

Reflection Anisotropy Spectroscopy as a Probe of the Metal/Liquid Interface and Molecular Adsorption

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Reflectance Anisotropy Spectroscopy (RAS) is a linear optical technique in which the difference of reflectivity at normal incidence of plane polarised light in two directions at right angles from the surface of a cubic material is measured. This geometry results in a cancellation of the bulk response by symmetry and RAS becomes a probe of the surface anisotropy. RAS has been extensively applied to the study of semiconductors [1] and as a monitor of semiconductor growth [2]. Recently it has been applied to the study of metal surfaces [3].

The RAS instrument was of the Aspnes design [4] operated in the range 1.5 to 5 eV. The measured RA signal is given by

$$\operatorname{Re}\left\{\frac{\Delta r}{r}\right\} = \operatorname{Re} 2\left\{\frac{r_{\parallel 001} - r_{\parallel \bar{1}01}}{r}\right\}.$$

In a recent work [5] we compared the RAS of a clean Au(110) (1x2) surface prepared in ultra high vacuum (UHV) with that of a Au(110) surface in an electrochemical cell and observed remarkably similar spectra.

In this work we apply the Reflection Anisotropy Spectroscopy to molecular interactions at surfaces. It is anticipated that this probe of the nature of the electronic structure of the interface can give information about the bonding between the adsorbate and surface.

Pyridine is known to adsorb onto an Au(110) electrode perpendicular to the surface through the nitrogen atom [6] at all potentials positive of -0.65V vs. SCE unlike the adsorption on the corresponding (100) and (111) face where a transition from the horizontal to vertical orientation occurs at $+0.3\text{V}$ vs. SCE.

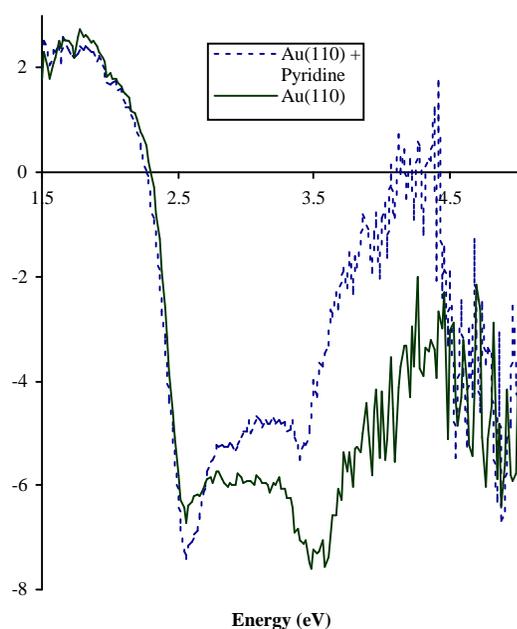


Figure 1

RAS Spectrum of (a) Au(110) in 0.1M NaClO₄ at 0V (solid line) and (b) Au(110) in 0.1M NaClO₄ + 1mM Pyridine at 0V vs. SCE (dashed line)

Figure 1 shows the spectrum obtained from Au(110) at 0V vs. SCE in the absence of pyridine (solid

line) and in the presence of pyridine (dashed line). The intensity of the peak at $\sim 2.6\text{eV}$ is enhanced due to the charge transfer excitations from the Fermi edge of the metal to the unoccupied π^* orbital of the molecule between 2 and 2.5 eV [7], while the peak at $\sim 3.7\text{eV}$ is reduced. The change in the spectrum at $\sim 4.8\text{eV}$ corresponds to the $^1A_1 \rightarrow ^1B_2$ transition in the optical spectrum of pyridine in solution but is broadened.

Pyridine bonds to the gold surface involve mainly an overlap of the non-bonding orbital with the electronic states of the gold and the π - π^* -orbitals of pyridine essentially do not participate in the formation of the chemisorption bond [8]. The interaction of the excited state with the substrate mainly involves a coupling of the dynamic dipole of the molecule to its image in the metal.

In an earlier study [5] we were able to account for the 1.6 eV and 3.7 eV transitions required in the empirical representation of the experimental RAS spectrum in terms of the results of electronic structure calculations of the Au(110) (1x2) surface [9]. In the notation of Xu *et al* we associate the low energy component with a transition at the Γ point between an occupied surface resonance, F, of odd symmetry arising from d states of yz character and an empty surface state, A, $\sim 0.3\text{eV}$ above the Fermi energy with even symmetry and predominantly p character. The 3.7 eV component is associated with a transition between an empty state R of even symmetry and predominantly sp character and a d derived filled surface state, I, of odd symmetry. The results of the calculations indicate that these two transitions occur between states with the appropriate symmetry and with energies of $\sim 2.0\text{eV}$ and 3.5eV which are consistent with the empirical results. The results of the calculations also provide some insight into the surface sensitivity of these transitions. The lower energy component is expected to be surface sensitive since it involves a surface state with an energy just above the Fermi energy. However the higher energy component should be less surface sensitive since it is a transition between an initial surface resonance and a final state which is dominated by contributions from the second layer of atoms.

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