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The local structure of SO_2 and SO_3 on Ni(1 1 1): A scanned-energy mode photoelectron diffraction study

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ABSTRACT

O 1s and S 2p scanned-energy mode photoelectron diffraction (PhD) data, combined with multiple-scattering simulations, have been used to determine the local adsorption geometry of the SO_2 and SO_3 species on a Ni(1 1 1) surface. For SO_2, the application of reasonable constraints on the molecular conformation used in the simulations leads to the conclusion that the molecule is centred over hollow sites on the surface, with the molecular plane essentially parallel to the surface, and with both S and O atoms offset from atop sites by almost the same distance of 0.65 Å. For SO_3, the results are consistent with earlier work which concluded that surface bonding is through the O atoms, with the S atom higher above the surface and the molecular symmetry axis almost perpendicular to the surface. Based on the O 1s PhD data alone, three local adsorption geometries are comparably acceptable, but only one of these is consistent with the results of an earlier normal-incidence X-ray standing wave (NIXSW) study. This optimised structural model differs somewhat from that originally proposed in the NIXSW investigation.

1. Introduction

SO_2 is an atmospheric pollutant, and the main source of 'acid rain', arising from the burning of fossil fuels, so its catalytic chemistry is of considerable practical importance. As a result, there have been quite a number of model surface science studies of its interaction with metal surfaces. At low temperatures, the molecule adsorbs intact on many surfaces, but some form of reaction typically occurs below room temperature to produce surface SO_x species, with disproportionation to coadsorbed atomic S and SO_3 being reported on many surfaces, including those of Ni. Reaction of SO_2 with surface atomic oxygen on these surfaces also leads to enhanced SO_3 production. Experimental quantitative structural investigations of both SO_2 and SO_3 have been performed on a small number of surfaces, including several on the low-index faces of Ni (on (1 0 0) [1,2], on (1 1 0) [3,4] and on (1 1 1) [1,5,6]). On all of these Ni surfaces S K-edge NEXAFS (near-edge X-ray absorption fine structure) measurements have indicated that SO_2 adsorbs with its molecular plane essentially parallel to the surface, while on Ni(1 1 1) the same technique has led to the conclusion that SO_3, produced by disproportionation, is adsorbed on the surface with its internal C_{3v} symmetry axis essentially perpendicular to the surface [6].

The local adsorption site in these adsorption systems is, however, less clear. In the case of the Ni(1 1 1) surface, the subject of the present study, two rather different adsorption geometries have been proposed for the intact SO_2 species. Using SEXAFS (surface extended X-ray absorption fine structure), Yokoyama et al. [1] favour a geometry in which the S atom occupies a bridge site, whereas Jackson et al. [5,6] conclude that their NIXSW (normal incidence X-ray standing wavefield) measurements are consistent with the molecule being centred over a hollow site. The hollow site geometry was also found to give the best quantitative fit in multiple-scattering simulations [7] of the experimental NEXAFS data published by Yokoyama et al. and reproduced by Jackson et al. A B3LYP density functional theory (DFT) cluster calculation [8] of this adsorption structure, in which the substrate was modelled by just four Ni atoms, was found to favour the bridge site model of Yokoyama et al. More recently, however, a DFT slab calculation (using the CASTEP code) [9] concluded that the optimised bridge and hollow geometries (Fig. 1) are energetically the most favoured structures, but the difference in calculated adsorption energies was too small to provide a reliable basis for identifying the preferred geometry. However, these same calculations also found that the structural parameter values (the exact lateral position of the molecule on the surface) for the bridge geometry did not agree with those of

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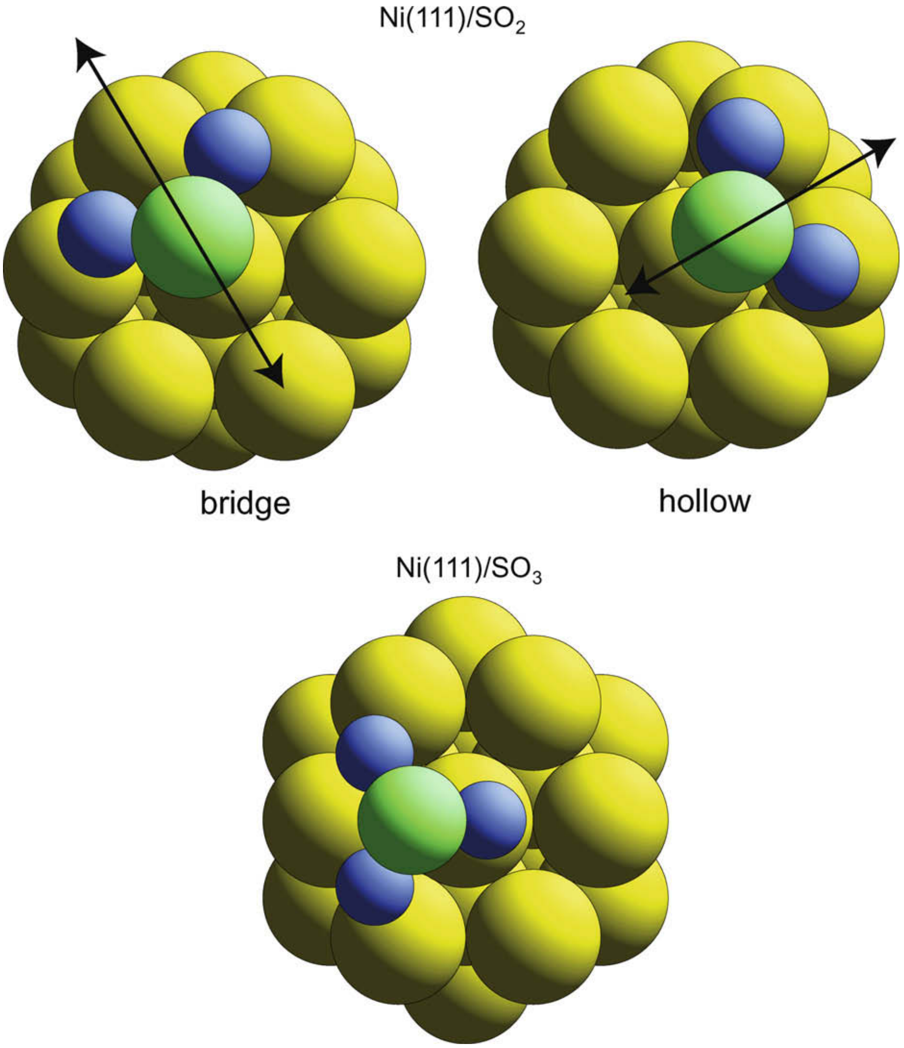

Fig. 1. Schematic plan views of the bridge and hollow SO_2 adsorption geometries on Ni(1 1 1), and of the NIXSW-optimised adsorption geometry for SO_3. For SO_2 the actual geometries shown here are those found in a recent DFT investigation [9]. Note that the original proposal for the bridge site model (based on SEXAFS experiments [1]) had the S atom (rather than the whole molecule) exactly in the bridging site. The arrows indicate the directions in which the molecules were displaced in the 'space-searching' PhD calculations.

the experimental SEXAFS investigation. In particular, while the SEXAFS experiments concluded that the S atom lies (exactly) in a bridging site, the DFT calculations yield an optimised bridging geometry for the molecule in which the S atom is displaced significantly towards an atop site (Fig. 1). Indeed, a DFT structural optimisation performed with the SEXAFS-derived structure as the starting model actually converged on the hollow site geometry. Of the two structural models proposed on the basis of experimental studies, these DFT results thus appear to favour the hollow adsorption site for SO_2 on Ni(1 1 1). However, new experimental data, from an entirely different structural technique, may provide a more definitive means of resolving this controversy.

With this objective in mind, we present here the results of an investigation of this adsorption system using scanned-energy mode photoelectron diffraction (PhD). Our investigation also includes a similar study of the local structure of the SO_3 species on Ni(1 1 1). Only one experimental determination of this structure has so far been published, by Jackson et al., based on NIXSW measurements [6]. The favoured adsorption geometry for this species corresponds to surface bonding through oxygen atoms, with the S atom (higher above the surface) in a bridging site relative to the outermost Ni substrate layer (Fig. 1). DFT calculations [9] yield a closely-similar optimal structure. Here we present the results of the experimental PhD investigation of these two adsorption systems, and also consider how these results may be reconciled with the detailed findings of the earlier experimental and theoretical investigations. We find further supporting evidence for the occupation of the hollow site by adsorbed SO_2; for SO_3 the optimal lateral positioning of the molecule on the surface differs from the conclusions of the earlier NIXSW study, but we show that the new geometry is, in fact, consistent with the NIXSW experimental data.

2. Experimental details and surface characterisation

The experiments were conducted in a conventional ultra-high vacuum surface science end-station equipped with the usual facilities for sample cleaning, heating and cooling. This instrument was installed on the UE56/2-PGM-1 beamline of BESSY II which comprises a 56 mm period undulator followed by a plane grating monochromator [10]. Different electron emission directions can be detected by rotating the sample about its surface normal (to change the azimuthal angle) and about a vertical axis (to change the polar angle). Sample characterisation in situ was achieved by LEED and by soft-X-ray photoelectron spectroscopy (SXPS) using