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The local structure of SO_2 and SO_3 on Ni(111)

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Abstract

The normal incidence X-ray standing wave (NIXSW) technique, supported by X-ray photoelectron spectroscopy and near-edge X-ray absorption fine structure (NEXAFS), has been used to determine the local adsorption geometry of SO₂ and SO₃ on Ni(111). Chemical-state specific NIXSW data for coadsorbed SO₃ and S, formed by the disproportionation of adsorbed SO₂ after heating from 140 K to 270 K, were obtained using S1s photoemission detection. For adsorbed SO₂ at 140 K the new results confirm those of an earlier study [Jackson et al., Surf. Sci. 389 (1997) 223] that the molecule is located above hollow sites with its molecular plane parallel to the surface and the S and O atoms in offatop sites; corrections to account for the non-dipole effects in the interpretation of the NIXSW monitored by S1s and O1s photoemission, not included in the earlier work, remove the need for any significant adsorption-induced distortion of the SO₂ in this structure. SO₃, not previously investigated, is found to occupy an off-bridge site with the C_{3v} axis slightly tilted relative to the surface normal and with one O atom in an off-atop site and the other two O atoms roughly between bridge and hollow sites. The O atoms are approximately 0.87 Å closer to the surface than the S atom. This general bonding orientation for SO₃ is similar to that found on Cu(111) and Cu(100) both experimentally and theoretically, although the detailed adsorption sites differ.

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1. Introduction

Sulphur dioxide, SO_2 , is an important air pollutant created by the burning of sulphur-contaminated fossil fuels, yet also has beneficial effects in

that it has also long been used as a sterilising agent, and there have been several investigations of its surface chemistry. It is known to adsorb intact on noble and transition metal surfaces at low temperatures, but chemical interaction occurs on all these surfaces other than Ag [1] as the temperature is raised, leading to dissociation or disproportionation and the presence of coadsorbed SO_x species in which x has been variously proposed on different surfaces to be 1, 3 or 4 e.g. [2-7]. In addition to quite a number of studies to characterise these surface chemical reactions, there have been a small number of structural studies on Ni [7-10] and Cu [11-14] surfaces aimed at establishing the local adsorption geometry, principally of the intact SO₂ species; a short review of much of this work to 1996 is available [15]. One of the difficulties involved in studying the local bonding geometry of the reaction products is that these usually show no long-range order and the presence of coadsorbed species, each containing S, renders even element-specific local structural probes such as surface extended X-ray absorption fine structure (SEXAFS) inadequate for separating out the individual components, although there have been several studies using this technique [12,13].

An alternative local structural probe which offers both elemental and chemical-state specificity is X-ray standing waves, notably performed near normal incidence to the Bragg scatterer planes (NIXSW) [16] which allows investigation of imperfect crystalline substrates (such a typical metal single crystals) [17,16]. This technique is a variant of the general XSW method [18] and exploits the fact that under conditions of a X-ray Bragg reflection in a crystal, the interference of the incident and scattered waves gives rise to a standing wave in, and outside, the crystal which has a periodicity in intensity equal to the scatterer plane spacing associated with the Bragg condition. As one scans through the Bragg condition in incident angle or photon energy, there is a finite range over which the standing wave exists; within this range, the standing wave is systematically displaced in phase relative to the scatterer planes. The profile of the X-ray absorption at a particular atom as one scans through this range is characteristic of the spacing of this absorber relative to the extended scatterer plane positions. By measuring such layer spacings for two or more sets of (non-parallel) scatterer planes, the absolute location of the absorber can be established by triangulation. If the X-ray absorption is monitored by the photoemission signal from the absorbing (photoionised) atom, the 'chemical shifts' in the photoelectron binding energy, widely exploited in conventional X-ray photoelectron spectroscopy (XPS) allows one to separate the absorption profiles for atoms of the same element in different chemical states [19-21]. In the case of SO₂ interactions with surfaces, this means that shifts in the S1s photoelectron binding energy can be used to obtain separate NIXSW structural data from coadsorbed SO_x species [14]. Photoemission detection does, however, require special precautions in the data analysis; non-dipole effects in the photoemission create a forward/backward asymmetry in the angular dependence of the photoemission relative to the direction of photon propagation which means that the photoemission from the incident and reflected X-rays are not detected in an equivalent fashion by a detector having a finite acceptance angle [22]. However, this now seems to be well understood [23], and the method of data analysis can be modified to account for this effect [24].

In the case of SO_2 interaction with Ni(111), a NIXSW investigation of the intact adsorbed SO₂ at 150 K was conducted by our group several years ago, but at that time (using a bending magnet source of synchrotron radiation on the SRS (synchrotron radiation source) at Daresbury Laboratory, we were unable to perform the chemicalstate specific study necessary to investigate the surface reaction products [10]. This earlier study also predated our current understanding of nondipole effects in photoemission-detected NIXSW, so some small systematic errors are present in the analysed data. Here we present the results of a newer investigation exploiting the high brilliance undulator beamline (ID32) on the third-generation source of the ESRF (European synchrotron radiation facility) in Grenoble which allows chemical-state specific NIXSW experiments to be performed. We also consider the implications of the revised methods of data analysis which take account of non-dipole effects in photoemission.

2. Experimental details and surface characterisation

The Ni(111) sample, oriented by Laue X-ray diffraction, was mechanically polished and then cleaned in situ in the UHV end-station of the ESRF beamline by cycles of 2 keV argon ion bombardment and annealing at 630 °C. Low energy electron diffraction (LEED) was used to confirm the presence of a (1×1) ordered surface whilst the quality of the near-surface sample order and cleanness could be also assessed by the substrate NIXSW profiles and by electron-stimulated Auger electron spectroscopy. The beamline was fitted with an in-vacuum double-crystal monochromator using Si(111) crystals. Photoelectron and Auger electron emission spectra were recorded using the Physical Electronics concentric hemispherical dispersive analyser (fitted with multi-channel detection) installed at 45° to the incident X-radiation the (horizontal) plane of polarisation. SO_2 dosing was effected by introducing the gas (99.99% manufactured purity) into the main experimental chamber with the sample at low temperature (120-140 K), checking the purity in the UHV vessel with a mass spectrometer. Nominal exposures of about 10×10^{-6} mbar s were found to produce an essentially saturated layer of the adsorbate; to investigate some of the surface reaction products brief heating to specified temperatures were used, but NIXSW data were always recorded at the lowest temperature after subsequent re-cooling to minimise the effects of thermal vibrations.

The interaction of the SO_2 with the Ni(111) surface was first characterised by XPS using a nominal photon energy of 3060 eV (chosen to be well away from the standing wave excitation energy range), mainly in the S1s photoelectron energy range. Following SO₂ dosing onto the sample at low temperature the sample was briefly heated to higher and higher temperatures, taking XP spectra after each heating. No absolute calibration of the photoelectron binding energies was undertaken, so all such energies are nominal although, of course, the relative energies of the different S1s chemically shifted components should be reliable. The results are summarised in Fig. 1. Fig. 1(b) shows the set of S1s spectra obtained in this way which are compared with similar data collected in the earlier investigation using the SRS [10] in Fig. 1(a). Fig. 1(c) shows on a larger scale S1s spectra recorded at 140 K and after heating to 270 K taken during NIXSW measurements including some fitting of the components (see below). The overall trend of these spectra is as previously discussed [10]. At the lowest temperature the main peak at a nominal binding energy of approximately 2472 eV is assigned to the intact adsorbed SO₂. There is a clear shoulder on the high binding energy (low kinetic energy) side which has also been observed by Yokoyama et al. [8], and, indeed a similar effect has been seen in conventional



Fig. 1. S1s XP spectra recorded at a photon energy of 3060 eV from SO₂ adsorbed on Ni(111) at low temperature followed by heating to successively higher temperatures. The spectra in panel (b) are from the present study while those in (a) are from an earlier study [10] and are included for comparison. (c) shows two of the spectra from (b) on an expanded scale with the three component peaks labelled.

(laboratory-based) XPS on the S2p photoemission peaks be Zebisch et al. [4]. It is not clear whether this feature is due to partial occupation of a second SO₂ adsorbed layer or to an intrinsic satellite of the main chemisorbed SO_2 peak, although the fact that it seems to be present at all temperatures at which the SO₂ peak is seen rather suggests that it is an intrinsic feature of this one state. Heating causes this SO₂ feature to be replaced by two new peaks with nominal binding energies of approximately 2474 eV and 2469 eV. At the highest temperature only the lowest binding energy peak survives, and this is clearly assigned to chemisorbed atomic S, the energy being identical to that seen from a Ni(111)(2 \times 2)–S surface [10]. The identification of the 2474 eV peak is somewhat more controversial; the general consensus is that it can be assigned to SO_3 although on Cu(100) Polcik et al. have argued that it should be attributed to SO [5]. However, on Cu there are compelling arguments on the basis of vibrational spectroscopy [3], S1s XPS and NEXAFS [12] and S2p and O1s XPS [25], that the intermediate is SO₃, produced by the disproportionation reaction $(3SO_2 \rightarrow 2SO_3 + S)$. The fact that the relative binding energies of these features on Cu and Ni surfaces are the same, and that the NEXAFS of this intermediate state on Ni(111) (see below) is also essentially identical to that assigned to SO₃ on Cu(111), leads us to the clear conclusion that this intermediate in our present study on Ni(111)can also be assigned to this sulphite species.

To provide further characterisation of these different surface species S K-edge NEXAFS spectra were recorded from both the as-deposited SO₂ adsorbate at 140 K and from the same surface after heating to 270 K at different grazing incidence angles to the surface. Because the plane of incidence is the same horizontal plane as that of the polarisation of the incident synchrotron radiation, these grazing incidence angles also correspond to the angle of the polarisation vector relative to the surface normal. NEXAFS data were recorded by measuring the intensity of the S KLL Auger peak at approximately 2108 eV (SO₂) and 2111 eV (SO₃) at each photon energy in 0.2 eVsteps. The results are shown in Fig. 2, together with the associated S KLL Auger electron spectra.



Fig. 2. S K-edge NEXAFS from Ni(111) exposed to SO₂ at low temperature, and after heating briefly to 270 K, at different grazing incidence angles as labelled. Also shown are the S KLL Auger spectra used to monitor the X-ray absorption.

For the low temperature state, attributable (almost) entirely to SO_2 , the spectra show the behaviour already shown to be characteristic of this surface [8,10]. There is a strong polarisation dependence of the edge feature at a nominal photon energy of 2473 eV which is assigned to a transition to a final state of π -symmetry. The fact that this peak is intense at grazing incidence and vanishes at normal incidence clearly indicates that SO_2 adsorbs with its molecular plane parallel to the surface as previously established. In the case of the data taken after heating to 270 K, the XPS data of Fig. 1 show clearly that in this case one has coadsorbed S and SO₃. However, the large chemical shift in the S KLL Auger peak associated with this species appears to help considerably in separating these components. The NEXAFS spectra for this surface show a pronounced peak at much lower photon energies (approximately 2467 eV) attributable to the near-edge 'white line' of the chemisorbed atomic S, but the edge jump associated with this component is guite small, indicating that the two features around 2477 and 2479 eV can be assigned entirely to the SO₃. As remarked above, these features, and their polarisation angle dependence, are essentially identical to the behaviour seen for the reaction product obtained by heating SO_2 adsorbed at low temperature on Cu(100) [12] and Cu(111) [14]. In these cases the two peaks are attributed respectively to transitions of e and a₁ symmetry in SO₃, so the fact that the lower energy peak is strongest at normal incidence indicates that the C_{3v} symmetry axis of the SO₃ is essentially perpendicular to the surface.

In order to obtain quantitative information on the adsorption geometries, NIXSW absorption profiles using both the chemical-state specific S1s and O1s photoemission peaks were recorded for both the (111) and (111) Bragg reflections. To achieve this, photoelectron energy distribution curves (EDCs) were measured around the S1s and O1s peaks for a succession of photon energies in 0.2 eV steps in a range of 14 eV centred on the Bragg condition. The EDCs were recorded using an analyser pass energy of 30 eV in 0.25 eV steps in kinetic energy over a range of 18 eV for the S1s and 12 eV for the O1s spectra. The overall spectral resolution was 0.3 eV. To extract NIXSW absorption profiles the component peaks of these EDCs were fitted by Doniach-Sunjic line-shapes, and the resulting peak areas were plotted as a function of photon energy after normalising to the beam current monitor to correct for the timedependent decay of the photon flux. XP spectra were recorded before after each NIXSW measurement to check that there was no significant change in the adsorbate spectra due to radiation damage

or contamination. We should, perhaps, stress that the use of chemical-state resolved NIXSW means that the structure determinations are not sensitive to the exact surface preparation conditions (temperature, exposure) which may give rise to different relative surface coverages of the different coadsorbed species. The one caveat to this statement, of course, is that we assume that the local adsorption site of each species is not significantly influenced by the relative coverage of each coadsorbate; to some extent, the fact that each species appears to have a single well-defined S1s photoelectron binding energy, validates this assumption.

3. NIXSW results

The NIXSW absorption profiles from the chemically shifted S1s and O1s photoemission signals from the SO₂ and SO₃ adsorbate species are summarised in Fig. 3; the experimental data are shown as individual data points and the best-fit theoretical curves are shown as continuous lines. To achieve these fits we first determine the key nonstructural parameters of the absolute energy and the energy broadening of the monochromated incident X-rays by fitting to the bulk absorption profile extracted from the inelastically-scattered electron background signal below the photoemission peaks. A further check was to fit similar absorption profiles extracted from monitoring



Fig. 3. Experimental NIXSW absorption profiles for the S and O atoms in SO_2 and SO_3 on Ni(111) (data points) compared with the best-fit theoretical curves (full lines). The structural parameters found for these fits are given in Tables 1 and 2.

the Ni $2p_{3/2}$ photoemission signal through the XSW range, although in this case an approximate correction for the forward–backward asymmetry of the photoemission had to be applied (a rigorous treatment is not currently available for emission from p-states [23,24]). Using these values of the non-structural parameters derived from the substrate absorption profile the adsorbate S and O1s photoemission signals for each reflection were fitted to two structural parameters, the coherent position, d_{hkl} , and the coherent fraction, f_{hkl} , including full corrections for non-dipolar effects in the angular dependence of the photoemission [24]. Fig. 3 shows clearly that the quality of the resulting fits is good.

Table 1 shows the structural parameter values obtained in this way for the SO₂ adsorbed at 140 K. Also included (in square brackets) are the values obtained in an earlier investigation in which no correction was included for non-dipole effects in the photoemission [10]. The two experimental data sets yielded almost identical absorption profiles, and the difference in structural parameter values is almost entirely due to these non-dipolar corrections. By far the largest difference in these values is in the coherent fraction for the $(\overline{1}11)$ reflection, $f_{(\bar{1}1)}$, for the O absorbers; the non-dipole correction reduces this value from 0.70 to 0.29. These nondipolar corrections most commonly lead to (modest) reductions in the coherent fraction, although for certain combinations of parameter values there can be, as in this case, much larger changes in the coherent fraction and for some parameter combinations even substantial changes in the coherent positions. It transpires (see below) that this reduction in $f_{(\bar{1}11)}$ for the O atoms improves the fit to the structural model proposed earlier [10].

Interpreting these pairs of coherent position values to determine the adsorption site by triangu-

lation is simplest when a single high symmetry site is occupied. In particular, on an fcc(111) surface, there are three such high symmetry sites, atop a surface layer substrate atom, in a 'hcp' hollow atop a second layer atom, and in a 'fcc' hollow atop a third layer atom. If the substrate scattering plane spacing is $D_{(111)}$, then for these three geometries the expected value of $d_{(\bar{1}11)}$ are, respectively, $d_{(111)}/3$, $(d_{(111)} + D_{(111)})/3$ and $(d_{(111)} + 2D_{(111)})/3$. Taking the values specific to the S atom in SO₂ on Ni(111) the predicted $d_{(\bar{1}11)}$ values are thus 0.67 Å (atop), 1.75 Å (hep hollow) and 2.03 Å (fcc hollow). The experimental value of 0.71 Å is therefore in reasonable agreement with the atop site and clearly quite different from the other predicted values. Notice, incidentally, that the value of $d_{(\bar{1}11)}$ expected for equal occupation of the hcp and fcc hollow sites (and also for occupation of the lower symmetry bridging sites) is $(d_{(111)} +$ $1.5D_{(111)}$ /3 of 1.88 A, also far from the experimental value. The same arguments show that the predicted $d_{(\bar{1}11)}$ value for the O atoms for the atop site of 0.65 Å is also much the closest to the experimental value of 0.74 Å, although the discrepancy is a little larger.

While simple triangulation of the coherent positions thus favours occupation of atop sites for both the S and O atoms in adsorbed SO₂, it is clear that the $f_{(\bar{1}11)}$ coherent fraction values of 0.3 for both S and O are small, indicating that this simple identification of high symmetry sites is not valid. For low symmetry adsorption sites a real NIXSW measurement must average over all symmetrically equivalent positions on the surface, and for a set of Bragg scatterer planes not parallel to the surface such as ($\bar{1}11$) (at 70.5° to the surface) this means that the measurement averages over several different values of the spacing of the absorber site from the scattering planes, and this summation leads to

Table 1

Best-fit structural parameter values for NIXSW from the SO2 species adsorbed at 140 K on Ni(111)

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Absorber	$d_{(111)}$ /Å	$f_{(111)}$	$d_{(\bar{1}11)}$ /Å	$f_{(\bar{1}11)}$
s	2.02(5) [1.95]	0.90(5) [0.90]	0.71(5) [0.66]	0.30(5) [0.25]
0	1.94(5) [2.03]	0.74(5) [0.75]	0.74(5) [0.66]	0.29(5) [0.70]

The numbers in round brackets are the estimated precision in the last significant figure. The numbers in square brackets are the values obtained in an earlier study [10] which did not include any correction for non-dipole effects in the photoemission.

a coherent position which is generally a weighted average of these spacings, while the coherent fraction falls from its ideal value of unity for a single spacing. A simple procedure for performing this summation, which can be visualised as a sum of vectors in an Argand diagram, the amplitude and phase of the vectors being determined by relative occupation and layer spacing respectively, has been described previously [26]. Using this approach one can map the values of the two structural parameters, $d_{(\bar{1}11)}$ and $f_{(\bar{1}11)}$ as a function of the lateral position on an fcc(111) surface for a particular value of $d_{(111)}$ [10,16]. Fig. 4 shows the result of this exercise in the form of grey-scale maps with associated contours for each parameter over a rectangular region with the area of a primitive unit mesh on this surface. For this figure, however, an additional assumption has been made that the adsorbate does not distinguish between the two inequivalent (hcp and fcc) hollow sites, effectively introducing a mirror plane which is present in the outermost layer alone but not in the underlying substrate. Fig. 5, which we will discuss later in the context of the SO₃ data, shows the same coherent fraction map over a larger area of the surface and without the grey scale, allowing the contours to be seen more clearly. We have discussed previously the need for the added mirror plane in interpreting data for the $Ni(111)/SO_2$ system [10] and the equivalent map obtained without this additional assumption has been presented elsewhere [16]. In particular, without this additional symmetry our NIXSW structural parameters cannot be reconciled with any position of the SO_2 molecule on the Ni(111) surface.

Fig. 4 shows a rather surprising result of these simple calculations, namely that only two values of $d_{(\bar{1}11)}$ can occur, one corresponding to atop triangulation, the other to the mixture of hcp and fcc hollows (or equivalently, bridge sites), for *any position of the adsorbing atom on the surface*. This is why the nominal grey-scale map of $d_{(\bar{1}11)}$ in Fig. 4 has only two different levels, black (corresponding to the atop value) and white (corresponding to the value for the mixed hollows). As one displaces an adsorbate from an exact atop site across the surface the atop value of $d_{(\bar{1}11)}$ remains constant but the coherent fraction, $f_{(\bar{1}11)}$, falls steadily. Fig. 4. Grey-scale maps (with superimposed contours) of the $(\bar{1}11)$ coherent positions and coherent fractions for an adsorbate atom located at different lateral positions on a Ni(111) surface. The calculation sums over all symmetrically equivalent positions for low symmetry sites, and also assumes that the adsorbate does not distinguish between the two inequivalent (hcp and fcc) hollow sites, thus imposing an additional mirror symmetry plane. In the coherent position map, only two possible values are allowed; one of these corresponds to that expected for atop adsorption and is represented by black. The other value is that expected for mixed hollow site occupation and is shown as white. The lateral positions of outermost layer Ni atoms are labelled. In the coherent fraction map, contours are shown at spacings of 0.1 and a few of these contours are labelled with the values. The white rings superimposed on the map correspond to those regions in which the coherent position is that for an atop site but the coherent fraction is 0.30 ± 0.05 , as found for both the S and O atoms for adsorbed SO2. A local adsorption geometry for SO₂ consistent with these constraints is superimposed on the figure.

Eventually, $f_{(\bar{1}11)}$ falls to zero and a further displacement causes $d_{(\bar{1}11)}$ to switch to the mixed hollow value and $f_{(\bar{1}11)}$ to rise again. Notice that this sudden switch of the $d_{(\bar{1}11)}$ value occurs when the

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Fig. 5. ($\overline{1}11$) coherent fraction contour map for different positions on Ni(111) as in the lower panel of Fig. 4 but with the grey scale omitted and the map repeated over several unit meshes. The black ring corresponds to a ($\overline{1}11$) coherent position consistent with mixed hollow sites and a coherent fraction of 0.15 ± 0.08 as found for the S atom in adsorbed SO₃. The projection of an adsorbed SO₃ species in a geometry described in the text is superimposed on the map.

associated coherent fraction is zero and so the value of the coherent position at this location on the surface is meaningless. It is now straightforward to identify the regions on these maps which correspond to our measured coherent position and fraction values. Specifically, the coherent positions indicate atop triangulation and thus imply positions of both the S and O atoms within the area defined by the black levels in the coherent position map. Within this area we must place the atoms on the coherent fraction contour corresponding to 0.3, but within a range defined by the estimated precision. The white arcs superimposed on the coherent fraction map correspond to these regions, and superimposed on this map are possible positions of the S and O atoms within an adsorbed SO2 molecule. The S-O bondlength used in this diagram is 1.48 Å, the value obtained experimentally by SEXAFS on this surface [8]. The O-S-O bond angle in this diagram is 110°,

to be compared with the value for SO_2 in the gas phase of 119.5°. Clearly some modest distortion of this kind is not unreasonable as a result of the chemisorption. This same basic model and analysis was used to interpret the results of the earlier NIXSW study, but in this case the apparently much higher value of 0.70 for $f_{(\bar{1}11)}$ of the O atoms implied that the O atoms were significantly closer to the true atop sites, requiring a larger distortion of the O-S-O bond angle and a substantial expansion of the S–O bondlength. Using the non-dipole corrections, the true value of this coherent fraction is found to be much smaller, consistent with the O atoms being displaced further from the atop sites and thus a much smaller implied distortion of the adsorbed SO₂.

Fig. 3 also shows the NIXSW adsorption profiles and best-fit calculations for the S and O absorber atoms in the adsorbed SO₃ species, while Table 2 shows the resulting structural parameter values. Notice that in this case the value of $d_{(111)}$ for the S atom has had one (111) substrate interlayer spacing added to give a value which may be consistent with realistic S-Ni nearest neighbour bondlengths. An intrinsic feature of the XSW technique is that the true adsorbate-substrate layer spacing may differ from the coherent position by any integral number of substrate interlayer spacings, the correct number to be used being readily identified by simply considering the plausibility of adsorbate-substrate bondlengths. In this particular case the value of the coherent position used in the fitting was 0.65 Å, but it is clearly not possible for this to represent a true S-Ni interlayer spacing (even in the highest-coordination hollow sites this would infer a S-Ni nearest neighbour distance of 1.58 Å which is unrealistically short); adding one interlayer spacing overcomes this problem (and

Table 2

Best-fit structural parameter values for NIXSW from the SO_3 species adsorbed Ni(111) after briefly heating an SO_2 -covered surface from 140 K to 270 K

Absorber	$d_{(111)}/\text{\AA}$	$f_{(111)}$	$d_{(\bar{1}11)}/\text{\AA}$	$f_{(\bar{1}11)}$
S	2.69(5)	0.80(5)	2.08(5)	0.15(8)
0	1.82(5)	0.62(10)	1.04(5)	0.08(8)

The numbers in round brackets are the estimated precision in the last significant figure.

adding two such spacings is incompatible with any plausible combination of SO₃-Ni bondlengths). The value of $d_{(\bar{1}11)}$ for S has been similarly modified. Despite these corrections the $d_{(111)}$ value for the S absorbers of 2.69 Å is significantly longer than one might expect for a Ni-S chemisorption bond, whereas the equivalent value for the O absorbers is much shorter, but has a value which could be more readily reconciled with a Ni-O chemical bond, particularly as the nearest neighbour bondlength must be larger than $d_{(111)}$ for any adsorption site other than atop. We therefore infer that the SO_3 bonds to the surface through the O atoms with the S atoms higher above the surface, as has been found for SO₃ on Cu surfaces [12,14].

As may be seen from Table 2, the $f_{(\bar{1}1)}$ values for both the S and O atoms are extremely low, clearly indicating that these atoms are not in single high-symmetry adsorption sites, but we first consider the possibility of simple triangulation of the two coherent position values for each atom. In the case of the S, the measured $d_{(111)}$ value can be used to calculate the expected $d_{(\bar{1}1)}$ values for the different high-symmetry adsorption sites. The values thus derived are 0.90 Å (atop), 1.58 Å (hcp hollow), 0.22 Å (fcc hollow) none of which is close to the measured value of 2.08 Å. However, the value expected for mixed hcp + fcc hollows (or bridge sites) is 1.92 which is much closer to the experimental value. In this regard we note that, as shown in Fig. 4, for adsorption on (single) low symmetry sites on Ni(111) in which the hcp and fcc sites are not distinguished, this value of the coherent position is the one alternative to the atop site value. While the agreement between the expected and measured values of $d_{(\bar{1}11)}$ is therefore not very good, adsorption of SO₃ with the S atom in this part of the surface seems the most reasonable interpretation. Fig. 5 shows the same $f_{(\bar{1}11)}$ coherent fraction map of the surface as in Fig. 4 with the grey shading omitted and drawn over a wider area of the surface. Superimposed on this map is a black ring corresponding to the region of the surface around one of the Ni surface atoms for which both the coherent fraction and the coherent position correspond to the values found experimentally for the S atom.

Turning to the O NIXSW coherent position values, a similar prediction of the $d_{(\bar{1}11)}$ values to be expected for single high-symmetry adsorption site occupation gives values of 0.61 Å (atop), 1.29 Å (hcp hollow), 1.97 Å (fcc hollow) and 1.63 A (mixed hollows), none of which is reasonably close to the experimental value of 1.04 Å. In truth, this is not surprising. This procedure is formally only consistent for occupation of these high symmetry sites, although for a single low symmetry adsorption site (and all its symmetrically equivalent positions), the coherent position map of Fig. 4 shows that (with the added mirror symmetry) this type of triangulation must return one of two values, that for atop or that for mixed hollows. However, as is clear from Fig. 5, if the S atoms of SO₃ occupy a low symmetry site, and the C_{3v} molecular axis is perpendicular to the surface (as

molecular axis is perpendicular to the surface (as implied by the NEXAFS data), then the three O atoms cannot occupy equivalent sites, and must actually occupy at least two inequivalent low symmetry sites. This situation is not covered by the contour maps of Figs. 4 and 5 and further modelling is required. For this purpose our starting point is the fact

that the $d_{(111)}$ values for the S and O absorbers differ by 0.87 Å. If we assume that this represents the projection of the S–O bonds onto the C_{3v} axis, and that the S–O bondlengths are 1.50 Å (as in Na_2SO_3), then the angle of the S–O bonds to this symmetry axis is 55° and the length of the S–O bond projection onto the plane perpendicular to the symmetry axis is 1.22 Å. We now note that the $d_{(\bar{1}11)}$ value for O is between that expected for atop sites and for the hollow sites, so some combination of off-atop and off-hollow sites may give a better fit to the experiment. The model of SO_3 superimposed in the coherent fraction contour map of Fig. 5 has these properties. Note that the O atom in the off-atop site will lie higher above the surface than those O atoms in the sites roughly between the hollow and bridge sites. Taking a plausible value for the Ni-O nearest neighbour bondlength of 2.0 Å, these two layer spacings are estimated to be 1.98 Å and 1.48 Å. This would actually imply a tilt of the C_{3v} axis of the SO₃ away from the surface normal of 14°, small enough to be consistent with the NEXAFS conclusion that this

axis is perpendicular to the surface (typical precision estimates for this assignment in NEXAFS are $\pm 10-20^{\circ}$). More importantly, this height difference for the three O atoms above the surface is calculated to cause a 25% reduction in $f_{(111)}$, almost exactly the difference between the measured values of this parameter for the S atoms (in identical sites) and the O atoms (in the two different sites). The model defined by the superimposed SO_3 on Fig. 5 also allows us to determine the expected (111)coherent fraction and coherent position values for the individual O atoms which may be combined to give the values expected experimentally; a simple calculation yields values of 0.13 and 1.01 A respectively, both falling well within the estimated precision limits of the experimental values. This model is therefore clearly consistent with all of the experimental data; we have been unable to identify any other such model.

Finally, we should note that our NIXSW measurements of the surface annealed to 270 K also provided information on the local adsorption geometry of the chemisorbed atomic S. The coherent positions obtained were 1.59 Å for (111) and 1.73 A for (111). On the basis of this (111) value the predicted values for $(\bar{1}11)$ are 0.53 Å (atop), 1.21 Å (hcp), 1.89 Å (fcc) and 1.55 Å (mixed hollow or bridge). The closest fit is therefore to the fcc hollow site, although the measured value may be rationalised by partial co-occupation of the hcp hollow site. However, while the measured (111) coherent fraction was high (0.90) that for the (111) reflection was low (0.30) clearly indicating that the true situation must be more complex. In this regard, we may note that equal occupation of hcp and fcc hollow sites leads to a highest possible $f_{(\bar{1}11)}$ value of 0.50, so if there is some co-occupation of the hcp hollow, some reduction of this coherent fraction is to be expected; however, this cannot entirely account for the low value measured here. The origin of this effect is most probably partial local reconstruction of the surface. Atomic S chemisorbed on Ni(111) forms several ordered phases, two simple overlayers (2×2) and $(\sqrt{3} \times$ $\sqrt{3}R30^{\circ}$ and one reconstructed phase, $(5\sqrt{3} \times 2)$ rect. In the reconstructed phase, with equal co-occupation of the three rotationally-equivalent domains, NIXSW experiments show the value of $f_{(\bar{1}11)}$ is zero [27]. The simple Ni(111)($\sqrt{3} \times \sqrt{3}$)R30°–S phase, which should have a single well-defined S high-symmetry adsorption site and for which NIXSW triangulation indicated fcc site occupation, gave a low value of $f_{(\bar{1}11)}$ of only 0.50 [27], and is this was attributed to partial coverage of the reconstructed phase. A very similar effect could account for the results for the atomic chemisorbed S in the present experiments.

4. Conclusions

This new NIXSW study of the interaction of SO_2 with Ni(111), reinforced by measurements using XPS and NEXAFS, has refined the structure found for the intact SO_2 species adsorbed at low temperature in an earlier such study [10] and has determined the local geometry of the SO₃ species formed by the disproportionation reaction which occurs on heating. For adsorbed SO₂ the new data are essentially identical to the old, and the only real difference is in corrections applied to the data analysis to account for non-dipole effects in the photoemission which cause some modification of the derived structural parameter values, most notably the $f_{(\bar{1}1)}$ coherent fraction value for the O atoms. As a result of these corrections the originally-proposed model is confirmed. SO₂ lies above hollow sites with its molecular plane parallel to the surface and the S and O atoms in off-atop sites. The corrected NIXSW structural parameters, however, greatly reduce the chemisorption-induced distortion which was first thought to occur. Specifically, with the revised analysis the S-O bondlengths used are those found in an earlier experimental SEXAFS study [8], while only the O-S-O bond angle is modified by some 10° relative to its value in the gas phase. Note that this adsorption site is quite different from that proposed on the basis of the SEXAFS study of Yokoyama et al. [8] which concluded that the S occupied bridge sites, although these authors only considered high-symmetry locations for the S atoms. Our data are clearly not compatible with S atoms in bridge sites. This S-bridging model has been supported by total energy cluster calculations [28], but these calculations do not appear to have considered our structure in clusters with more than four Ni atoms.

For adsorbed SO_3 our data are shown to be compatible with a model in which the C_{3v} symmetry axis is slightly tilted (but by only about 14°) relative to the surface normal, the S-O bonds bent out of plane such that the O atoms are closer to the surface by some 0.87 Å, implying the adsorbate-surface bonding is through these O atoms. The molecular species occupies an off-bridge site such that one O atom is quite close to atop a surface Ni atom and the other two O atoms are roughly between hollow and bridge sites. There appears to be no previous determination of the structure of SO₃ on a Ni surface. However, previous investigations of this species on Cu(111) by NIXSW [14], and on Cu(100) by SEXAFS [12] have both concluded that the C_{3v} axis is essentially perpendicular to the surface and that the O atoms are closer to the surface and thus involved in the adsorbate substrate bonding. For Cu(100) this bonding geometry is also favoured by total energy calculations [29]. This similarity of behaviour for SO₃ on Cu and Ni surface is in contrast to the differences seen for SO₂, which adsorbs with its molecular plane parallel to Ni surfaces but perpendicular to Cu surfaces.

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