra of SO₂/Ni(111) against the parameter X in the vicinity of the hcp site, where X is defined as the distance between the S atom and the atop site as indicated in the inset.

So we exclude the possibility of SO₂ adsorbed in the vicinity of the hcp hollow site, which was suggested in [2]. Now we investigate the case where the SO₂ is adsorbed in the vicinity of the fcc site. The S K-edge NEXAFS spectra are very sensitive with respect to the parameter X in figure 7. It is easy to find that there exist two X values, i.e. $X = 1.43$ Å (fcc site) and $X = 1.0$ Å (vicinity of fcc), where the calculated NEXAFS curves are in good agreement with the experimental spectra. These positions seem to be two singularities when X changes from 0.7 Å (close to the atop site) to 1.7 Å (close to the bridge site), in which one is the fcc site; another one ($X = 1.0$ Å) is that proposed to be the correct adsorption site of SO₂ on Ni(111) by Jackson *et al* [2]. Hereinafter a question arises: is the fcc site the most preferable adsorption site of SO₂/Ni(111)? To facilitate the comparison, R -factor analyses have been performed to determine an exact X value.

3.2.4. R -factor analyses. We take account of the R -factor among four kinds of R -factors which are defined by Van Hove *et al* and Pendry [16, 17] for every x-ray incident angle while we define the average R -factor as follows.

$$R_i = \frac{1}{3}[R_i(90^\circ) + R_i(55^\circ) + R_i(15^\circ)]$$

where $R_i(90^\circ)$, $R_i(55^\circ)$ and $R_i(15^\circ)$ are R -factors for normal incidence ($\theta = 90^\circ$) and two grazing incidences ($\theta = 55^\circ$ and $\theta = 15^\circ$), respectively. The result of R_x has been plotted in figure 8(a). Obviously, a well-defined minimum is seen at $X = 1.43$ Å, which corresponds

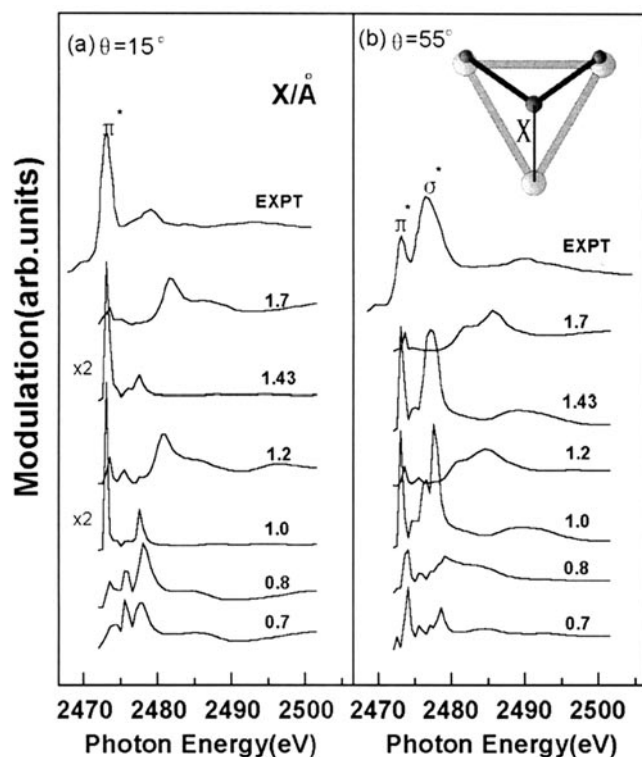


Figure 7. Plot of the calculated S 1s NEXAFS spectra of SO₂/Ni(111) against the parameter X in the vicinity of the fcc site, where X is defined as the distance between the S atom and the atop site as indicated in the inset.

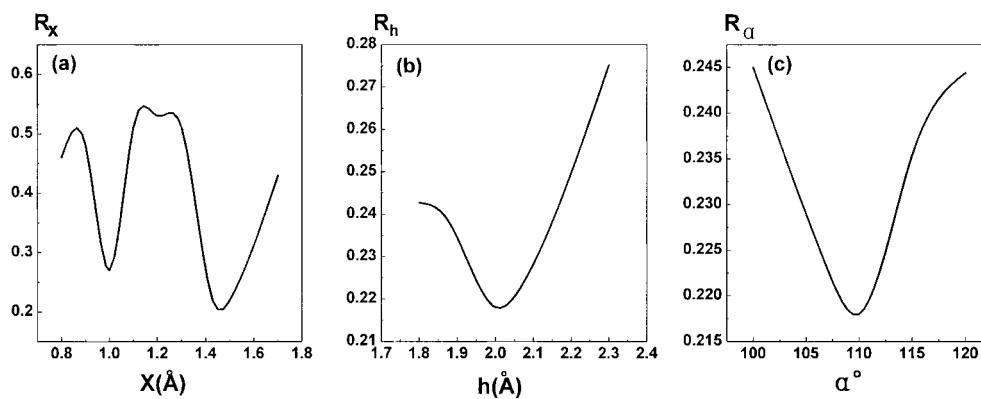


Figure 8. Plot of the average R -factors against three structural parameters: (a) asymmetrical parameter X ; (b) adsorption height h ; (c) bonding angle α .

to the fcc threefold hollow site. Meanwhile a local minimum appears at $X = 1.0 \text{ \AA}$, which is one of the asymmetric adsorption sites suggested in [2]. Our R -factor analysis confirms the conclusion that the fcc threefold hollow is the preferable adsorption site. The result indicates that both the O and S atoms are implicated in bonding with the substrate when SO₂ is adsorbed on Ni(111).

To obtain the clear best fit of the adsorption height (h) and the molecular bond angle (α), we perform the R -factor analyses for the two structural parameters. The results have been plotted as a function of the two structural quantities in figure 8(b) and (c). The well defined minima are seen at $h = 2.0 \text{ \AA}$ and $\alpha = 110^\circ$, which confirms the conclusion of the visual inspection of figure 5. We can deduce that L_{S-Ni} equals $2.5 \pm 0.1 \text{ \AA}$ and $L_{O-Ni} = 2.0 \pm 0.1 \text{ \AA}$ from the adsorption height (h) and the molecular bond angle (α).

4. Conclusions

We have calculated the S K-shell NEXAFS spectra of the SO₂ molecule as well as SO₂ adsorbed on the Ni(111) surface in terms of the MSC method. The results are inferred by induction as follows:

- (a) In SO₂/Ni(111), the sulphur atom is adsorbed on the fcc hollow site while the two oxygen atoms occasionally locate close to the top site. The S and two O are implicated in bonding to the substrate Ni atoms with $L_{S-Ni} = 2.5 \pm 0.1 \text{ \AA}$ and $L_{O-Ni} = 2.0 \pm 0.1 \text{ \AA}$. These structures can be considered as the η^3 -SO₂ configuration as suggested in [2].
- (b) A broad structure, labelled as A, exists in S K-shell NEXAFS spectra either for a flat-lying SO₂ molecule or for SO₂ adsorbed on the Ni(111) surface, which exhibits a shape resonance character.
- (c) In SO₂/Ni(111), the S–O bond length is equal to $1.50 \pm 0.02 \text{ \AA}$; it is longer than that of the gas-phase molecule. The O–S–O bond angle is equal to $110^\circ \pm 5^\circ$. The elongation of L_{S-O} and the reduction of O–S–O bond angle are due to the interaction between the adsorbate and substrate atoms.
- (d) R -factor analysis exhibits a local minimum in the vicinity of the fcc threefold hollow site, which was just proposed by Jackson *et al*

Acknowledgments

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References

- [1] Yokoyama T, Terada S, Yagi S, Imanishi A, Takenaka S, Kitajima Y and Ohta T 1995 *Surf. Sci.* **324** 25
- [2] Jackson G J, Lüdecke J, Driver S M, Woodruff D P, Jones R G and Chan A 1997 *Surf. Sci.* **389** 223
- [3] Wilde L, Polcik M, Haase J, Brena B, Cocco D, Comelli G and Paolucci G 1998 *Surf. Sci.* **405** 215
- [4] Terada S, Yokoyama T, Sakano M, Kiguchi M, Kitajima Y and Ohta T 1999 *Chem. Phys. Lett.* **300** 645
- [5] Terada S, Yokoyama T, Okamoto Y, Kiguchi M, Kitajima Y and Ohta T 1999 *Surf. Sci.* **442** 141
- [6] Stohr J 1992 *NEXAFS Spectroscopy (Springer Series in Surface Science Vol 25)* ed R Gomer (Berlin: Springer)
- [7] Tang J C, Feng X S, Shen J F, Fujikawa T and Okazawa T 1991 *Phys. Rev. B* **44** 13 018
- [8] Tang J C, Fu S B, Ji H and Chen Y B 1992 *Sci. China A* **35** 965
- [9] Hu X F, Chen C J and Tang J C 1996 *Surf. Sci.* **365** 319
- [10] Wang L, Zhuang F and Tang J C 1999 *Surf. Sci.* **436** 91
- [11] Zhu P, Tang J C and He J P 2000 *Phys. Chem. Chem. Phys.* **2** 1123
- [12] Zhu P, Tang J C and He J P 2000 *J. Phys. Chem. B* **104** 10 597
- [13] Li C H, Lubinsky A R and Tong S Y 1978 *Phys. Rev. B* **17** 3128
- [14] Fujikawa T 1981 *J. Phys. Soc. Japan* **50** 1321
- [15] Bodeur S and Esteva J M 1985 *Chem. Phys.* **100** 415
- [16] Van Hove M A, Tong S Y and Elconion M H 1977 *Surf. Sci.* **64** 65
- [17] Pendry J B 1980 *J. Phys. C: Solid State Phys.* **13** 937