

The Study of Solid/Liquid Interfaces with X-ray Standing Waves

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The principles and applications of the x-ray standing wave technique are described. Emphasis is placed on its utility for the study of structure, composition, and distribution of interfacial species especially at solid/liquid interfaces.

STRUCTURE, COMPOSITION, AND DISTRIBUTION OF CHEMICAL species and their variations caused by various stimuli are key aspects that are intimately related to interfacial reactivity. Their study can provide valuable insights on areas of fundamental, technological, and economic relevance, including catalysis, adsorption, electron transfer, corrosion, and the potential and ionic gradients at charged interfaces such as colloids, electrodes, and biological membranes (1, 2). Many of the above-mentioned areas involve solid/liquid interfaces and this has made their direct study rather elusive since most techniques sensitive to surface structure, composition, and distribution can only operate under high or ultra-high vacuum.

Because of their short wavelengths and significant penetration depths, x-rays represent a unique tool with which to study the structure, composition, and distribution of interfacial species. The advent of powerful x-ray synchrotron sources (3) had made many of these investigations feasible and has sparked a renewed interest in such studies. Thus, the development and application of techniques such as surface EXAFS (4) (extended x-ray absorption fine structure), surface diffraction (5), and x-ray standing waves (XSWs) (6).

The interference of two coherently related plane waves with wavelength λ generates a standing wave with a period D given by

$$D = \lambda/2\sin\Theta \quad (1)$$

where 2Θ is the relative angle between the waves. If the angle of incidence is increased, the value of $2\sin\Theta$ increases and thus the period of the standing wave decreases. In addition, the standing wave can be moved with respect to position by changing the relative phase between the incident and reflected waves.

Consider a species A at some fixed location where the standing wave exists and assume that there is an interaction of the standing wave with this species that gives rise to a characteristic response dependent on, for example, the electric field intensity of the standing wave at the location occupied by A. By monitoring the intensity of the characteristic response of A as we move the standing wave (by changing the relative phase) we can ascertain the location of A, its distribution, and the total amount of A present. This simple

description contains all the essential elements of standing waves, and we shall elaborate on this below.

The generation of a standing wave requires a strong reflected wave. Within the x-ray region of the spectrum, a strong reflected wave can be generated through total external reflection or through Bragg reflection (Fig. 1B) (7), and this dictates the type of standing wave generated. XSWs generated through Bragg reflection on single crystals have periods that are typical of crystallographic d -spacings; that is, of the order of a few angstroms. The use of layered synthetic microstructures (LSMs) in Bragg reflection allows for the generation of XSWs with periodicities in the range of 20 to 200 Å. Finally, XSWs generated through total external reflection have periods in the range of hundreds of angstroms. Thus, by the judicious choice of experiment one can change the characteristic length-scale of the technique.

X-ray standing waves based on Bragg reflections. In the vicinity of a Bragg reflection (Fig. 1, A and B), an incident plane wave (with wave vector $\mathbf{k}_O$) and a reflected wave (with wave vector $\mathbf{k}_R$) interfere to generate a standing wave with a periodicity equivalent to that of the (h,k,l) diffracting planes. The properties of such a standing wave are described by the theory of dynamical diffraction of x-rays (8). The nodal and antinodal planes of the standing wave are parallel to the diffracting planes. The standing wave develops not only in the diffracting crystal, but also extends well beyond its surface. As the angle of incidence is advanced through the strong Bragg reflection, the relative phase between the incident and reflected plane waves (at a fixed point) changes by π , and as a result the antinodal planes of the standing wave field move inwards in a direction normal to the diffraction planes by $1/2$ of a d -spacing, from a position halfway between the (h,k,l) diffracting planes (or their projection) at the low angle side of the Bragg reflection to a position that coincides with them at the high angle side of the Bragg reflection (Fig. 2). Thus, the standing wave can be made to sample an adsorbate, overlayer, or distributed layer at varying positions above the substrate interface.

For an atomic overlayer which is positioned parallel to the diffracting planes, the nodal and antinodal planes of the standing wave will pass through the atom plane as the angle of incidence is advanced. By choosing the incident x-ray beam energy to be at or beyond an absorption edge for the atoms in the overlayer, characteristic fluorescence can be excited. As the angle of incidence is advanced across the Bragg reflection, the fluorescence emission yield for the atoms in the overlayer, which by dipole approximation will be directly proportional to the electric field intensity at the atom's center, will exhibit a characteristic modulation dependent on the position of the adlayer relative to the diffraction planes. Figure 3 depicts the angular dependence of the fluorescence yield which would be observed for an adsorbate layer located at varying positions with respect to the diffracting planes. Notice the distinct differences in these profiles for positions that only differ by fractions

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of a d -spacing. This makes XSW measurements extremely sensitive to distributions normal to the diffraction planes.

The phase and amplitude of the modulations (or so-called coherent position and coherent fraction) are a measure of the mean position $\langle Z \rangle$ and width $\sqrt{\langle Z^2 \rangle}$ of the distribution of atoms in the overlayer. Standing wave measurements of $\langle Z \rangle$ and $\sqrt{\langle Z^2 \rangle}$ can be accurate to within 1 and 2% of the d -spacing, respectively (9). The coherent fraction is a model-independent quantity which reflects the width of the distribution of atoms in the adlayer. For example, if all the atoms were at the same position (a delta function; that is, zero width), the coherent fraction would be one. On the other hand, if the atoms were randomly distributed (normal to the surface) the coherent fraction would be zero. For intermediate cases the coherent fraction would have a value between zero and one. The coherent fraction (f_c) and coherent position (p_c) can be incorporated into an expression for the fluorescence yield as

$$Y(\theta) = |E_0(\theta)|^2 \{1 + R(\theta) + 2\sqrt{R(\theta)} f_c \cos[\nu(\theta) - 2\pi p_c]\} \quad (2)$$

where Y is the fluorescence yield, E_0 is the incident electric field amplitude, R is the reflectivity, and ν is the phase. It should be mentioned that the yield at angles removed from the Bragg reflection (off-Bragg yield) represents an integral measurement of all

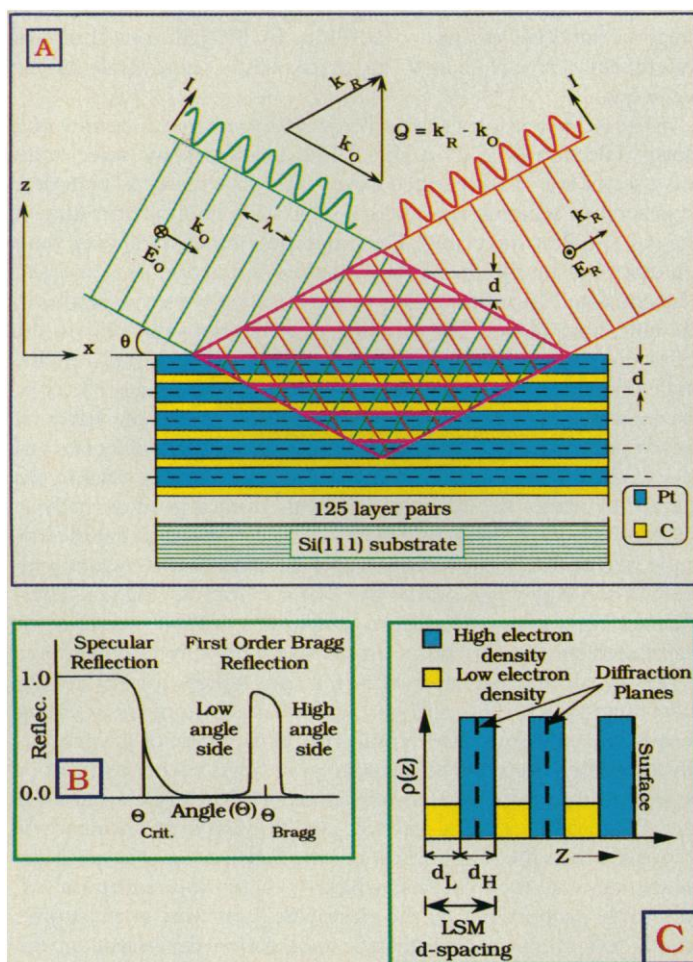


Fig. 1. (A) Depiction of the generation of an x-ray standing wave by Bragg reflection from a Pt/C-layered synthetic microstructure. k_0 and k_R refer to the wave vectors of incident and reflected plane waves, respectively, and Q is the momentum transfer. (B) Generic reflectivity profile depicting total external (specular) and Bragg reflection. (C) Diagrammatic depiction of an LSM.

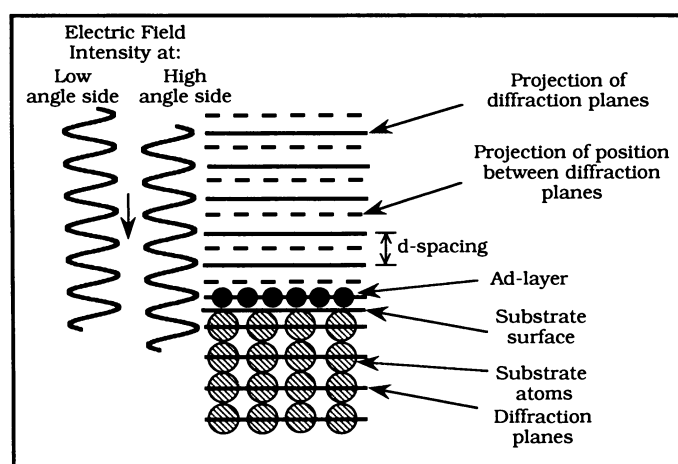


Fig. 2. Depiction of the movement of the electric field intensity of a standing wave as the angle of incidence is scanned from the low to the high angle side of a Bragg reflection.

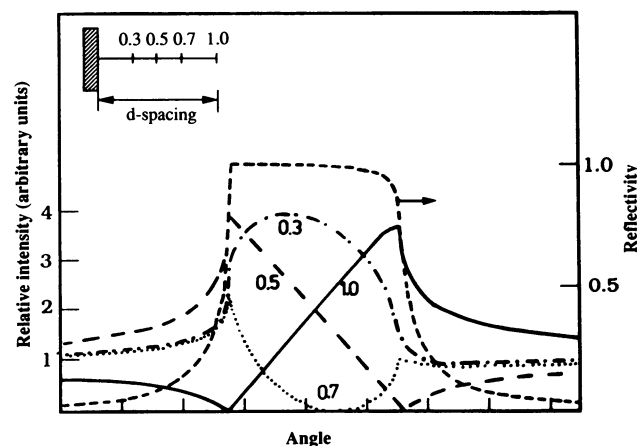


Fig. 3. Angular dependence of the reflectivity and the fluorescence yield (or electric field intensity) for an atomic layer located at various positions with respect to the diffraction planes.

absorbing species and thus provides a measure of concentration.

Although the characteristic length scale of a few angstroms for XSWs generated by Bragg reflection from single crystals is ideal for determining bond lengths between atom layers at single crystal surfaces, it is inappropriate for the structural determination of systems extending over several tens of angstroms, such as ionic distributions at charged surfaces. An alternative to single crystals is the use of LSMs (10, 11) which are depth-periodic structures consisting of alternating layers of high and low electron density materials (such as platinum and carbon), and which are of high enough quality to produce strong Bragg reflection (Fig. 1, A and C) so that a well-defined standing wave can be produced. LSMs are advantageous because they can be made with fundamental d -spacings ranging from 20 to 200 Å, and these give rise to long-period XSW standing waves which are optimally suited to investigate systems that are distributed over such distances.

X-ray standing waves generated by total external reflection. A second way of generating an XSW is through total external reflection (12, 13). This is based on the fact that at x-ray energies the index of refraction of matter is slightly less than one (7), so that if x-rays impinge on a surface at angles below the critical angle θ_c (typically a few milliradians), the beam undergoes total external reflection and only an exponentially damped evanescent wave penetrates into the

medium. The incident and reflected waves can thus interfere to generate a standing wave. Analogous to XSW generation by Bragg diffraction, there is a change in the relative phase (by π) between the incident and reflected waves which occurs as we scan across the total external reflection regime ($\theta = 0$ to $\theta = \theta_c$). The angular dependence of the total external reflection XSWs can be described using the general formalism discussed previously. When the angle of incidence is zero, there is a node at the mirror surface (the incident and reflected waves are completely out of phase), and since the period D is infinite [$D = \infty$ since $\sin(0) = 0$; Eq. 1], the first antinode is at infinity. As the angle of incidence is increased, the first antinode moves inward, in a direction normal to the surface, until at the critical angle it coincides with the mirror surface. The subsequent antinodes follow behind with a periodic spacing given by Eq. 1. Thus, the angular variation of the total external reflection XSWs can be visualized as a wave that is compressing and shifting downwards towards the surface as the angle of incidence is advanced (that is, both the period and the phase are changing simultaneously).

Experimental Aspects and Data Analysis

An XSW experiment consists of monitoring the angular dependence of some signal arising from the species of interest and which is proportional to the standing wave electric field intensity (such as characteristic fluorescence). A typical experimental set up consists of a well-collimated beam of monochromatic x-rays (typically from a synchrotron source) that impinges on the sample which is mounted on a stage with high angular resolution. Signals that are monitored include the incident and reflected beam intensities as well as the characteristic fluorescence (measured with a solid-state detector) arising from the species under study. Of particular importance is the angular resolution of the sample stage since the typical reflection width for a single crystal will be of the order of tens of microradians and a few milliradians for LSMs.

Analysis of XSW data is based on a fit of the data (reflectivity and fluorescence yield) to predictions from theory. Fitting of the desired characteristic fluorescence emission line to an assumed functional form (usually a combination of Gaussian functions) and subtraction of an extrapolated polynomial background render the data suitable for reconstruction of the fluorescence yield as a function of the angle of incidence.

In order to fit the data, the electric field intensity at a particular point must either be calculated from dynamically diffraction theory (8) or from an optical theory approach based on a stratified medium formalism in which the medium is divided into parallel slabs (10, 14). The layered medium approach is particularly well suited for analysis of standing waves in multilayered structures (10, 15).

Incorporation of coherent position and coherent fraction into Eq. 2 (or analogous expressions) allows a fit to be obtained in terms of three parameters: normalized coverage of absorber, coherent position, and coherent fraction.

Selected Examples

As electrochemists, our interest lies in the use of the XSW technique to study solid/liquid interfaces, in general, and the electrode/solution interface in particular. We are especially interested in being able to follow potential dependent variations in the distribution of species in the vicinity of the electrode surface. Such variations are a strong function of the applied potential and can cover distances as small as a few and as large as hundreds of angstroms. Furthermore, the use of x-rays as probes allows for the in

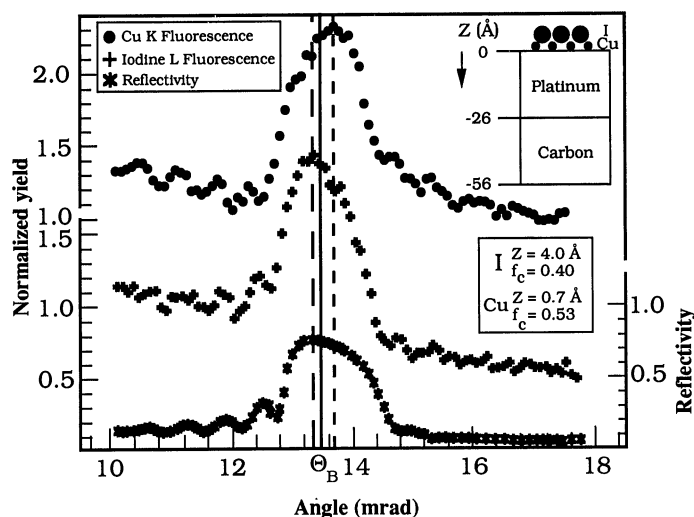


Fig. 4. Reflectivity profile and normalized fluorescence yields for I and Cu for a Pt/C LSM with an electrodeposited layer of copper and adsorbed iodide. Inset: Depiction of the location of the I and Cu layers on the Pt/C LSM.

situ characterization of such systems. Thus, the ability to use an in situ probe whose characteristic length scale can be varied over such a broad range, makes XSWs ideal for the study of solid/liquid interfaces in general.

In our studies, the substrate material on which the reflected wave is generated also serves as the electrode whose potential we wish to change over a broad range. As a result, in our work we have relied heavily on Pt/C LSMs as substrates since they fulfill all of our requirements.

Electrodeposition of copper on an iodine-treated Pt/C LSM. One of our earlier XSW studies involved the adsorption of iodide onto a platinum/carbon LSM followed by the electrodeposition of a layer of copper (16). Radiation (9.2 keV) from the Cornell High Energy Synchrotron Source (CHESS) was used to excite L-level and K-level fluorescence from the iodide and copper, respectively. Initially, the LSM was exposed to a 35 mM aqueous solution of sodium iodide for 15 minutes. It was then studied by the XSW technique. The angular dependence of the characteristic iodine L fluorescence indicated that the iodine layer was on top of the platinum surface layer. The LSM was then placed in an electrochemical cell and half a monolayer of copper was electrodeposited. The LSM (now with half a monolayer of copper and a monolayer of iodide) was again analyzed by the XSW technique. Since the incident x-ray energy (9.2 keV) was capable of exciting fluorescence from both copper and iodide, the fluorescence intensity of both elements (as well as the reflectivity) were obtained simultaneously. The results presented in Fig. 4 show the reflectivity curve and the modulations of the iodide and copper fluorescence intensities. The most important feature is the noticeable phase difference between the iodide and copper modulations, that is, the location of the iodide and copper fluorescence maxima, with the copper maximum being to the right of the iodine maximum. Since the antinodes of the XSW move inward as the angle increases, the order in which these maxima occur can be unambiguously interpreted as meaning that the copper layer is closer than the iodide layer to the surface of the platinum. Since the iodide had been previously deposited on the platinum, this represents unequivocal evidence of the displacement of the iodide layer by the electrodeposited copper. Similar findings based on Auger intensities and low-energy electron diffraction (LEED) patterns have been previously reported by Hubbard and co-workers (17, 18).

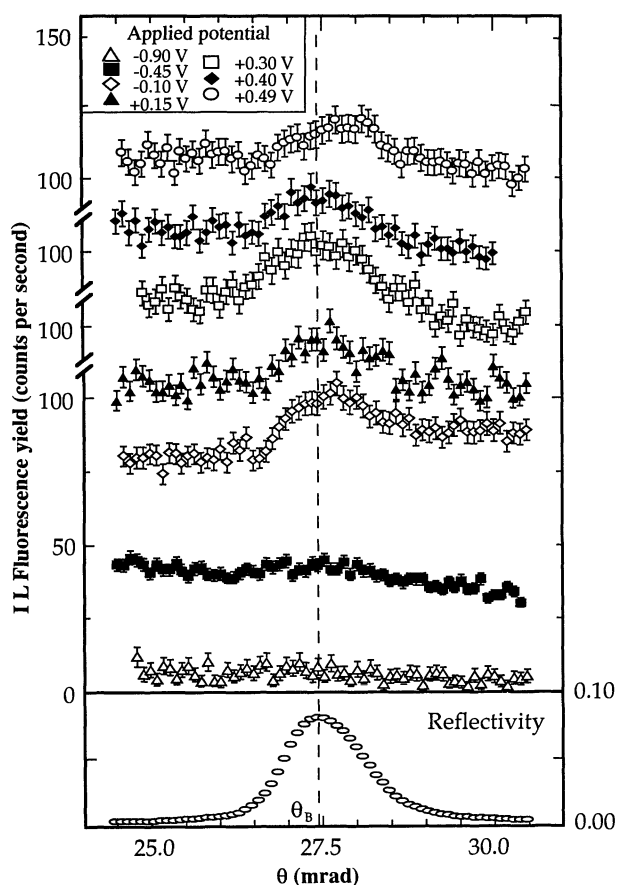


Fig. 5. Angular dependence of the I_L fluorescence intensity as a function of applied potential and reflectivity profile.

From an analysis of the copper fluorescence intensity we were able to determine that the copper layer had a significant degree of coherence ($f_c = 0.53$) and that its coherent position was $0.70 \text{ \AA}$ above the platinum surface. Similar analysis of the iodine fluorescence gave values of 0.40 and $4 \text{ \AA}$ for the coherent fraction and position, respectively. This case exemplifies the study of systems whose distribution extends over a very short range close to the electrode surface.

Iodine on Pt: Packing density and potential dependent distributional changes. The adsorption of iodine on polycrystalline and single crystal Pt electrodes has been widely investigated using LEED, Auger, EXAFS, and voltammetric techniques. It is generally accepted that immersion of a Pt(111) surface into aqueous iodide (or HI) solutions results in the formation of an ordered ad-layer of iodine atoms. Furthermore, the Pt(111)/I system possesses a rich potential-dependent coverage isotherm, which has been characterized by Auger spectroscopy for the emersed case (19), and in situ by x-ray absorption spectroscopy (20). Its features are explained in terms of potential dependent structural and distributional changes. The aim in this work was to study in situ, by means of the XSW method with LSMs, the potential dependence of structural changes in the distribution of iodine species, and to relate features of the aforementioned isotherm to observations from this measurement (21). In this study we employed a $40.8 \text{ \AA}$ d -spacing Pt/C LSM (Pt as the topmost layer) in contact with a $0.1 \text{ M Na}_2\text{SO}_4$ solution of pH 6.7 containing $10 \text{ \mu M NaI}$.

As mentioned previously, coherent position and coherent fraction can be used to describe the distribution of species determined from XSW measurements. However, these terms are relevant only when describing symmetrical atomic distributions centered around a given

mean $\langle z \rangle$ position. For an extended (that is, a distribution with width $> d$), unsymmetrical distribution $N(z)$, coherent position and coherent fraction are inadequate in characterizing the angular dependence of the XSW fluorescence yield. In this case, a model for $N(z)$ must be chosen and the standing wave electric field intensity $I(\Theta, z)$ must be averaged over the entire distribution:

$$Y(\Theta) = \int I(\Theta, z) N(z) dz \quad (3)$$

We chose a simple model consisting of three basic components to describe the iodine distribution: (i) a step at the electrode's surface extending over a few angstroms, describing the specifically adsorbed iodine atoms; (ii) an exponential tail with a characteristic decay length k , extending out into solution from the iodine ad-layer, portraying iodide anions attracted to the electrode surface (the diffuse layer); and (iii) a second step, with a width equal to the thickness of the solution layer, depicting bulk iodide. Analytically, this model can be expressed as follows:

$$N(z) = \begin{cases} N_{\text{ad}} & 0 \leq z \leq t_{\text{ad}} \\ N_{\text{diff}} \exp(-z/k) + N_{\text{bulk}} & t_{\text{ad}} < z \leq t_{\text{sol}} \end{cases} \quad (4)$$

where N_{ad} is the concentration of iodine atoms specifically adsorbed, t_{ad} is the ad-layer thickness, N_{diff} is the initial concentration of iodide in the diffuse layer, k is the decay length of this diffuse layer, N_{bulk} is the iodide bulk concentration, and t_{sol} is the thickness of the solution layer. The choice of an exponential decay to model the diffuse layer was motivated by its mathematical simplicity as well as its frequent usage in simple theoretical descriptions of the electrical double layer (22). The standing wave yield can now be calculated with the distribution $N(z)$ defined above (Eq. 4) in the integral in Eq. 3. Computationally, N_{diff} and N_{bulk} were expressed as fractional values of N_{ad} , and the distribution was normalized with the condition:

$$Y_{\text{OB}} = \int_{z=0}^{t_{\text{sol}}} N(z) dz \quad (5)$$

where Y_{OB} is the measured off-Bragg fluorescence yield; a value proportional to the total number of I/I^- species present in the solution layer (t_{sol}). The effect of including a diffuse layer along with the adsorbed layer in the model (Eq. 4), corresponds to a superposition of a random-like component to the coherent XSW yield from the ad-layer (provided that the thickness t_{ad} is narrow with respect to the substrate's d -spacing), in a ratio proportional to the population in each layer with the number of atoms in the diffuse layer being controlled by the decay length k and the initial concentration N_{diff} . From theoretical calculations, we find that the XSW technique is very sensitive to these distributional changes. For example, adding a diffuse layer with a fall-off length of only $10 \text{ \AA}$ produces a dramatic change in both the amplitude and the phase of the calculated signal. Furthermore, appreciable differences are seen when the diffuse layer population is changed by varying N_{diff} . Thus, in principle, the XSW method is extremely sensitive to subtle changes in atomic/ionic distributions at the electrode/electrolyte interface.

The I_L fluorescence yield as a function of the angle of incidence Θ , for each of the potentials studied, is shown in Fig. 5. Changes in both the phase and amplitude of the standing wave signal are indicative of distributional changes in the direction normal to the substrate surface. In addition, the potential dependent changes in the background slope, peak position, and modulation amplitude, provide further insights as to the distribution of species. All of the variations in these parameters can be understood in terms of changes in the distribution of iodine/iodide species at the electrode/electro-

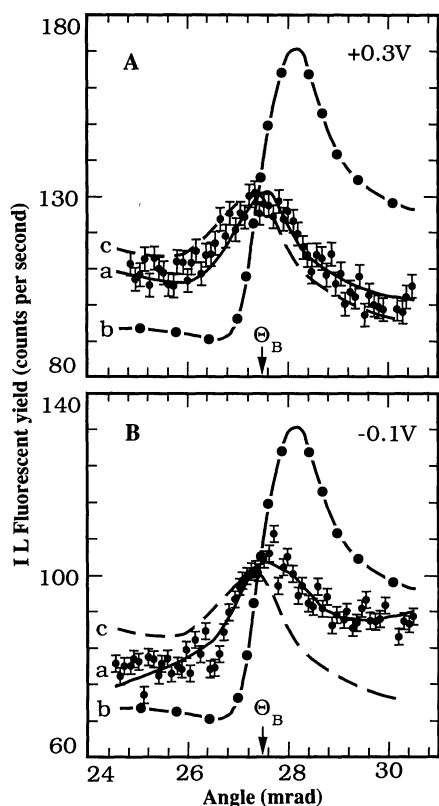


Fig. 6. Theoretical fits (a) of I_L fluorescence intensity obtained at +0.30 (A) and -0.10 (B) V. Also shown on both panels are the theoretical yields predicted for a 10 Å iodine ad-layer alone (b) as well as for a random distribution of iodide in solution (c). Errors bars represent ± 1 standard deviation.

lyte interface as described by the above-mentioned model.

In order to obtain a quantitative assessment of the contribution of the various components, we have χ^2 fitted the data to theoretical yields based on the model defined in Eq. 4. Figure 6 shows two typical theoretical fits and points out the noticeable differences produced in the fluorescence yield by two different iodide distributions. Referring to this figure, if the diffuse layer had been a negligible component of the iodide distribution, the observed fluorescence yield would have followed the theoretical yield calculated for an ad-layer alone (b; dot-dash lines). On the other hand, if the bulk or diffuse layer contributions were dominant, the fluorescence yield would have been that calculated for a random distribution (c; dashed lines). In both cases the best fit (a; points and solid lines), represents a combination of these two limiting cases.

By taking the off-Bragg yield at each potential and subtracting the contribution due to the diffuse layer, as determined from the fitting parameters k and $N_{\text{diff}}/N_{\text{ad}}$, we could determine the changes in ad-layer normalized coverage with applied potential. These variations are analogous to packing densities observed on Pt(111) from dilute NaI solution determined in situ by x-ray absorption spectroscopy (20) and on emersed Pt(111) electrodes by Auger electron spectroscopy (19). In these cases, the variations are attributed to structural changes in the iodine ad-layer. Since the changes observed in the normalized coverage in this experiment are in excellent agreement with the changes in the packing density measured on a Pt(111) electrode surface, we believe that a similar structural transition takes place for the iodine ad-layer formed at the Pt surface of the Pt/C LSM employed in this work.

From an analysis of the standing wave and off-Bragg yield measurements, we obtain a picture of the interface where we note a marked accumulation of iodide in the diffuse layer, weakly associat-

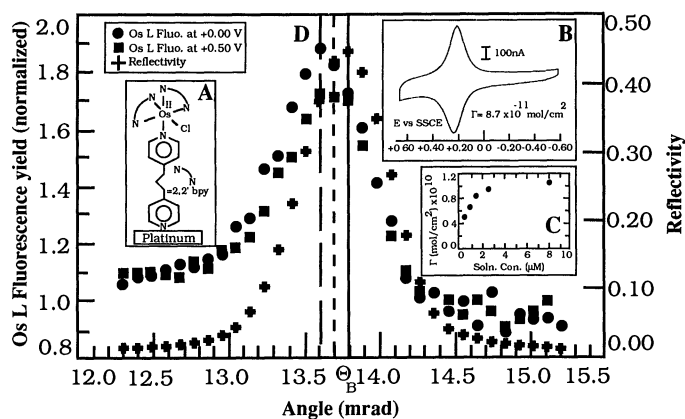


Fig. 7. (A) Structure of self-assembling, redox active osmium complex. (B) Cyclic voltammetric response in dichloromethane for the osmium complex adsorbed on a platinum electrode. (C) Isotherm for the adsorption of the osmium complex onto a platinum electrode surface. (D) Reflectivity profile and angular dependence of the Os_L fluorescence intensity at 0.00 and +0.50 V for a Pt/C LSM coated with a monolayer of the osmium complex.

ed with the adsorbed iodine, when the Pt surface is not saturated by iodine adatoms (-0.10 V). This striking association of iodide with the iodine ad-lattice is perhaps driven by the hydrophilic character of the unsaturated Pt surface. Furthermore, the increase in the adsorbed iodine packing density to saturation coverage is accompanied by an abrupt decrease in the concentration of this accumulated iodide. Thus, we suggest that the potential dependent structural transformation in the iodine ad-lattice could be viewed as a phase transition, in which iodide anions in the liquid-like arrangement of the diffuse layer are incorporated into the crystalline-like structure of the iodine ad-lattice, resulting in a saturated Pt surface, possibly hydrophobic, and the concomitant decrease in the concentration of iodide in the diffuse layer, associated with the adsorbed iodine.

In this work, we were able to follow, in situ, distributional changes for a minute amount of an ionic content, with angstroms resolution in the direction normal to the surface. Although the model chosen to describe the distribution was primitive, it was consistent with all experimental observations. The use of standing wave measurements over higher-order Bragg reflections as well as the total external reflection regime may allow for the use of more sophisticated theories.

X-ray standing wave study of a redox active self-assembling monolayer. The study of reactions within organized media, both in solution as well as at interfaces, has received a great deal of attention in the recent past (23, 24). Within the present context, it is reactions taking place at interfaces of controlled and deliberate architecture that are of interest and specifically those which involve redox active components. There is much interest in the study of electron transfer kinetics for surface immobilized redox species especially with regards to the distance dependence of the rate since it is believed that such studies may provide very valuable insights on long-range electron transfer processes within biological systems (25). Because they are structurally simpler (and ostensibly better characterized), these model studies may allow for a clearer and more direct interpretation. We describe here some preliminary results of an XSW study of a redox active self-assembling monolayer (26) and point to some of the advantages and difficulties of such measurements.

The system studied was the osmium complex $[Os(bpy)_2(dpyp)Cl]^+$ [where bpy is 2,2' bipyridine and dpyp is 1,3-di-(4-pyridyl) propane] whose structure is presented in Fig. 7A. In this material the remote pyridine group provides a site of attachment to an electrode surface. The complex exhibits reversible electrochemis-

try and is stable in both oxidized and reduced forms. This material adsorbs very strongly to platinum electrodes and the surface-immobilized complex exhibits very well behaved electrochemistry (Fig. 7B) in numerous solvents. A saturation coverage representing a compact monolayer (one monolayer represents 1×10^{-10} mol/cm²) is achieved for solution concentrations above 4 μ M. A typical adsorption isotherm is presented in Fig. 7C.

In this experiment we employed a 40.8 Å d-spacing Pt/C LSM as the electrode. A monolayer of complex was adsorbed from solution and the electrode was mounted in an electrochemical cell similar to that used in previous studies. An incident x-ray beam energy of 11.1 keV was employed to excite Os_L fluorescence. In all cases a reflectivity profile was collected simultaneously with the Os_L fluorescence intensity. Experiments were carried out at applied potentials of 0.0 and +0.50 V where the osmium center within the complex is present as Os(II) and Os(III), respectively. It should be noted that the overall charge on the complex changes from +1 to +2 upon electrochemical oxidation.

Data for the Os_L fluorescence intensity at 0.0 and +0.50 V as well as a reflectivity profile are presented in Fig. 7D. Again, as in the previous examples we focus on the angular position and amplitude of the fluorescence profiles. As can be seen in Fig. 7D, the maximum in the fluorescence at 0.0 V occurs at a lower angle than at +0.50 V. In addition, the fluorescence intensity is lower at +0.50 V relative to the values at 0.0 V. There are some qualitative observations that may be made. The fact that upon oxidation at +0.50 V the fluorescence maximum shifts to a higher angle suggests that, on average, the osmium centers are closer to the electrode surface than at 0.0 V. It is worth mentioning that the distance between the osmium center and the electrode surface would be 12 Å for a fully extended chain.

The fact that the fluorescence intensity is lower at +0.50 V relative to 0.0 V would suggest that there is a broader distribution of distances. This might be due to increased coulombic repulsion between adjacent molecules since upon oxidation the charge on each molecule increases from +1 to +2. Thus, the coulombic repulsion is expected to be approximately four times as large and, in order to release the repulsive forces, the molecules may adopt a broader distribution in terms of distance. Although these are preliminary findings, our interpretation is consistent with the data. In addition, additional electrochemical evidence is also consistent with the interpretation given above (26).

We are now preparing analogous molecules with varying chain length between the pyridines in order to carry out a systematic study of potential dependent variations as a function of chain length. We feel confident that these studies will provide a wealth of information on electron transfer rates and reactivity of redox monolayers on electrodes.

Future Prospects and Applications

In addition to measurements based on Bragg reflection, the use of the very long period XSWs generated by total external reflection provides a means for studying systems distributed over ranges of

hundreds of angstroms. The applicability of such a technique was recently demonstrated by Bedzyk and co-workers in a study on ionic distributions at a phospholipid membrane (27). It is clear that the XSW technique is a powerful probe of the structure, composition, and distribution of interfacial species and is of particular value in the study of solid/liquid interfaces. The fact that the length scale that it probes can be controlled is an especially attractive feature. In addition, the construction of new synchrotron radiation facilities will also make this technique accessible to a broader range of practitioners. As more emphasis is placed on the investigation of interfacial properties of biological systems and new materials, we feel confident that the XSW technique will play an increasingly prominent role in these investigations.

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