ELECTROCHEMICAL CONTACT ADSORPTION SITE CHANGES DRIVEN BY FIELD AND CHARGE: FACT AND THEORY.

by

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Electrochemical Contact Adsorption Site Changes Driven by Field and Charge. Fact and Theory

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measurements and deductive reasoning using simple models, electrochemists have evolved a detailed 'standard model' of the disposition of ions, water, and organics adsorbed on the electrode in the range of potentials where the electric double layer is thermodynamically stable. There is evidence that the anions are physisorbed. However, it is only in more recent years through a variety of in situ probes of vibrational properties (ftir and raman) and geometry (sexafs and gixs) that this model is being really tested.

This paper briefly surveys what is known about contact adsorption and the electric double layer of noble metal electrodes. Some of the in situ experimental probes in current use are described. Then we describe how theory in the form of self consistent field (scf) model cluster calculations has provided some detailed insight into the nature of the adsorption bond. The interplay between experiment and theory is illustrated through discussion of a series of progressively more complex ligands. Starting with halides like chloride (Cl\textsuperscript-), diatomics like cyanide (CN\textsuperscript-), small polyatomics like azide (N\textsubscript{3}\textsuperscript-) and thiocyanate (SCN\textsuperscript-) and concluding with some larger more complex ligands like sulphate (SO\textsubscript{4}\textsuperscript-) and bisulphate (HSO\textsubscript{4}\textsuperscript-).
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ABSTRACT

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(HSO\textsubscript{4}).

INTRODUCTION

Understanding the adsorption of ions on surfaces from solution is a chal-
lenging scientific problem comparable in difficulty to any other involving buried
interfaces. It is also of significant technological interest in connection the basis
for understanding complex electrochemical phenomena associated with battery
chemistry, dissolution of metals in acids, electroplating, electropolishing, incipience of oxide films, and passivation of surfaces.

Revolution in Electrochemical Science.

During the last fifteen years a quiet revolution has been occurring in electrochemical science driven by the development of experimental techniques that provide direct atomic scale information about the nature of the electrochemical interface. Most important of these are in situ structure probes using x-ray light from synchrotron sources. Next is the medley of ex situ techniques adapted from ultra high vacuum (uhv) surface science and applied to electrodes that have been immersed into inert gas atmosphere and then transferred into uhv. Then come a variety of spectroscopic methods one at least (surface enhanced raman scattering or sers) was first discovered in electrochemical cells. Most recent to impact the area are theoretical studies utilizing modern ab initio quantum chemistry calculations to explore possible geometry-bonding relationships. Following closely are molecular dynamic and Monte Carlo simulations of the interface. The standard model of the electrochemical interface evolved over thirty or so years study by chronocoulometric techniques. The new measurement techniques and advanced computational theory methods are beginning to impact the standard model in significant ways. It is an exciting time to be doing research in electrochemistry.

Electrochemical Interface and the Double Layer.

Since the early forties electrochemists have accumulated a vast amount of knowledge concerning the workings of metal electrode-aqueous electrolyte interfaces [1 - 4]. Initial experiments relied on the fact that electric charge can be measured with very high precision. In the mid forties Grahame [1] used a dropping mercury electrode to avoid surface contamination and in a classic series of classic experiments, measured the capacitance of the double layer as a function of electrolyte composition and potential. This was the beginning of the modern era of electrochemistry and the birth of what we call here the standard model of the interface (see Fig.1). A fairly detailed picture of adsorption on the surface and concurrent structural changes in the inner and outer part of the double layer has been evolved over the years. Consider for the moment a hydrated chloride ion approaching the surface by some diffusional process. Before the ion can make contact some of the weakly bound water molecules between the electrode and the ion are displaced. The thermodynamic equilibrium involves a delicate balance of opposing free energy interactions. The most important of these are: electrostatic interaction between ion and metal, enthalpies of hydration of ion and surface atoms, and entropy of displaced water molecules. Generally speaking large ions (iodide, cesium) contact adsorb whereas small ions (fluoride, calcium) do not. Verification of contact adsorption has been demonstrated by a variety of techniques including: differential capacitance [3], radio tracer [5], ftir [6], and surface exafs [7 - 8].

According to the standard model the electric double layer consists of two parts. The part closest to the electrode is called the compact layer and it is delimited by the outer Helmholtz plane OHP (see Fig.1). The OHP is the point of closest approach of fully solvated cations that do not contact adsorb. The compact part consists of approximately two monolayers of water molecules, contact adsorbed ions, and visiting counter ions. On the basis of capacitance measurements it is traditional to further subdivide the compact layer into an inner part and an outer part at the hypothetical inner Helmholtz plane (see IHP in Fig. 1). This plane cuts through the adsorbed ion centers. The second part of the electric double layer, called the diffuse part, consists of fully hydrated ions moving under
Figure 1. Immersed Electrode. Schematic picture of the standard model of the electrode - aqueous electrolyte interface. Water dipoles of hydration shells of ions shown. Anions contact adsorbed, cations not adsorbed. Charge on metal is not shown. IHP and OHP are the inner and outer Helmholtz planes.

Figure 2. Schematic diagram showing ionic adsorption vs. electrode charge. Halides and pseudohalides adsorb strongly whereas adsorption of perchlorate and nitrate is much weaker.
the influence of thermal forces in the combined electric fields of the metal electrons and the adsorbed ions. The diffuse layer, described by Gouy-Chapman theory [3–4], screens the charge on the electrode. Direct measurement of the diffuse layer distribution has been described recently using x-ray fluorescence from zinc ions [9].

Ions have been classified according to their adsorbing ability by Anson [10]. Figure 2 shows schematically two classes of ion. Inside the compact layer the specifically adsorbed ions accumulate on the electrode driven there by the Gibbs free energy of adsorption. They can change the sign of the charge felt by ions in the diffuse layer. Put another, way negative ions like iodide adsorb strongly on negatively charged metal electrodes, requiring the diffuse layer to screen a larger effective charge. Likewise adsorption of anions on positively charged metal electrodes can lead to an overall negative charge to be screened by the diffuse layer. The thermodynamics of contact adsorption has been well studied within the frame work of the standard model. Tables of Gibbs free energies are given in a number of texts see for example Bockris and Reddy [11]. The main point for this discussion is that for large radius ions the water-electrode and ion-electrode interactions are roughly constant and opposing. The determining effect is the variation in ion-water interaction. So large radius ions tend to adsorb strongly, even if their charge is deeply buried as in the case of tetraalkyl ammonium ions. In the last ten years many new experimental techniques (stm, sers, ftir, shg, ex situ uhv, sfg, sexafs, gixs) together with improvements in time tested techniques like chronocoulometry, differential capacitance, ellipsometry, etc., applied to single crystal electrodes have provided new information requiring a much more detailed picture than currently available. The standard model with its flat charged hard wall electrode needs much further development.

It is anticipated that improvements in the model will come in two main areas. Knowledge of adsorption site geometry will require the development of detailed local models utilizing all the power at the disposal of quantum chemistry programs. Rigorous statistical mechanical models utilizing the correlation function approach of Henderson and co-workers [12–13] or the brute force power now available on work stations to perform molecular dynamic or Monte Carlo calculations [14–17] of the double layer structure.

What we want to know.

At the most fundamental level the information we would like to know about electrochemical interfaces concern its structure, dynamics and chemistry. Although we are still a long way from being able to picture the surface with the precision available to surface scientists in uhv. However with the new x-ray tools and developments in scanning tunneling microscope (stm) techniques and photoemission through liquid films, for example, our knowledge of electrochemical interfaces is improving rapidly. Structural properties of the compact part of the double layer of greatest interest are: nature of the chemisorption bond, geometry of the adsorption site, orientation of the adsorbates, solvation of adsorbed ions, coverage vs external potential, orientation of surface water molecules, electronic structure of metal surface, and magnitude of interfacial electric fields. To complete the picture we must also understand the dynamics of the interfacial species. Typical diffusion constants for molecules in bulk water are 3 nm²/nsec. Physisorbed water is expected to be immobilized. This will greatly affect diffusion of ions and water in and out of the compact layer. Another aspect of dynamics is to understand why adsorbate vibration frequencies shift with the applied external electrode potential. This will be a topic discussed at length later.
EXPERIMENTAL PROBES

The effort at the Almaden Research Center has focussed on in situ techniques, and this naturally will form the focus of what is to be discuss here. Space is not sufficient to detail the enormous contributions made solely with the classic techniques or the ex situ ones. Rather we summarize salient points relevant for proper perspective.

Classical electrochemical probes.

The strategy of classical electrochemical investigations has been to determine the thermodynamics of adsorption by measuring interfacial surface tension accurately enough as a function of electrolyte composition, electrode potential, temperature etc. The Lippmann equations [11] can then be used to determine all other thermodynamic quantities of interest, including how the concentration of surface species change with intensive variables. The enormous drawback to this approach is that metal surface tensions can only be readily measured for mercury and its amalgams. Consequently the strategy for solid metals has been to determine some other thermodynamic property like capacitance, or attempt to measure adsorption directly. Methods used with varying degrees of success have been ellipsometry, uv-vis absorption spectroscopy, and frequency shift of a quartz crystal oscillator [18]. The draw back of all these latter methods is their insensitivity to details of the surface structure.

In situ geometric probes.

There are now a set of probes that return information with atomic scale features that can be used whilst maintaining the electrode under full potentiostatic control. Surface extended x-ray absorption fine structure (sexafs) measured with high brilliance x-ray sources can be analyzed to determine the local geometry around the atom absorbing the x-ray. This works well for high atomic number adsorbates. Figure 3 shows a sexafs experiment schematically. An x-ray adsorption spectrum is measured by recording the action spectrum of the fluorescence emission. In the case of a monolayer of copper under potentially deposited (upd) on gold (111) single crystals in the presence of sulphate electrolyte the fine structure has been analyzed in terms of the model shown schematically in Figure 4. A second powerful x-ray technique utilizes grazing incidence x-ray scattering (gixs) from the surface to determine long range surface structure. This technique has been successfully applied to the study of lead, bismuth, and silver upd layers on noble metals [19].

As exciting as the x-ray measurements are developments in the use of scanning tunnelling microscopy (stm) [20]. Initially attempts to use this probe were frustrated by the existence of large ionic conduction currents that totally swamped the signal from the tunnelling electrons. This problem has been solved by coating the tip in glass or plastic such that only a minute region some 0.1 nm² at tip end is bare metal. Images recorded with the electrode under full potentiostatic control have been applied to the study of step migration, the adsorption of metal overlayers and chalcogenides. A surprising new development has been the recording of photoelectron spectra. Photoemission into solution as an experimental technique had been stymied by the very rapid thermalization of the photoemitted electrons and concomitant loss of information. This draw back has been overcome to some large degree by positioning a collector electrode a few nanometers from the photocathode. The emitted electrons traverse a very thin film of liquid electrolyte before capture by the anode [21].
Figure 3. Schematic diagram of SEXAFS and GIXS structure determining experiments.

Figure 4. Proposed model for adsorption of sulphate ions on Cu monolayer underpotentially deposited on Au(111) electrode surface.
In situ spectroscopic probes.

Whereas our knowledge of adsorbate organization versus coverage is in its infancy, our understanding of bonding is substantial albeit somewhat qualitative. Surface enhanced raman scattering (sers) provided a window to observe rather directly the vibrations of adsorbates on copper, silver and gold electrodes [22]. These metals have accessible interfacial plasmon-like modes on roughened surfaces that can enhance the raman cross-section by factors of 10^6 in optimum cases. This technique cannot be applied to smooth surfaces, though in principle one could use prisms or gratings to enhance the raman cross-section, it has not been reduced to useful routine practice. However sers remains the sole practical method for the measurement of direct metal-ligand vibrations in the 100-400 cm⁻¹ region [23].

More widely applicable is in situ ftir [24]. This works best in the regions where water adsorbs light weakly, namely 1000-1400 cm⁻¹, and 2000-3000 cm⁻¹. Figure 5 shows schematically an arrangement we have used a great deal at Almaden in combination with a commercially available ftir instrument designed by Brueker. The ir beam is focussed through a polarization modulator on the prism-electrolyte interface, whence it passes through a compensator onto an ellipsoidal mirror which focuses the beam onto the detector. The thickness of the electrolyte film between prism and electrode is controlled by a precision micrometer. The modulator allows simultaneous recording of s- and p-polarized spectra. The final spectra consist of the ratio (I_p-I_s)/(I_p+I_s) versus reciprocal centimeter. Figure 6 shows a schematic detail of the prism, electrolyte film and electrode in cross-section, and Figure 7 shows some sample spectra taken in the 2000-3000 cm⁻¹ window region for carbon monoxide adsorbed on platinum, cyanide on gold and azide on silver. In each spectrum the bands labelled A correspond to the surface adsorbed species. Note that there is an easily measured frequency shift with electrode potential. The potentials were measured relative to the AgCl/Ag reference electrode except in the case of the spectra for carbon monoxide which are referenced to normal hydrogen electrode (NHE). The main advantage of the polarization modulation technique is its independence of electrode potential. There are variants that improve on surface sensitivity by recording the difference between ir spectra as the electrode potential is modulated from a state where there is more adsorption to one where there is less adsorption on the surface. So called snifters is one such widely used technique [24]. Increase in surface sensitivity is at the expense of ease of interpretation. Water molecule can reorganize and the surface reconstruct when the potential is switched.

Powerful as ftir spectroscopy has proved there is another probe of vibrational properties that has greater sensitivity for planar surfaces, namely sum frequency generation (sfg) spectroscopy [25,26]. The idea is to use the absence of center of symmetry at the surface to probe the vibrational modes of surface species in a non-linear experiment. This technique has demonstrated its power in resolving thiocyanate spectra on platinum beyond that available from ftir [27–28].

Another application of non-linear spectroscopy has been the use of second harmonic generated (shg) light. Basically this is a second order susceptibility experiment that occurs at surfaces because of the absence of a center of symmetry. It has been argued that in principle the potential of zero charge (pzc) of the electrode could be measured this way. This is important since the current route is through the thermodynamic analysis of the electrocapillary (surface tension) data. However progress in this direction has been impeded by a useable theory of second harmonic-light generation at metal surfaces [29,30].
Figure 5. Schematic diagram of in situ surface FTIR experiment using polarization modulation.

Figure 6. Schematic diagram showing detail of the prism-electrolyte-electrode interface in the thin film electrochemical cell designed for in situ FTIR spectroscopy.
Figure 7. Representative examples of in situ IR spectra of simple diatomic ligands adsorbed on polycrystalline metal electrodes.

Figure 8. Schematic diagram showing the emersion of an electrode into gas under potentiostatic control.
**Ex situ probes.**

In completing this survey of experimental techniques mention must be made of a battery of ex situ methods that draw on UHV surface analysis [31 - 34]. There are two stages. First the electrode is processed in a small cell under an inert gas like argon. Then under potentiostatic control the electrode is immersed, as shown schematically in Figure 8. The compact part of the double layer is withdrawn along with an indeterminate part of the diffuse layer to maintain charge neutrality. Next the electrode is transferred into UHV were the surface is examined by Iedd, auger, eels, etc., to determine surface structure. Numerous systems have been studied this way, and a great deal has been learnt about halide adsorption on Pt(111). Space does not permit justice to be paid to this area.

**QUANTUM CHEMISTRY CLUSTER CALCULATIONS.**

There are several routes to understanding the bonding of ligands to surfaces from the point of view of electronic structure. Each offer a unique perspective, whilst having limitations that must be properly appreciated.

**Jellium half space.**

The approach of treating the metal as a jellium half space and using local density theory to derive equations to solve for the bonding has been developed by Lang [35]. This method appears to treat the metal electrons in a superior way, but is computationally intensive for polyatomic ligands. It has been used to study the bonding of atoms to jellium.

**Superlattice slab method.**

Another approach used extensively for semiconductor surfaces can be described as a slab method with finite number of atomic layers of metal forming a superlattice in the direction normal to the basal plane and translational symmetry along x and y. Local density approximation is used to adsorb electron correlation. This method has enjoyed much success in understanding metal properties, and is being used to study exchange coupling between ferromagnetic materials [36]. It has not been widely used to study the bonding of electrochemically interesting ligands to metals. However Hoffmann [37] has been developing the slab LCAO method for studying reaction pathways on metals.

**Cluster method.**

The third method utilizes a cluster as a model for the metal [38]. Once the model is defined the full force of modern quantum chemical programs can be brought to bear without resorting to further approximations. The cluster method appears to be qualitatively good for understanding: local bonding including potential energy surfaces, adsorbate geometry, and the local effect of electric fields. Since correlation can be included (at a price!) it also appears to include be able to include dispersion interactions.

There are aspects of surfaces that it cannot adequately treat. Practically anything involving metallic properties like screening. Others of note are band structure effects like those that operate when the Fermi level is altered. This is precisely what happens when the electrode potential is changed. Effects due to collective properties like surface plasmons. The full image effect involves plasmon modes and so also can never be treated adequately by the cluster approach.
One of the successes of the cluster approach has been its application to adsorption of electrochemically interesting species on metal electrodes. It is clear from calculations described in detail in this book for example, that the bonding of carbon monoxide to copper is representative of dative covalent bonding. Carbon monoxide is a by-product of the electrochemical oxidation of methanol to carbon dioxide and water, that binds strongly to platinum and inhibits further oxidation. The primarily electrostatic bonding of halide and pseudohalide anions appears in accord with experiment.

CONTACT ADSORBED SMALL LIGANDS.

The adsorption geometries of some small ligands are depicted schematically in Figure 9. Monatomics in hollow site will have an allowed ir and raman active mode polarized perpendicular to the surface. Diatomics are expected to have two main modes, a low frequency frustrated translation and a high frequency internal mode. For linear triatomics the picture has essential complications with dipole allowed angle bends.

Monatomic ligands.

The adsorption of halides on polycrystalline and selected single crystal metal electrodes has been well studied by many of the techniques alluded to above. Chloride, bromide and iodine contact adsorb with the largest ion most strongly bound. Fluoride does not adsorb because it is so strongly hydrated. Sers for polycrystalline silver shows low frequency bands at 240 cm⁻¹, 180 cm⁻¹ and 120 cm⁻¹ for chloride, bromide and iodide respectively. The chloride band has a strong potential dependence shifting to higher frequency as the electrode is polarized more positive. The tuning rate is between 20-30 cm⁻¹/V, in other words a large fraction (ca. 0.1) of its value [39] The results of cluster calculations can be summarized as follows [40]. For monatomic ligands in three fold hollow sites of Ag(111) represented by compact silver clusters with n (n = 4, 6, 7, and 10) atoms it was found that the bonding to be essentially ionic with a very small (< 10%) but increasing covalent contribution with increasing size of the halogen. Applied static electric of 0.01 atomic field units (10⁸V/cm) caused a large change in the equilibrium nuclear positions and vibrational frequencies. Bond shortening of 10% and upward frequency shifts of 25% were calculated. The absolute agreement between calculated and sers frequencies is very poor as one would expect at the scf level for such small vibration frequencies. More important is the qualitative agreement in the tuning rate. The geometry change at the site should be measurable by sexafs. Preliminary experiments by Gordon and co-workers suggest reconstruction in the case of bromide on Ag(111) [41]. The mechanism for frequency shift is compression of the potential energy surface perpendicular to the plane of the surface brought on by Pauli repulsion of filled shells.

Diatomics.

For the diatomic ligands like neutral CO and ionic CN cluster calculation give a contrasting picture in bonding. These two ligands are isoelectronic and experimentally have comparable tuning rates for their high frequency internal stretching mode at ca. 2000 cm⁻¹[42,43]. See the spectra shown in Figure 7. It is tempting to ascribe similar mechanisms to their bonding to surfaces. Nothing could be further from the truth according to the cluster calculations. Quite different bonding is found. Several clusters have been studied for carbon monoxide and cyanide, in particular clusters Cu₁₀(5,4,1) and Cu₁₄(5,4,5) for an on top site on the (100) plane [44,45]. For CO there is dπ-π* back donation of approximately 0.25e and no σ bond. The low frequency mode v(Cu-C) is affected little
Figure 9. Schematic diagram of adsorption geometries of polyatomic anions on small metal clusters.

Figure 10. Schematic representation of adsorption of a sulphate ion on a metal cluster.
by the dc field, whereas the high frequency mode $\nu(C-O)$ couples strongly through its' dynamic dipole. In contrast cyanide CN exists as the anion, and its equilibrium position $r$(Cu-C) depends strongly on the applied field. Both the low and high frequency modes shift in the applied field because of the operation of a wall effect that constrains the physical space that the nuclei can move in. Orientation of the CN ligand has been extensively studied including N atom down and CN parallel to the Cu(100) surface. In the case of N down the tuning rate is reduced because the dynamic dipole is reversed over C down, and in this orientation opposes the action of the wall. There is no experimental evidence suggesting that cyanide can adsorb N down at electrochemical interfaces.

Triatomics.

The vibrational spectra of azide and thiocyanate ions adsorbed on noble metal electrodes has been studied by sers and ftir and in one case sfg. Azide at low bulk concentrations appears to adsorb flat, in particular it has been argued to lie preferentially in the Ag(110) grooves [46]. Sers spectra indicate that the symmetric raman active stretching mode at ca. 1400 cm$^{-1}$ has no potential dependence, whereas the ir active mode seen in ftir experiments has a large positive tuning rate. [47,48]

Simple model cluster calculations show that azide remains an ion next to a silver atom or positive ion. This crude model is adequate for delineating some effects of ligand orientation relative to the surface, on electronic structure and internal vibrational frequencies. The silver surface was represented by a simple but useful approximation of a single Ag$^0$ atom or Ag$^+$ ion. The effect of the electric field on the two high frequency internal modes was studied. In each case it was found that the asymmetric stretch ($\nu \approx 2100$ cm$^{-1}$, ir active in the isolated ion) was strongly field dependent, whereas the symmetric mode ($\nu \approx 1340$ cm$^{-1}$, Raman active in the isolated ion) was not [48].

The experimental evidence for thiocyanate orientation is more extensive. Both sers and surface ftir show the presence of multiple bands in the region of the internal C-N stretching mode at ca.2000 cm$^{-1}$ [49,50]. These have been interpreted as adsorption with S- and N-atom down in accordance with correlations known between crystal structure and ir spectra of inorganic coordination complexes [51]. Cluster calculations for Ag$_n$ (n = 1, 5 and 10) show there to be two possible orientations [50,52]. N down has the configuration axis perpendicular to the surface plane, whereas S-down lies almost flat. Applying a repulsive electric field causes the ligand to orient perpendicular. These results are in accord with known experimental observations including the crystal structure of AgNCS which has zig-zag chains in which the AgNCS are essentially collinear units with the NCS-Ag angle around 100 degrees.

PROGRESS WITH LARGER LIGANDS.

In aqueous solution sulphate belongs to the class of anion known to undergo specific adsorption in the range of electrode potential corresponding to a thermodynamically stable electric double layer. There are numerous orientation to consider some shown schematically in Figure 10 for a (111) surface. Sexafs [7,8] and lead [34] have proposed top site models for sulphate adsorption on copper. In the sexafs experiments the ion occupied an on-top site with the Cu-O-S parallel to the normal of the (111) surface plane. The on-top and bridged site geometries were proposed for adsorption on Cu(100) obtained by immersing the electrode from acidic sulphate solution prior transfer into uhv where lead was performed [34].
The high symmetry T₄d of isolated sulphate ion means that there are many internal vibration modes that are exclusively ir or raman allowed, thereby suggesting it may prove to be a useful probe of forces influencing orientation and the local field within the double layer. On the other hand the polyatomic nature of sulphate makes a daunting task of interpreting spectra to a level achievable for smaller ligands like CO or cyanide. Nevertheless because of the existence of several proposed structures on Cu surfaces and the variety of other data bearing on adsorption site geometry and structure it is clear that quantum chemistry calculations performed at the scf Hartree-Fock level could play a crucial role in elucidating geometry, structure and bonding at the adsorption site.

The first calculations were for sulphate oriented over a single copper atom and positive copper ion. Then a cluster was built up in which the top site atom was given a realistic environment of neighbours. For a single Cu atom the preferred orientation has higher coordination of Cu by sulphate oxygens as charge or field (attractive) increased. This trend was significantly changed for a larger cluster where three oxygens eclipsed three surface coppers at the bulk metal separations. In this case the configuration with three feet down was significantly more stable than others by about 0.5eV [53].

SUMMARY AND OUTLOOK

Future advances in the science of electrochemical interfaces are tied to new experimental techniques that provide atomic scale information about surface site geometry and changes driven by external parameters like the electrode potential. Theoretical calculations of bonding, geometry and electronic structure have a vital role to play primarily as a guide to interpreting experimental results and also as a means of gaining greater insight into underlying physics.

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