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## ARUPS of water adsorption on Si(100) and Si(111) surfaces

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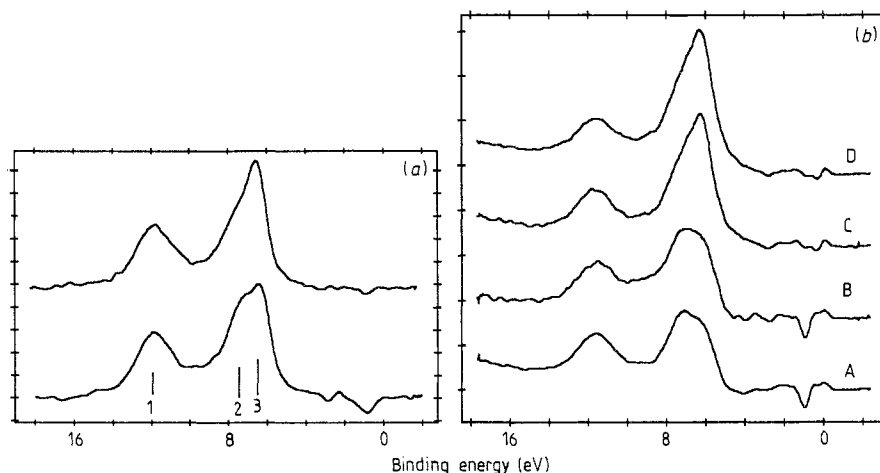
**Abstract.** Water adsorption on Si(100) and Si(111) surfaces at room temperature has been investigated by angle-resolved ultraviolet photo-electron spectroscopy (ARUPS) using synchrotron radiation. Earlier angle-integrated UPS studies have suggested that the adsorption is non-dissociative on (100) and dissociative on (111). The ARUPS data indicate that the adsorption is dissociative on both surfaces; the adsorbate-related valence features are similar and their binding energies agree closely with a self-consistent calculation of quasi-molecular SiOH. In this common dissociative-adsorption scheme there is no conflict between UPS and other techniques. The calculation provides an assignment of features which may allow the adsorption geometry to be probed by the application of photo-emission selection rules.

### 1. Introduction

Ultraviolet photo-electron spectroscopy (UPS) has a central role in the investigation of adsorption on surfaces: spectral features reflect the adsorbate-related electronic density of states. In the adsorption of molecular species, it is important to know if the molecule dissociates on the surface. In principle, a comparison of gas-phase and adsorbate-phase UPS will supply the answer; in practice, the comparison is often ambiguous. Where this question has been satisfactorily answered, for example for carbon monoxide on transition metal surfaces, angle-resolved UPS (ARUPS) can probe the bonding environment in considerable detail (Plummer and Eberhardt 1982). However, where there is ambiguity, as is often the case for water vapour, then UPS, ARUPS and *a priori* modelling have to iterate to a conclusion which is consistent with the results of other techniques.

The adsorption of water on silicon surfaces provides a ready example of the problem. For Si(111)7 × 7, UPS indicates that the adsorption is dissociative at room temperature (Schmeisser and Demuth 1986); a wide range of other surface techniques are in agreement. However, for Si(100)2 × 1, UPS has been interpreted as indicating non-dissociative adsorption, whereas all other techniques indicate dissociative adsorption. This conflict is a barrier to more detailed studies of this system. In this paper we argue that UPS of the

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**Figure 1.** (a) ARUPS spectra of H<sub>2</sub>O adsorption on vicinal Si(100), recorded at normal incidence; the clean surface contribution has been subtracted. The lower spectrum was recorded with light polarised in the [011] azimuth and the analyser also in the [011] azimuth at 20° from the surface normal. The upper spectrum was recorded with light polarised in the [0 $\bar{1}$ 1] azimuth and the analyser at 70° from the surface normal in the [011] azimuth. (b) ARUPS difference spectra of H<sub>2</sub>O adsorption on Si(111): A, recorded at 70° incidence, normal emission; B, at 45° incidence, normal emission; C, at normal incidence, 70° emission; D, at 20° incidence, 70° emission.

H<sub>2</sub>O–Si(100)2 × 1 system should be interpreted as indicating dissociative adsorption, i.e. that there is no such conflict. This conclusion is based on the comparison of recent self-consistent calculations of the electronic levels of SiOH (McMillan 1988) with ARUPS measurements of the (100) and (111) surface adsorption systems.

## 2. Results

ARUPS spectra were recorded on station 6.2 at the Daresbury Laboratory SRS. This comprises an ADES 400 spectrometer coupled to a toroidal grating monochromator. The photon energy was 36 eV. The (100) sample had a vicinal surface off-cut by 5° towards [011], resulting in a single-domain surface (McGrath *et al* 1988). Fuller details of sample preparation and water dosing procedures are given elsewhere (McGrath *et al* 1988).

Figure 1 shows difference spectra obtained by subtracting clean and adsorbate spectra following suitable scaling (Briggs and Seah 1983). Figure 1(a) shows spectra for single-domain Si(100)2 × 1; the spectra in figure 1(b) are for Si(111)7 × 7. For both surfaces the spectra comprise a single feature at ≈12 eV and a doublet feature centred at ≈7 eV with respect to the Fermi level; these features are numbered according to binding energy. For the (100) surface, as shown in table 1, peak 1 is located at 11.9 eV and peaks 2 and 3, the two components of the doublet, are at 7.5 and 6.5 eV respectively. For the (111) surface the recorded binding energies are 0.3 eV lower, but the same separations of the features are maintained.

For the two spectra in figure 1(a) the electron emission vector is in the plane perpendicular to both the (100) surface and the mirror plane containing the dimers; the choice of this plane is discussed in § 3 below. For the lower spectrum the polarisation vector is also in this plane, i.e. a ‘symmetric’ geometry; for the upper spectrum the

**Table 1.** Binding energies of orbitals predicted by theories for H<sub>2</sub>O dissociation on Si(100), compared with the experimentally determined values.

	Experiment (eV)	Ciraci and Wagner (1983)	Katircioglu (1987)	McMillan (1988)
<b>Peak 1</b>				
Content		Si s + O p	Si s + O p	Si-O
Label		Oσ	Oσ	
Energy	11.9	18.5	18.8	19.99
<b>Peak 2</b>				
Content		O p-H s	O p-H	OH
Label		3σ	3σ	
Energy	7.5	14.8	16.0	15.58
<i>Separation</i> 1 and 2	<b>4.4</b>	3.7	2.8	<b>4.4</b>
<b>Peak 3</b>				
Content		OH 1π	O p	O p
Label		O π	O π	
Energy	6.5	12.1	12.2	14.38
<i>Separation</i> 1 and 3	<b>5.4</b>	6.4	6.6	<b>5.6</b>

polarisation vector is perpendicular to this emission plane, i.e. an 'antisymmetric' geometry. The (111) surface has no mirror plane symmetry and the spectra range from normal emission at grazing incidence (lowest curve) to grazing emission at near-normal incidence (uppermost curve).

### 3. Discussion

The background to this topic has recently been reviewed by Thiel and Madey (1987): Schmeisser and co-workers have used UPS extensively to study water adsorption on silicon surfaces (Schmeisser *et al* 1983, Schmeisser 1984, Ranke and Schmeisser 1984, Ranke *et al* 1985). The observation of three valence features for (100) as against two for other surfaces is the main basis for interpreting the adsorption as non-dissociative. Against this, infra-red reflection-absorption spectroscopy (Chabal 1985 and references therein) and electron energy loss spectroscopy (Nishijima *et al* 1986 and references therein) show vibrational features characteristic of dissociation; two recent core-level photo-electron studies (Larsson *et al* 1987a, McGrath *et al* 1988) also favour dissociation, as do recent electron-stimulated desorption ion angular distribution (ESDIAD) methods (Larsson *et al* 1987b). There is further support for dissociation from two theoretical studies (Ciraci and Wagner 1983, Katircioglu 1987), although these are limited by non-self-consistency.

The earlier UPS measurement (Schmeisser *et al* 1983) on the (100) surface shows essentially the same three features which are evident in figure 1. In that work a direct comparison was made with gas-phase UPS of water. Peak 1 was aligned with the 1b<sub>2</sub> level of water vapour and peaks 2 and 3 were assigned to the 3a<sub>1</sub> and 1b<sub>1</sub> levels respectively. This required differential shifts in binding energy of -0.4 eV for 3a<sub>1</sub> and +0.6 eV for 1b<sub>1</sub>; the rationale given was that the latter shift is due to Si-H<sub>2</sub>O bonding via this lone pair orbital, while the former shift is due to a concomitant weakening of OH bonding

within the water molecule. The authors rejected dissociative adsorption on the grounds that gas-phase OH could contribute only two orbitals, whereas three spectral features are observed (for dissociation into OH and H, the photo-emission cross-sections show spectra to be dominated by OH levels). They commented that chemisorbed OH would result in a third ( $\text{Si } 2s + \text{O } 2p_z$ ) feature as provided by the calculation of Ciraci and Wagner (1983), but the mismatch in binding energy (see table 1) was too great.

Given the conflict between this interpretation and the results of other techniques, it seems reasonable to consider dissociative adsorption further. The orbital spectrum of molecular OH should comprise a  $\sigma$  O–H bond and (at lower energy) a doubly-degenerate non-bonding  $\pi$  level. As a first step, the UPS of the adsorbate can be discussed in terms of these levels by equating  $\sigma$  with peak 1 and  $\pi$  with peaks 2 and 3; the doublet nature of the  $\pi$  feature can be attributed to the lifting of the degeneracy of the  $\pi$  levels in a non-normal bonding configuration. An earlier ARUPS study of the vicinal (100) surface (McGrath *et al* 1988) adopted this assignment as the basis for the application of the mirror-plane selection rules. This paper implies that the two features seen in the OH gas-phase UPS data of Katsumata and Lloyd (1977) are the  $\sigma$  and  $\pi$  levels; these features arise from final-state effects on the  $\pi$  emission. The analysis is limited by the unknown contribution of the silicon substrate emission.

In the measurements presented here the contribution of silicon substrate emission has been removed. From figures 1(a) and (b) it is apparent that adsorption on the (100) and (111) surfaces results in very similar adsorbate spectra: the same three features with identical peak separations, their relative intensities depending on the photo-excitation/emission geometry. This strongly suggests that the adsorption mode, i.e. molecular or dissociative, is the same for both surfaces. As noted by Schmeisser *et al* (1983), these experimental peak separations are at odds with the (dissociative) calculation of Ciraci and Wagner (1983); this is also the case with the later (also dissociative) calculation of Katircioglu (1987). That both these calculations are not self-consistent underlines the very good agreement between the experiment and the fully self-consistent calculation of McMillan (1988). As shown in table 1, the experimental energy separations agree with those calculated for SiOH to within the combined experimental and calculation accuracy of 0.2 eV. It is therefore concluded that the room-temperature adsorption of water on both (100) and (111) surfaces is dissociative, in agreement with other techniques. This is the primary conclusion of this paper.

A significant corollary of this conclusion is the positive identification of the character of the three features by the calculation: peak 1 is the Si–O bond, peak 2 is the O–H  $\sigma$  bond and peak 3 is the O–H  $\pi$  non-bonding orbital. This re-opens the possibility of applying ARUPS selection rules, especially for the low-symmetry, single-domain, (100) surface. In terms of a simplified ‘oriented molecule’ approach such as that discussed above, the relevant  $\sigma/\pi$  comparison lies in peaks 2 and 3 rather than in peaks 1 and 2/3 as previously considered (McGrath *et al* 1988). To pursue this approach it is necessary to establish the emission plane which contains the OH molecular axis (if any). Recent ESDIAD data suggest that this molecular axis could be preferentially in the plane which is perpendicular to the dimer mirror plane; this model is the basis of the choice of emission plane in figure 1(a), and it is encouraging that peak 2 ( $\sigma$ ) appears stronger in the symmetric geometry.

It must be emphasised that the value of this result is limited by an incomplete application of the symmetry selection rule. The antisymmetric geometry is achieved by rotating both the sample and analyser azimuths (the polarisation of the storage ring is fixed!). The analyser geometry constrained the ‘out-of-plane’ emission angle to a

minimum of 70° and manipulator problems constrained the 'in-plane' emission angle to a maximum of 20°, i.e. the emission angles were very different. The same intensity variation could simply result from a differential polar dependence of peaks 2 and 3, independent of the azimuth. Certainly this is the only possible interpretation of the intensity variations in the spectra in figure 1(b), i.e. for the (111) surface; a similar conclusion for the (100) surface cannot be excluded with the limited (100) dataset and further (100) measurements are required.

It may be instructive to pursue this similarity further. Assuming a plane-wave final state, the (111) data suggests that the  $\sigma$  orbital associated with peak 2 is closer to the normal than the surface, and *vice versa* for the  $\pi$  orbital associated with peak 3. Indeed, the intensity variations tend to pair peaks 1 and 2 against peak 3, which would have the entire SiOH complex (which McMillan (1988) predicts to have a bond angle of approximately 120°) tending to the normal. It is conceivable that this geometry obtains on both surfaces. Equally this may not be entirely at odds with the ESDIAD model which was proposed for a low-temperature phase; clearly, such temperature effects should be looked for in ARUPS. Finally, it is worth noting that this pairing of peaks 1 and 2 would require the 'molecular water' adsorbate envisaged by Schmeisser *et al* (1983) to be inclined towards the surface.

#### 4. Conclusions

From a comparison of ARUPS spectra of water adsorbed on both (100) and (111) silicon surfaces with a self-consistent calculation of the species SiOH, it is concluded that the room temperature adsorption mode on both surfaces is dissociative. The adsorbate-induced features have been assigned and the application of simplified photo-emission selection rules to elicit the adsorption geometry has been discussed. Experiments to include low-temperature effects are planned for the near future.

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