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13 The essence of this AFOSR project is investigation of the structure, composition, mode of attachment and reactivity of the surface molecular species which form when metals come into contact with fluids. A series of findings, advances in investigative technology and 91 scientific articles have occurred thus far during this project. These include: i) determination of the orientations and modes of attachment of organic molecules attached to electrode surfaces; ii) demonstration that each orientation of an adsorbed molecule manifests different chemical and electrochemical reactivity; iii) discovery that electrodeposition of metals at single-crystal surfaces produces highly-ordered layers; iv) discovery that contact between metal surfaces and ionic solutions forms chemically unique, ordered layers; v) adaptation of electron energy-loss spectroscopy (EELS) for measurement of vibrational spectra of molecules adsorbed at metal surfaces from solutions; vi) systematic study of 150 adsorbed phenols, acids, amines, pyridines, mercaptans, alcohols, alkenes and aromatics as to structure (LEED), composition (Auger), molecular construction/mode of surface attachment (EELS), chemical reactivity (all methods), and electrochemical reactivity (cyclic voltammetry, CV); vii) demonstration of the stability of these adsorbed layers toward vacuum and electron beams used in surface spectroscopy by performing CV before and after the electron spectra were obtained; and, viii) studies of surface structure by means of Auger electrons. These results have practical usefulness as well as fundamental significance: any substance present in any practical amount on virtually any solid metal surface can now be identified, quantitated and characterized; chemisorbed intermediates can be characterized and their electrochemical reactivity can be explored; molecular species formed at metal surfaces as a result of lubrication, coating, immersion, electrolysis, adhesive action, combustion and other high pressure processes can now be characterized as to composition, molecular structure, mode of surface attachment, and other physical and chemical properties; and studies begun with Pt surfaces have now been extended to various non-noble metals.

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ABSTRACT

The essence of this AFOSR project is investigation of the structure, composition, mode of attachment and reactivity of the surface molecular species which form when metals come into contact with fluids. A series of findings, advances in investigative technology and 91 scientific articles have occurred thus far during this project. These include: i) determination of the orientations and modes of attachment of organic molecules attached to electrode surfaces; ii) demonstration that each orientation of an adsorbed molecule manifests different chemical and electrochemical reactivity; iii) discovery that electrodeposition of metals at single-crystal surfaces produces highly-ordered layers; iv) discovery that contact between metal surfaces and ionic solutions forms chemically unique, ordered layers; v) adaptation of electron energy-loss spectroscopy (EELS) for measurement of vibrational spectra of molecules adsorbed at metal surfaces from solutions; vi) systematic study of 150 adsorbed phenols, acids, amines, pyridines, mercaptans, alcohols, alkenes and aromatics as to structure (LEED), composition (Auger), molecular construction/mode of surface attachment (EELS), chemical reactivity (all methods), and electrochemical reactivity (cyclic voltammetry, CV); vii) demonstration of the stability of these adsorbed layers toward vacuum and electron beams used in surface spectroscopy by performing CV before and after the electron spectra were obtained; and, viii) studies of surface structure by means of Auger electrons. These results have practical usefulness as well as fundamental significance: any substance present in any practical amount on virtually any solid metal surface can now be identified, quantitated and characterized; chemisorbed intermediates can be characterized and their electrochemical reactivity can be explored; molecular species formed at metal surfaces as a result of lubrication, coating, immersion, electrolysis, adhesive action, combustion and other high pressure processes can now be characterized as to composition, molecular structure, mode of surface attachment, and other physical and chemical properties; and studies begun with Pt surfaces have now been extended to various non-noble metals.

I. REPORT OF RESEARCH

A. Some Motivations for Research in Surface Electrochemistry.

Before proceeding to a discussion of recent studies of pyridine derivatives, let us take a few moments to reflect on the underlying reasons for making studies of this type. There is a need to detect, identify and quantitate the species which form at metal surfaces under conditions typical of practical situations such as bonding of materials, protection of metal surfaces, lubrication of metals, storage of electrical energy, cleaning of materials, fabrication of electronic devices and sensors, and others. Thus far, we have adapted LEED, Auger spectroscopy, EELS, surface IR spectroscopy and voltammetry/coulometry for this purpose, and we will continue to invest part of our time in improvements of investigative methodology. With these methods we can detect, quantitate and identify virtually any surface species in any practical amount.

Identification of surface species (atoms, ions, molecules and oligomers) will be an important aspect of any future discovery, development and testing of new surface-related processes and devices by designed approaches rather than trial and error. Investigation of the mode of bonding of chemical substances and materials to surfaces provides valuable clues by which to understand the behavior of metallic and other solid surfaces in contact with fluids. Substrate surface characterization (structure, cleanliness, electronic properties) is becoming increasingly important with the continuing discovery of examples of substantial influences of roughness, trace elements, and other surface characteristics. Knowledge of the relative affinities of various classes of chemical substances for various categories of material surfaces is essential to design of surface-related processes and devices. Exploration of chemical families of well-characterized adsorbed species by various forms of surface-sensitive spectroscopy both in surveys and in detailed studies is vital to future explorations of surface processes and phenomena. Observations of the chemical reactivity and electrochemical redox of well-characterized adsorbed layers, and of the influence of such species on the reactions of unadsorbed reactants are reliable benchmarks of the surface sciences, including electrochemistry. Results from various laboratories around the world are adding emphasis to the realization that surface structure is an important factor in electrode reactions of organic molecules, and to the need for electrode surface characterization.

B. Adsorption and Reactivity of Pyridine and Derivatives at Pt(111).

Pyridine and its derivatives belong to a class of compounds which adsorb strongly at Pt electrodes in a vertical orientation with the plane of the ring approximately perpendicular to the surface (47). Evidence for vertical orientation of pyridine adsorbed from vacuum at low temperature and warmed to room temperature has also been reported (162-165). Accordingly, we undertook to study pyridine and some of its typical derivatives as an opportunity to learn about vertically-oriented adsorption and to compare it with the equally important horizontally-oriented adsorption of aromatic compounds (117).

Our latest studies of pyridine and its derivatives at Pt(111) electrode surfaces by means of LEED, Auger, EELS and voltammetry (125) have confirmed the vertical orientation but have produced some remarkable surprises, as well:

(i) 3-pyridine carboxylic acid (nicotinic acid, NA) binds to Pt surfaces through both the nitrogen atom and an oxygen atom of the carboxylate group when adsorption is carried out at relatively positive potentials. When adsorbed at relatively negative potentials NA binds exclusively through the N atom and has a highly active carboxylic acid pendant. These principles were deduced initially from EELS spectra which showed a prominent O-H stretch at 3566 cm^{-1} , Figure 1-A, which disappeared at positive potentials, Figure 1-B. This transition between coordinated and pendant carboxylate occurs smoothly with potential, and is not due to deposition of NA, as illustrated by the EELS and Auger data shown in Figure 2.

(ii) Evidence of the potential-dependence and pendant acidity of NA is seen in the retention of K^+ by the NA layer in alkaline solutions, Figure 3. K^+ ions are retained only at relatively negative potentials, in agreement with the implications of the EELS data. The pK_A of NA is less than 4. We have not yet devised an accurate method of measuring pK_A for such a favorable acid dissociation. This very active pendant invites utilization for a wide variety of fundamental studies and practical chemical modifications of surface behavior.

(iii) Pyridine adsorbs at virtually constant packing density ("coverage") at all dosages from 0.1 mM all the way to neat liquid pyridine, and displays a clear but complex LEED pattern shown in Figure 4. This LEED pattern corresponds to a Pt(111) $(3.324 \times 4.738, 77.1^\circ)\text{R}34^\circ\text{-PYR}$ unit mesh. In matrix notation this is:

$$\begin{array}{|c|c|} \hline a_1 & a_2 \\ \hline \end{array} = \begin{array}{|c|c|} \hline 1.684 & 2.145 \\ \hline -4.255 & 5.106 \\ \hline \end{array}$$

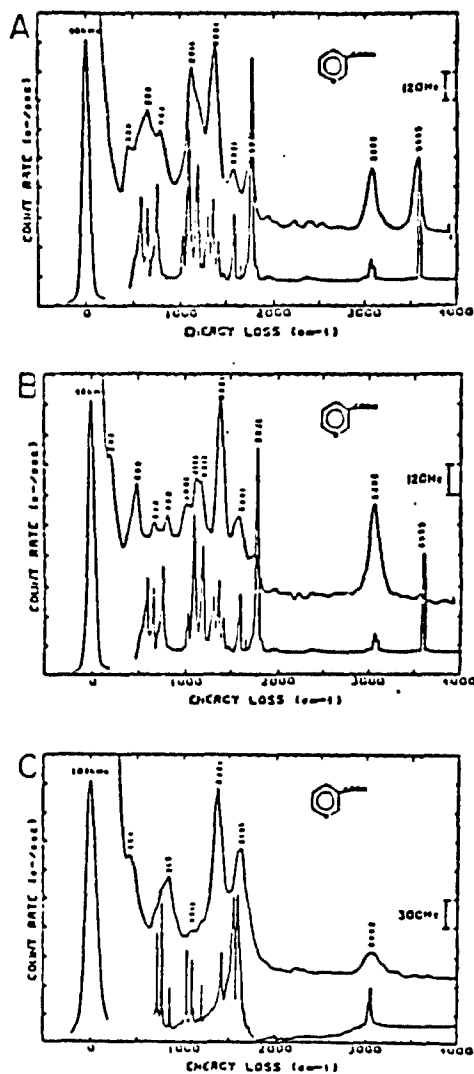


Figure 1 Vibrational spectra of NA.

- A. EELS spectrum of NA adsorbed at Pt(111), $-0.2V$, pH 3.
Lower curve in A and B is mid-IR spectrum of NA vapor (19).
- B. EELS spectrum of NA at Pt(111), $+0.6V$, pH 3.
- C. EELS spectrum of NA at Pt(111), $-0.3V$, rinsed at pH 10.
Lower curve is mid-IR spectrum of solid KNA.

Experimental conditions: adsorption from $1mM$ NA in $10mM$ KF, pH 3 (A and B) or pH 7 (C), followed by rinsing with $1mM$ HF (A and B, pH 3) or $0.1mM$ KOH (pH 10, C);

EELS incidence and detection angle 62° from surface normal; beam energy, $4eV$; beam current about $120pA$; EELS resolution, $10meV$ ($80cm^{-1}$) F.W.H.M.; IR resolution, $4cm^{-1}$.

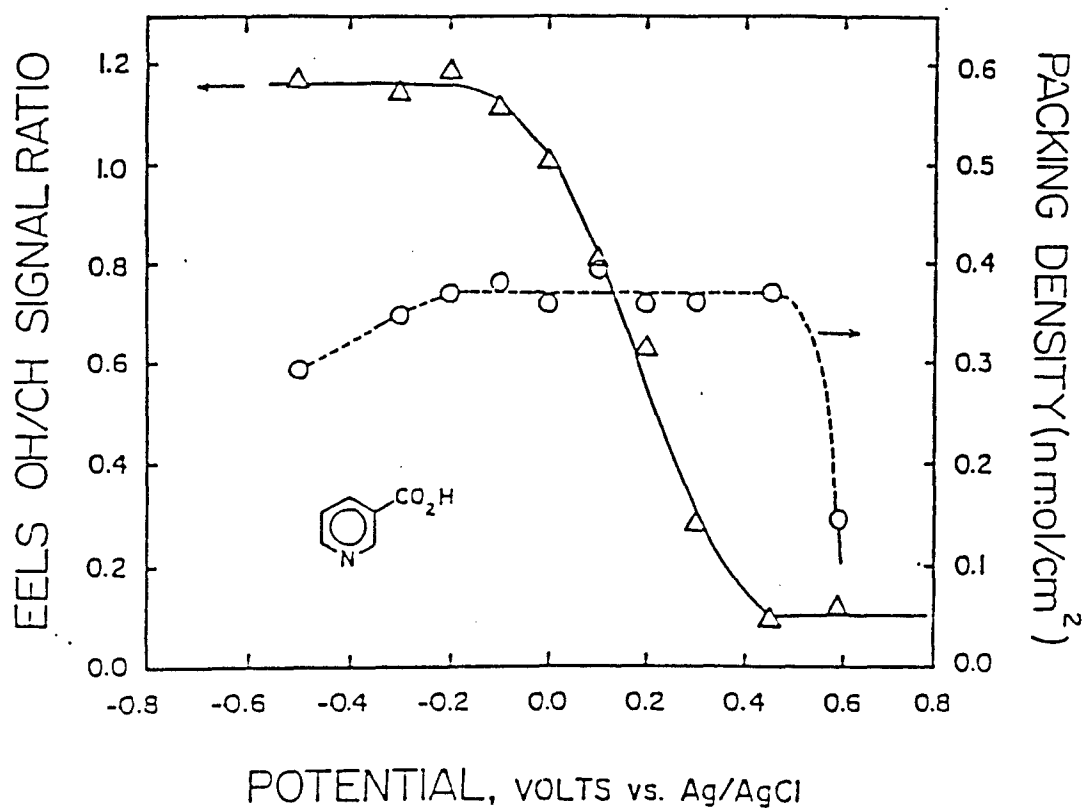


Figure 2. Ratio of EELS O-H (3566cm^{-1}) to C-H (3068cm^{-1}) peak height (Δ); Packing density of NA (o).

Experimental conditions: adsorption from 1mM NA in 10mM KF at pH 7, followed by rinsing in 2mM HF (pH 3); electron beam at normal incidence, 100nA, 2000eV.

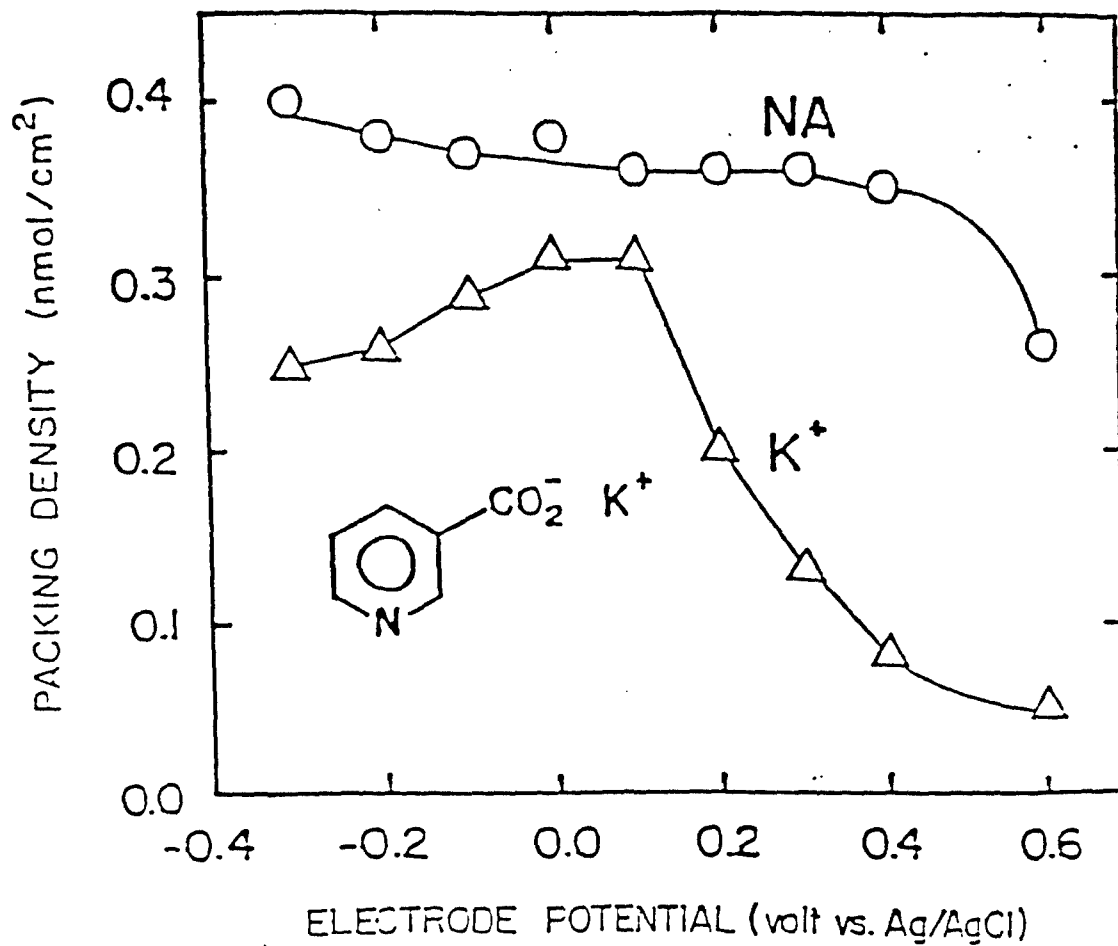


Figure 3. Packing density of K⁺ ions (Δ); packing density of NA (o).
Experimental conditions: adsorption from 1mM NA in 10mM KF (pH 3),
followed by 3 rinses in 0.1mM KOH (pH 10). EELS conditions as in Figure 1
Auger conditions as in Figure 2.

Pt(111)(3.324 x 4.738, 77.1°)R34.0°-PYR

1.684	2.145
-4.255	5.106

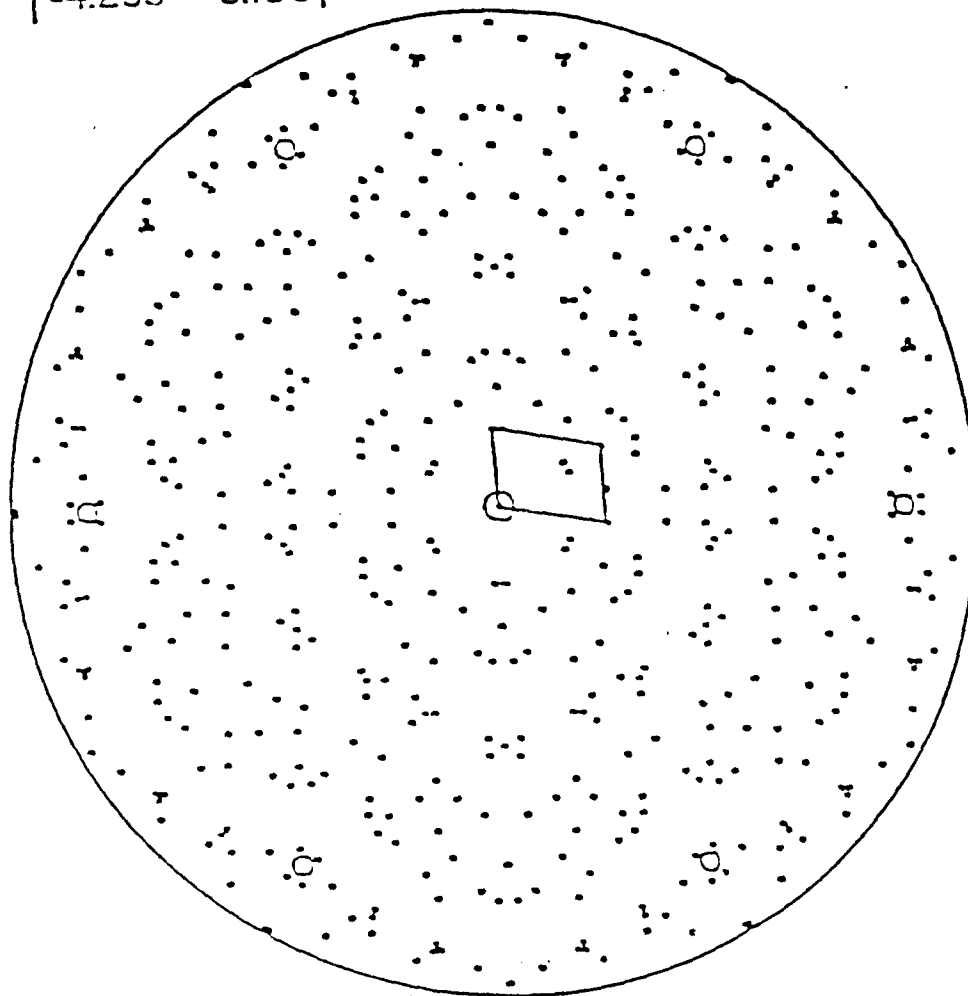


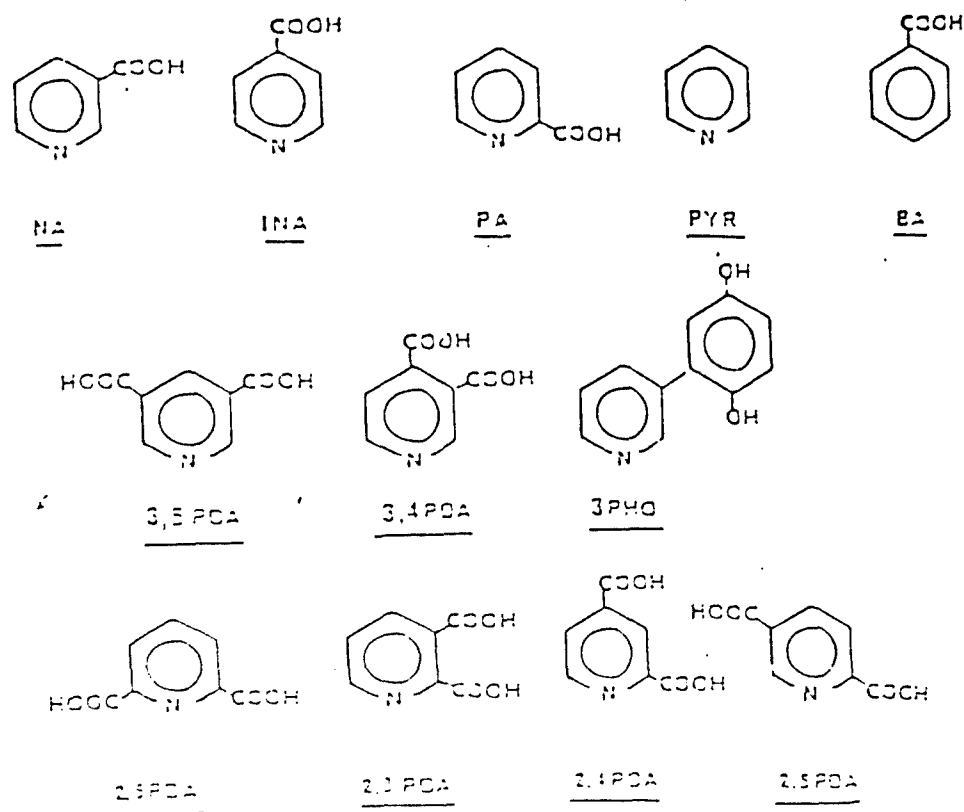
Figure 4. Diagram of the LEED pattern of PYR adsorbed at Pt(111), 51eV. Experimental conditions: adsorption from 1mM PYR in 10mM KF (pH 7) at -0.3V, followed by rinsing with 0.1mM KF (pH 7).

This is an incommensurate structure in which the pyridine molecules do not have integral periodicity with respect to the Pt surface atoms. The nearest commensurate structure, $(2\frac{1}{3} \times \frac{1}{2} 21, 79^\circ)R30^\circ$, and all other commensurate structures correspond to expected LEED patterns dramatically different from the observed pattern. Likewise, changes in the mesh vectors by more than about 0.1% from those stated above predict noticeably different patterns. Pyridine (and quite possibly its derivatives) favors an incommensurate (but ordered and oriented) structure.

(iv) Remarkable inertness of Pt-pyridine and Pt-NA monolayers is illustrated by the cyclic voltammograms in Figure 5. A horizontally-oriented adsorbate, benzoic acid, is relatively reactive by comparison, Figure 5-C.

(v) Packing densities of pyridine and derivatives are consistently intermediate between that expected for horizontal and perpendicular-vertical orientations, as illustrated by Figure 6. The angle, Θ , between the ring and the Pt surface is 70 to 75° for all of the pyridine derivatives studied. This tilted structure is consistent with the potential-dependent coordination behavior of NA, and as we shall see is also consistent with the behavior of the other compounds studied.

(vi) Studies similar to items (i - v) above were also carried out for all of the compounds shown below:



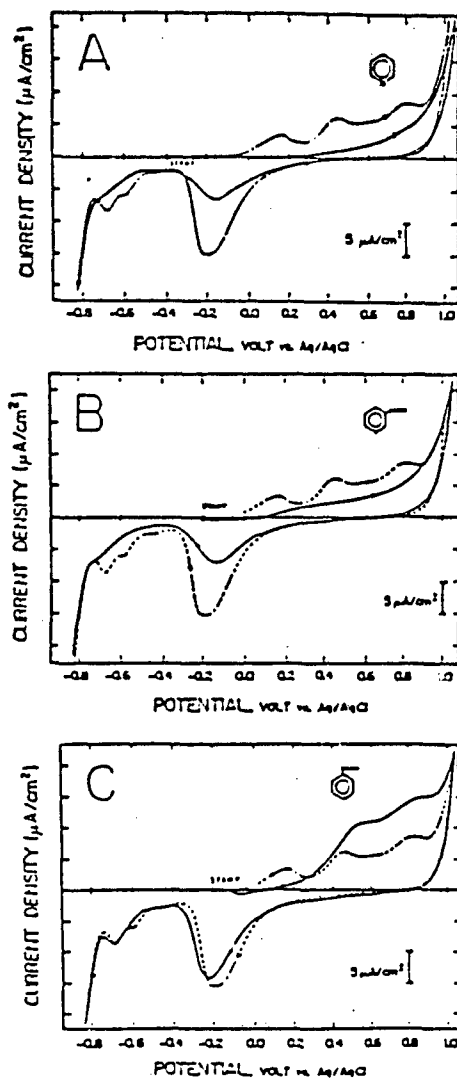


Figure 5. Cyclic voltammetry at Pt(111).

A. PYR

B. NA

C. BA

(—) Solid curves: adsorbed layer; (---) dashed curve: clean Pt(111).

Experimental conditions: adsorption from PYR (0.1mM, -0.1V), NA (1mM, -0.2V), or BA (1mM, -0.1V) in 10mM KF (pH 7); rinse and scan in 10mM KF (pH 7); 5mV/S.

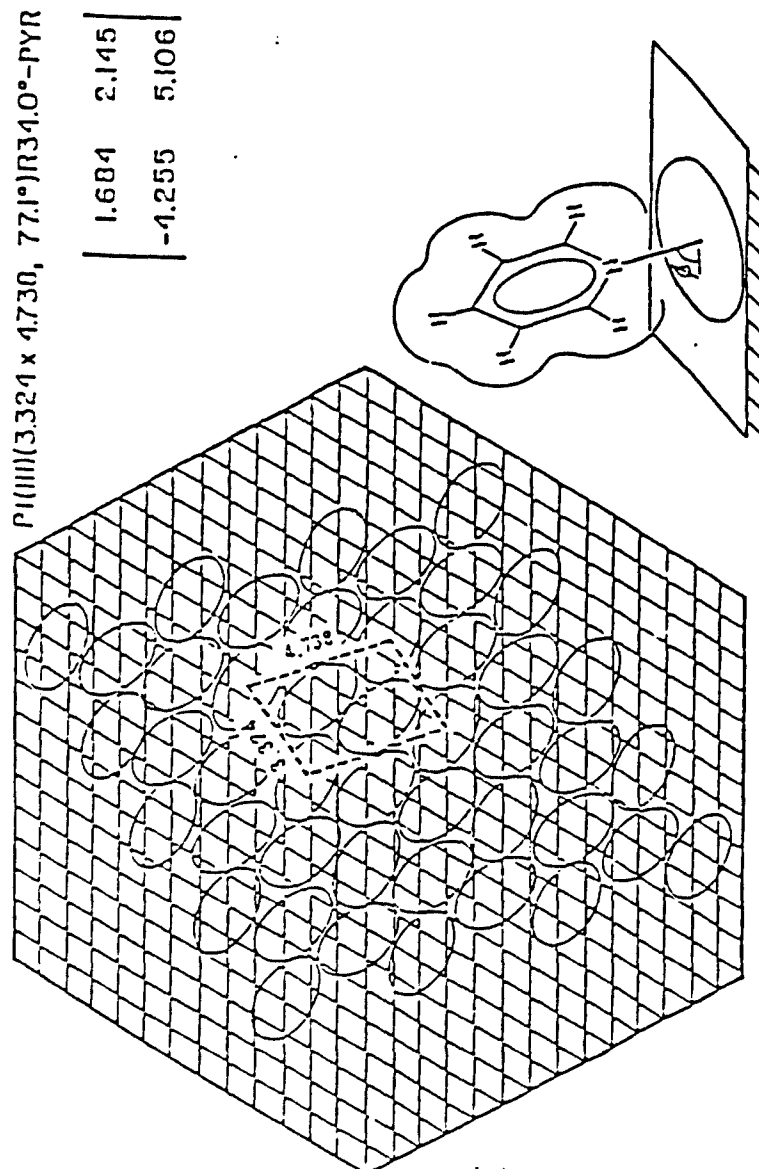


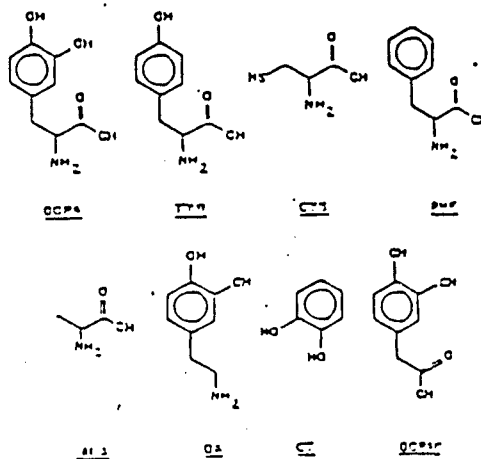
Figure 6. Model of the Pt(111)(3.324 x 4.730, 77.1°)R34.0°-PYR. The PYR packing density in this model is 0.421nmol/cm². Experimental conditions: adsorption from 1ml PYR in 10ml KF (pH 7) at -0.3V, followed by rinsing with 0.1ml KF (pH 7).

In a few words, the results are: carboxylate of INA is pendant at all potentials, as expected from the para structure of INA; on the other hand, the PA carboxylate group always interacts with the Pt surface, as expected from its proximity to the N and Pt. Similar trends are exhibited by the various pyridine dicarboxylic acids.

(vii) Cyclic voltammetry of the (3-pyridyl)hydroquinone adsorbed layer before and after one hour in vacuum yielded virtually identical results. A small decrease in background current was the only effect of evacuation. Experiments were also performed in which LEED, Auger and EELS were performed prior to voltammetry. Again, the voltammetric results were the same. The pyridine anchor and the hydroquinone pendant are sufficiently stable in vacuum and electron beams to allow their study by the methods we use. Please refer to Reference 125 for details.

C. Molecular Conformations and Reactivity of Amino Acids at Pt(111).

Combining the AFOSR instrumentation with operating support from the National Institutes of Health has allowed us to follow up the pyridine studies with further substantiation from studies of aromatic amino acids and related fragments (121):



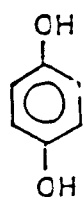
The essence of our findings is as follows: Two planes were studied to give us an indication of the influence of surface plane on adsorption and reactivity, namely, Pt(111) and Pt(100). Packing densities measured by two Auger spectroscopic methods indicate adsorption of DOPA, TYR, DA, CT and DOPAC with the aromatic ring parallel to the Pt surface. The side chains tend to be pendant at Pt(100) and coordinated at Pt(111), based upon packing densities. As a result, oxidation of the adsorbed layer is more extensive (larger n_{ox}) at

Pt(111) than at Pt(100). In contrast, CYS is adsorbed through the S atom, while ALA and PHE are attached through their amino acid moieties. Evacuation does not influence the voltammetric behavior of the adsorbed layers of these compounds. Vibrational (EELS) spectra of these adsorbed species reveal that the hydroxyl hydrogens of DOPA, TYR, DA, CT and DOPAC as well as the carboxylhydrogens at PHE and DOPAC, all horizontally oriented adsorbates, are partially or completely removed as a result of the adsorption process. CT forms an ordered layer at Pt(111), but the others do not have long range order as judged by LEED. Competition among the acid, amine, amino acid and aromatic moieties of these compounds for coordination to the surface is thus a function of the structure of the surfaces, resulting in a strong dependence of bonding and reactivity of surface species on surface structure. Details and further analysis of the results are given in References 121 and 128.

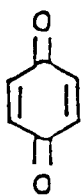
D. Adsorption and Reactivity of Phenols at Pt(111):

Studies were made of a group of phenols with respect to their adsorption at Pt(111), packing density and stoichiometry as judged by Auger spectroscopy, vibrational frequencies as judged by EELS, and electrochemical reactivity by use of voltammetry and coulometry (117, 119). Phenols were chosen for study because hydroquinone and catechol are electroactive and water soluble, allowing their study by electrochemical methods as well as the more general electron and photon spectroscopic techniques. Our goal in studying the phenols is of course to understand the surface electrochemistry and catalytic chemistry of aromatic compounds. These phenols are yielded results which have moved us substantially in the direction of our goal, and have served as a connecting link between electrochemical studies (described in about 45 AFOSR-supported publications) and the newer electron spectroscopic investigations. Details are given in References 117 and 119. Only a brief synopsis will be attempted here.

The compounds studied are:



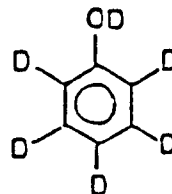
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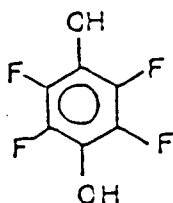
BQ



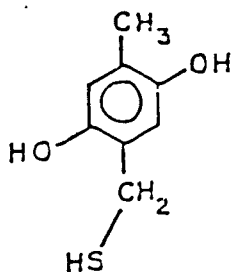
PL



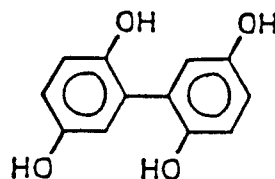
PDPL



TFHQ



DMEM



THEP

Packing densities measured by two independent Auger methods indicated adsorption of HQ, BQ, PL, DPDL and TFHQ with the ring parallel to the Pt(111) surface, while DMEM was attached through the sulfur atom with the ring pendant from the surface. EELS spectra of these adsorbed compounds are virtually the envelope of the IR spectrum, except that the OH hydrogens are partially or completely removed as a result of adsorption. Horizontal orientations of all but DMEM are much more stable at Pt(111) than at polycrystalline surfaces (47). Studies of deuterated compounds such as PDPL confirmed the EELS assignments based upon the IR spectroscopy literature, and demonstrated the purity of the adsorbed layer. HQ, BQ, PL and PDPL displayed substantial long-range ordering when adsorbed from dilute aqueous solutions. DMEM displayed reversible quinone—hydroquinone electroactivity in the adsorbed state. THBP formed a mixed layer,

the vertical component of which was electroactive. Electro-oxidation of adsorbed HQ, BQ, PL, and PDPL preceded irreversibly but completely to CO_2 . No significant changes in electroactive behavior of these adsorbed compounds occurred as a result of evacuation or electron spectroscopic characterization under the conditions of these experiments: electron spectroscopy is applicable to the study of typical aromatic compounds adsorbed at electrode surfaces.

E. Sulfide at Pt(111) and Pt(100):

AFOSR funded instrumentation was employed for study of the processes which take place when metals are treated with aqueous sulfide solutions (127). Voltammetry revealed that oxidative desorption of adsorbed S occurs at relatively positive potentials (primarily as SO_4^{2-} ions) but reductive desorption did not occur to a detectable extent. Absence of K^+ ions (based upon Auger spectroscopy) followed adsorption from K_2S solutions is evidence that the layer is composed of a neutral Pt S coordination compound. Adsorbed sulfur layers are highly ordered under all conditions of adsorption where the S layer is stable. LEED patterns are Pt(111)($\sqrt{3} \times \sqrt{3}$)R30°-S and Pt(100)($\sqrt{2} \times \sqrt{2}$)R45°-S. In particular, sulfide is one of the few adsorbates studied thus far which forms a primitive, highly ordered structure at room temperature on the otherwise complicated Pt(100) surface. EELS spectra of the sulfur layer have identified the Pt-S vibrational modes of these interesting adsorbed layers.

F. Comparison of Annealed and Electrochemically-Cycled Pt Surfaces.

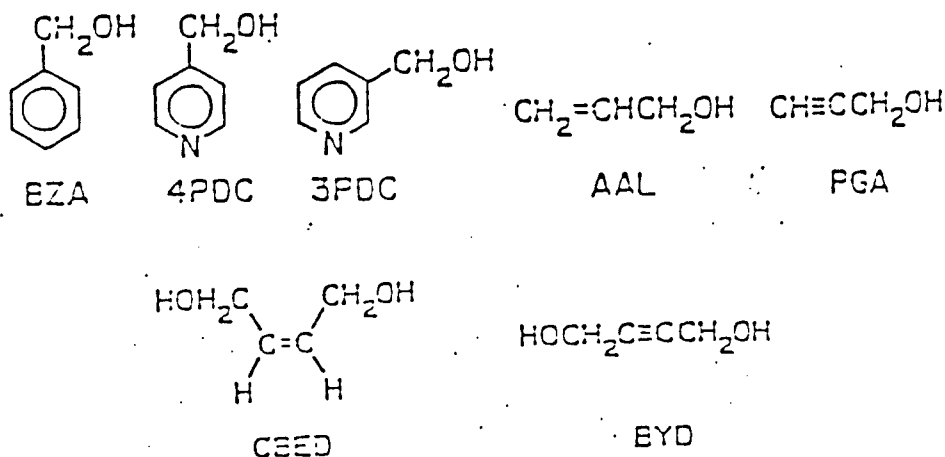
An intriguing series of experiments has been performed in which packing density, electrochemical reactivity and surface vibrational spectra are compared for various typical adsorbates at annealed Pt(111) and electrochemically-cycled Pt(111) surfaces (126,137). By "cycled" is meant the repeated oxidation (+1.4 V vs. Ag/AgCl) and reduction (-0.2 V) process by which electrochemists commonly clean their electrode surfaces.

The purpose of these experiments is, of course, to reveal the effects which the cycling process might have upon the nature of adsorbed species and electrocatalytic reactivity as judged by EELS, Auger spectroscopy, and voltammetry. Future work will add polycrystalline surfaces to the single-crystal surfaces already studied. Compounds

studied to date are: HQ, THBP, DMBM, 3PHQ, NA and 3-thiophene carboxylic acid (3TCA). Very striking differences are observed between annealed and cycled surfaces in all respects: electrochemical reactivity, vibrational spectroscopy and quantitative aspects (126,137). Elastic, specular reflection of slow electrons from the Pt surface is diminished 30-fold by cycling, evidence of surface roughness. Vibrational intensities and frequencies are profoundly altered. For instance, aromatic C-H stretching increases upon cycling, while O-H stretching in the pendant groups decreases. Spectral changes are greatest for HQ and THBP bound to the surface primarily in horizontal orientations, in contrast to the vertically oriented adsorbates DMBM, 3PHQ, NA and 3TCA. Evidently, cycling influences the bonding of the HQ aromatic ring to the Pt surface, leading to more pronounced spectral changes than for the vertical adsorbates which undergo less contact between the aromatic ring and the surface. Packing density as measured by Auger spectroscopy changes as a result of cycling. This is further indication that cycling causes profound changes in surface and adsorbed layer geometric structure and electronic properties.

G. Adsorption and Reactivity of Unsaturated Alcohols at Pt(111).

Unsaturated alcohols provide an opportunity to view the interplay between two competing adsorbates (OH and C=C) in the same layer, as well as between the electrochemical reactants in the same molecule (132). Also, this marks one of our first inroads into the study of neat organic liquids at well-defined surfaces. Compounds included in this initial study were:

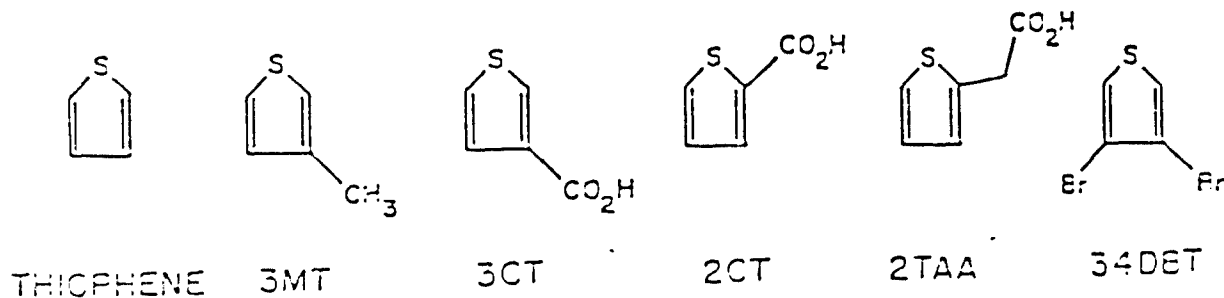


Chemisorption of the unsaturated center of each compound proves to be the principal mode of surface attachment (phenyl, pyridyl, alkenyl or alkynyl moiety). Electrochemical oxidation of adsorbed BZA, AAL, PGA, CBED and BYD in aqueous fluoride electrolyte proceeds efficiently to CO_2 , while adsorbed 4PDC and 3PDC are relatively inert. Evidently, the pyridine ring keeps the alcohol moiety out of contact with the pt surface. Oxidation of BZA, AAL, PGA, CBED and BYD in each case begins with the alcohol moiety, followed by oxidation at more positive electrode potentials of the unsaturated point-of-attachment to the surface. The adsorbed layer of each of these alcohols is stable in vacuum, such that surface spectroscopic methods in vacuum are directly applicable to the liquid-solid interfacial chemistry and electrochemistry of these compounds. 4PDC and 3PDC are adsorbed in a tilted vertical orientation, analogously to pyridine. The triple bonds of PGA and BYD are evidently converted quantitatively to double-bonds as a result of the adsorption process. However, the aromatic and alkene and alkene groups of adsorbed BZA, 4PDC, 3PDC, AAL and CBED remain essentially intact, with only small shifts in their vibrational frequencies (EELS).

H. Thiophene and Derivatives as Monomers and Polymers at Pt(111).

Thiophene and its derivatives polymerize relatively easily at an electrode surface under mildly oxidizing conditions in an aprotic solvent such as acetonitrile (166-171). Acetonitrile adsorbs strongly at transition metal surfaces (42,45), and this would be expected to compete with the polymer for attachment to the surface (105). Likewise, the thiophene monomers could attach to the surface prior to polymerization (172,173). In order to better understand the nature of the electrogenerated polymers and the role of solvent, monomer and electrolyte in polymer attachment to a solid surface, we have undertaken studies of thiophene monomers and polymers at Pt(111) surfaces using LEED, Auger, EELS and electrochemistry (129). Surface infrared spectroscopy will be performed in the near future on these layers.

Compounds studied to date are:

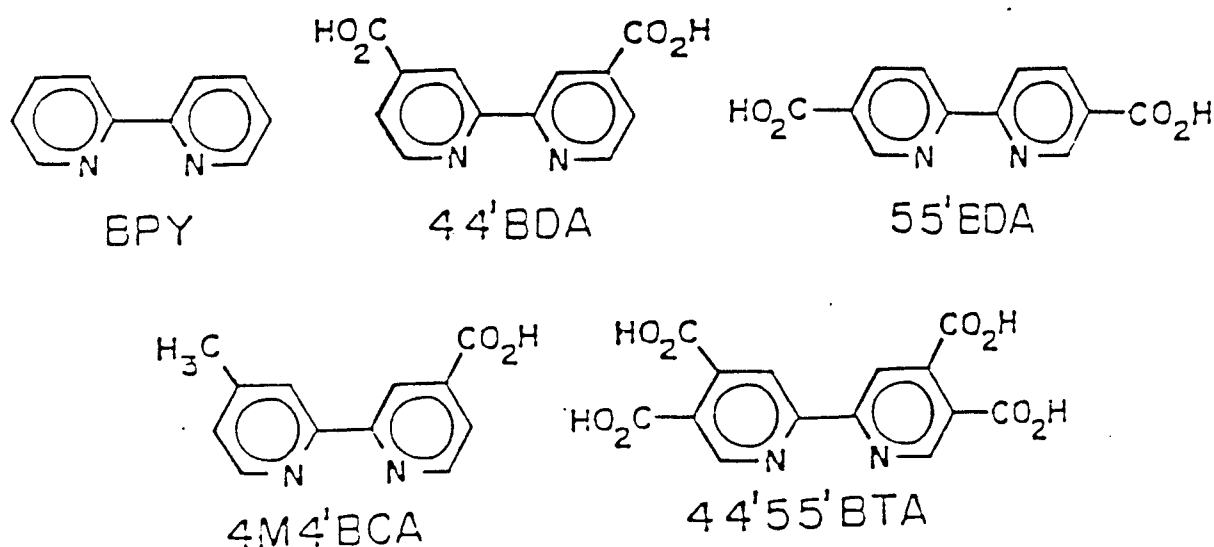


Each of these compounds proves to be strongly adsorbed at Pt(111) from aqueous solutions in a close-packed layer of tilted vertical orientation. However, adsorption from acetonitrile solutions occurs only at much higher concentrations (greater than 0.1 M) than were previously employed for electropolymerization reactions. Adsorbed monomer remains attached under the conditions used for polymerization. Evidently, filming of an electrode surface occurs in spite of the presence of a pre-adsorbed layer of solvent and/or monomer! Pendant carboxylate groups are present in the monomeric layer of 3CT, 2CT or 2TAA. Some coordination of carboxylate groups to Pt occurs at positive electrode potentials, but to a lesser extent than for NA and related pyridine derivatives. Accordingly, thiophene monomers and polymers are also excellent anchors for functional group attachment to surfaces. Unfortunately, some desulfurization occurs during adsorption. 34DBT has the interesting property that its electropolymerized film is relatively free of C-H bonds, as evidenced by EELS spectra of the polymer. Relatively inert and very adherent polymeric films might therefore be possible from monomers of this type. We are at a preliminary stage on this topic, and work is continuing.

I. 2,2'-Bipyridyl and Derivatives at Pt(111).

In collaboration with Professor Michael Elliot (Colorado State University) we are investigating 2,2'-bipyridyl and derivatives at Pt(111) (133).

Compounds studied to date are:



The objective of these studies was to determine whether the placement of the nitrogen atoms in BPY permits binding of both rings to the Pt surface in the usual tilted-vertical orientation. It does. We also experimented with the potential-dependence of the acid O-H stretching bonds in 44'BDA, 55'BDA, 4M4'BCA, and 44'55'BTA. Coordination of the carboxylate groups to Pt is less extensive in the PBY derivatives than in pyridine derivatives and chemisorption of BPY is weaker than pyridine.

J. Halide Films at Ag(111) Electrodes.

Along with future studies of noble metal surfaces our plans include non-noble metals and alloys. Studies of single-crystal stainless steel alloys were reported previously (81,83,85,109). Silver (114,115) and eventually silver alloys are another important avenue for future study.

Studies have been made by means of Auger spectroscopy, LEED, and voltammetry of the surface layers which are formed when an Ag(111) surface is immersed into aqueous halide solution (KF, KCl, KBr and KI) at controlled pH, and electrode potential. The full range of electrode potentials was explored (from water reduction to silver dissolution). Two pH's were studied: 4 and 10. Surface composition was monitored by means of quantitative Auger spectroscopy. Seven elements, F, Cl, Br, I, O, K and Ag entered into these studies. Strong adsorption of Cl, Br and I occurs throughout most of the potential range. F and K adsorption is negligible. Oxygen is present only at relatively positive potentials in alkaline solutions. One of the surprising characteristics of Ag surfaces not previously discovered is that halide is chemisorbed at virtually all potentials, and not merely on the positive side as commonly believed. In fact, chemisorption of Cl^- , Br^- , and I^- is a one-electron redox process spanning the entire useful potential range; adsorption of I^- is so strong that it cannot be removed by reduction in aqueous electrolytes at pH 4 or 10. Cl and Br form a highly ordered Ag(111) ($\sqrt{3} \times \sqrt{3}$)R30° monoatomic layer, while I yields some of the same complex structures as are found in Ag deposition at iodine-pretreated Pt(111). (See References 52-54 and 56-58.) In other words, Ag is essentially always halide-covered in Cl^- , Br^- or I^- media, and is structurally reconstructed in I^- solutions.

K. Electrodeposition of Bi, Tl, Pb and Cu at Ag(111) Electrodes.

A step in the direction of understanding electroplating of non-noble substrates has been taken through studies of electrodeposition of Bi, Pb, Tl and Cu at Ag(111) from aqueous solutions (115).

Electrodeposition of Bi from trifluoroacetic acid (TFA) solutions onto Ag(111) under linear scan voltammetric conditions takes place in an underpotential deposition (UPD) peak followed by deposition of bulk Bi. Both stages involve substantial activation barriers. The Bi UPD layer is stable at open circuit, contains 0.55 Bi atoms per Ag surface atom, and is hexagonally close-packed in a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ structure consisting of strip-shaped domains averaging $8.5\sqrt{3}$ silver unit meshes in width. Electrodeposition of Pb onto Ag(111) from non-chemisorbing electrolytes such as acetate, TFA, and perchlorate gives three UPD peaks, while deposition from Cl^- , Br^- , or I^- media result in only one UPD peak. The Pb layers are unstable at open circuit. That is, Pb corrodes away in acidic aqueous solutions to yield an ordered layer of PbO , the structure of which is different for each halide electrolyte. Use of aprotic electrolytes to stabilize the Pb deposit should be explored in future work.

Electrodeposition of Tl from TFA electrolyte gives four UPD peaks. The electrodeposited Tl layer is unstable at open circuit, giving an ordered TlOH layer having a $(3\sqrt{3} \times 3\sqrt{3})R30^\circ$ structure.

Electrodeposition of Cu at Ag(111) gives no UPD peaks (Cu and Ag are chemically similar). The bulk Cu electrodeposit is stable at open circuit, and consists of monolayers of Cu which yield diffuse LEED patterns. That is, the Cu covers the surface evenly but has insufficient long-range order to yield interpretable LEED patterns.

L. Alkenoic Acids at Pt(111)

Studies of the electrochemical oxidation of a series of straight-chain terminal alkenoic acids adsorbed at a Pt(111) electrode surface from aqueous electrolyte have been conducted (138). Compounds adsorbed were: propenoic acid (acrylic acid, PPA); 3-butenic acid (vinylacetic acid, 3BTA); 4-pentenoic acid (allylacetic acid, 4PTA); 6-heptenoic acid (6HPA); and 10-undecenoic acid (10UDA). Vibrational spectra of adsorbed layers were obtained by use of electron energy-loss spectroscopy (EELS). Molecular packing densities were measured by use of Auger spectroscopy. Electrochemical

oxidation of each adsorbed layer was explored by means of cyclic voltammetry in aqueous inert electrolyte (KF/HF). As the analogous aliphatic acids are not chemisorbed at Pt under the same conditions, the alkenoic acids evidently adsorb at Pt(111) predominantly through the C=C double bond. Molecular packing densities indicate that the carboxylic acid moiety is in contact with the Pt surface only in the case of PPA. EELS spectra also indicate that the carboxylate groups (other than in PPA) are present as pendants. The carboxylic acid O-H stretching bands of most of the adsorbed acids are red-shifted and broadened, evidently due to extensive intermolecular hydrogen bonding; the exceptions are PPA, for which the interaction is primarily with the Pt surface, and 3BTA, for which intermolecular interaction between the carboxylic acid pendants is apparently prevented by steric considerations. The surface-attached carboxylic acid moieties react with KOH solution, leading to retention of K⁺ ions, detected by Auger spectroscopy, and to changes in the vibrational spectra indicative of carboxylate anions; reactivity toward KOH decreases with chain length. Adsorbed alkenoic acids at Pt(111) surfaces are stable in water and in vacuum. Oxidation of the adsorbed short-chain acids PPA and 3BTA proceeds to completion, forming CO₂ as the principal product. Oxidation of the adsorbed long-chain acids converts the C=C moiety to 2CO₂, and transforms the remainder of the molecule to an unadsorbed diacid (likely possibilities are malonic acid from 4PTA; glutaric acid from 6HPA; and heptane-1,7-dioic acid from 10UDA).

M. Multinitrogen Heteroaromatics at Pt(111):

Surface electrochemical studies of several multi-nitrogen heteroaromatics and their carboxylic acid derivatives adsorbed at well defined Pt(111) electrode surfaces from aqueous solutions have been performed (139). The adsorbates studied include pyrazine (PZ), pyrimidine (PM), pyridazine (PD), 2-pyrazine carboxylic acid (PZCA), 2,3-pyrazinedicarboxylic acid (23PZDCA), 4-pyridazine carboxylic acid (4PDCA) and 1,3,5-triazine (TZ):



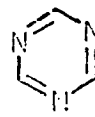
PZ



PM



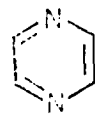
PD



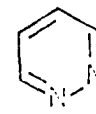
TZ



PZCA



23 PZDCA



4 PDCA

Packing densities (moles adsorbed per unit area) of each compound adsorbed from solution at controlled pH and electrode potential were measured by means of Auger spectroscopy. All of the above compounds except TZ adsorb strongly to Pt(111). Surface vibrational spectra of these adsorbed layers were obtained by electron energy-loss spectroscopy (EELS) and were compared with either vapor or condensed phase infrared (R) spectra of the parent compounds. The similarity of EELS and IR spectra indicate that the adsorbates retain their molecular structure unchanged as a result of adsorption. Adsorbed layers of these materials are stable in contact with aqueous fluoride solutions, and are stable also in vacuum. The adsorbed layer is electrochemically unreactive, and tends to passivate the Pt surface. Carboxylic acid substituents of these compounds interact with the Pt surface to an extent which depends upon the electrode potential. Long-range order is absent from the adsorbed layer, based upon LEED observations, although the Pt(111) surface remains ordered. The adsorbed molecules are attached to the surface primarily through the least hindered ring nitrogen atom, and are arranged in tilted-vertical orientation with the average ring-to-surface angles ranging from 73° to 86°, Figure 7.

N. Alkenols at Pt(111)

Studies of adsorption and electrochemical oxidation of a series of straight-chain terminal alkenols at a Pt(111) electrode surface have been conducted (141). Vibrational spectra of each adsorbed layer were obtained by use of electron energy-loss spectroscopy (EELS). Molecular packing density in the adsorbed layer was measured by means of Auger electron spectroscopy. Substrate surface structure was monitored by use of LEED. Electrochemical oxidation of each adsorbed layer was explored by means of linear potential scan voltammetry in an inert aqueous electrolyte (KF/HF). Compounds studied are: 2-propen-1-ol (PPEOH, allyl alcohol); 3-buten-1-ol (BTEOH); 4-penten-1-ol (PTEOH); 5-hexen-1-ol (HXEOH); and 10-undecen-1-ol (UDEOH). Attachment to the surface is primarily through the C=C double bond, Figure 8. Regardless of chain length each chemisorbed alkenol molecule occupies an area similar to that of PPEOH. EELS spectra indicate that the C=C double bond is preserved in the adsorbed state. Evidently, the C=C axis is parallel to the Pt(111) surface, and the aliphatic chain is pendant. The -OH moiety is in contact with the Pt surface only in the case of PPEOH.

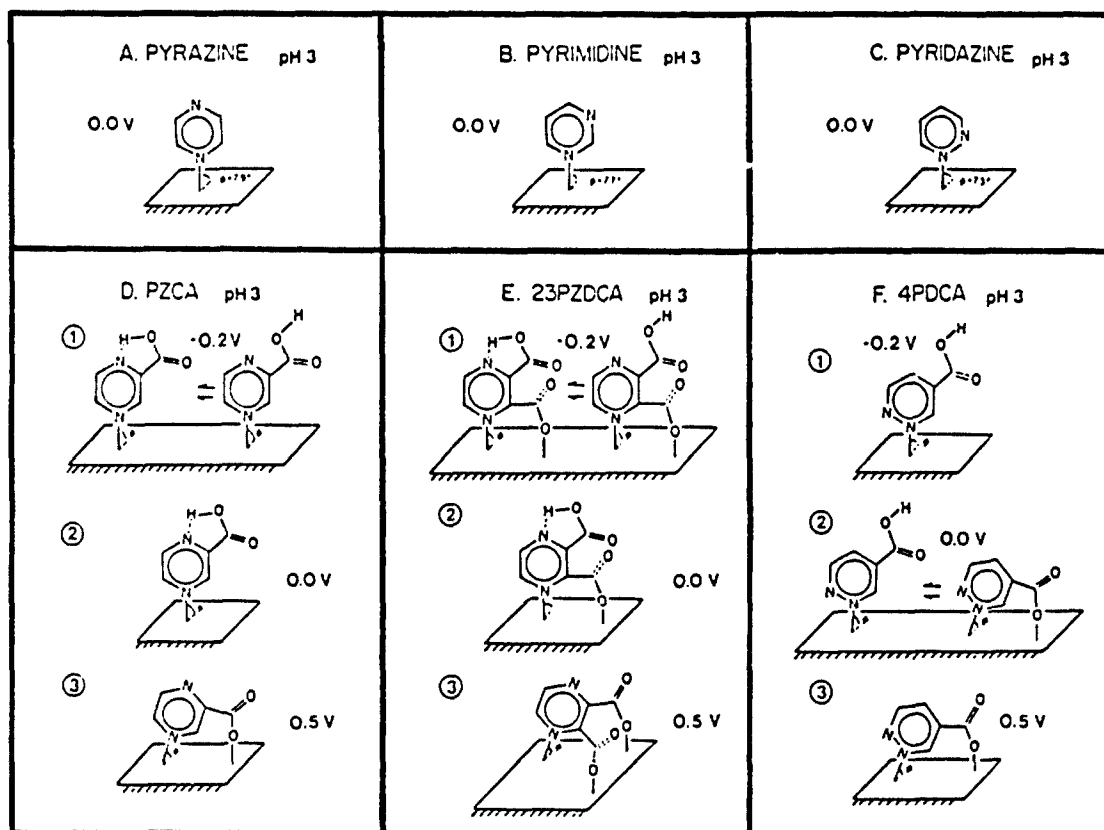


Figure 7: Structural models of adsorbed dinitrogen heteroaromatics (139). Values of θ based upon Auger data for adsorption from 1 mM adsorbate (pH 3) solution at 0.00 V are:

- | | |
|-------------------------------|------------------------------------|
| A. PZ ($\theta = 79^\circ$) | D. PZCA ($\theta = 86^\circ$) |
| B. PM ($\theta = 77^\circ$) | E. 23PZDCA ($\theta = 80^\circ$) |
| C. PD ($\theta = 73^\circ$) | F. 4PDCA ($\theta = 86^\circ$) |

An O-H stretching band is present only in the EELS spectrum of BTEOH; intermolecular hydrogen bonding (PTEOH, HXEOH, UDEOH) and interaction with the Pt surface (PPEOH) eliminate the O-H stretching bands of the other adsorbed terminal alkenols studied. Measurement of the average number of electrons, n_{ox} , required for catalytic electrochemical oxidation of an adsorbed molecule reveals that oxidation takes place primarily at the C=C double bond and one adjacent saturated carbon.

O. Alkenes at Pt(111)

Studies of the surface packing density, vibrational spectroscopy and electrochemical oxidation of a series of straight-chain terminal alkenes adsorbed from the vapor at a Pt(111) electrode surface have been completed (142). Compounds studied were: ethene (ETE), propene (PPE), 1-butene (BTE), 1-pentene (PTE), 1-hexene (HXE), 1-octene (OCE) and 1-decene (DCE). Vibrational spectra of the adsorbed layers were obtained by use of electron energy-loss spectroscopy (EELS). Molecular packing densities (nmol/cm^2) in the adsorbed layer were measured by use of Auger spectroscopy. Electrochemical oxidation of each adsorbed layer in aqueous inert electrolyte (KF/HF) was investigated by means of linear potential scan voltammetry. Attachment to the surface is through the C=C bond. Based upon molecular packing densities, the aliphatic chains are pendant; regardless of its chain length each chemisorbed alkene molecule occupies an area similar to that of chemisorbed PPE, Figure 9. The packing densities of ETE and PPE indicate an average orientation in which the C=C moiety is parallel to the Pt(111) surface. EELS spectra indicate that the C=C double bond is preserved in the adsorbed state of each 1-alkene studied. Measurement of the average number of electrons, n_{ox} , required to electro-oxidatively desorb an adsorbed 1-alkene molecule reveals that the catalytic electrochemical oxidation process involves primarily the C=C double bond and one adjacent saturated carbon atom.

Figure 8: Structural models of adsorbed terminal alkenols at Pt(111).

- A. PPEOH
- B. BTEOH
- C. PTEOH
- D. HXEOH
- E. UDEOH

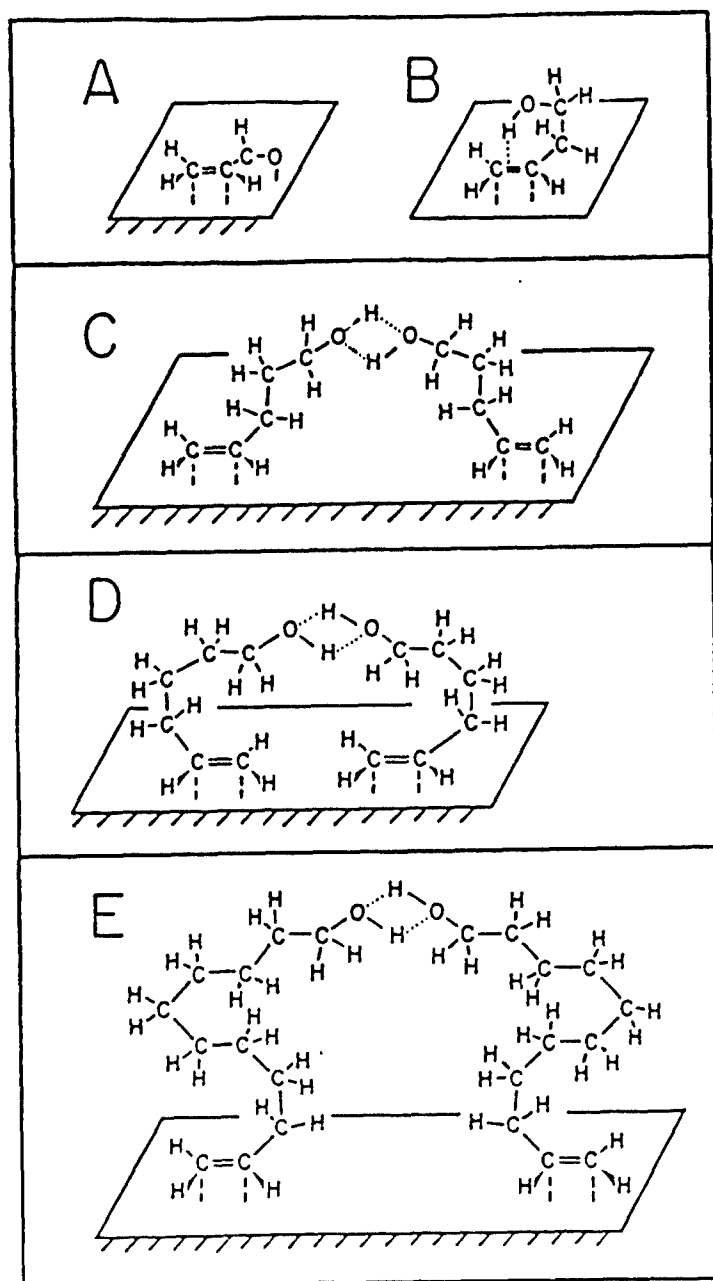
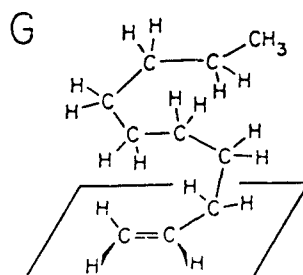
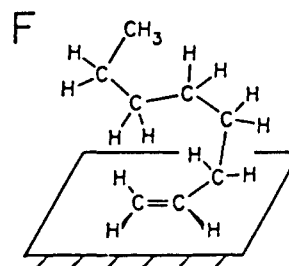
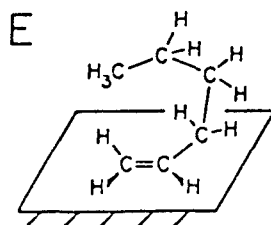
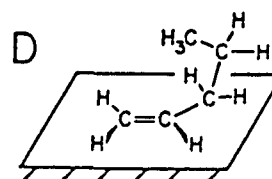
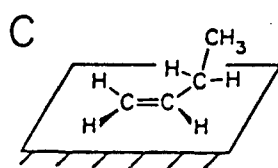
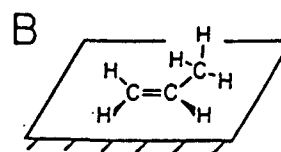
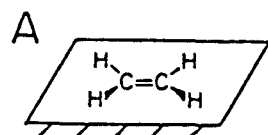


Figure 9: Structural models of adsorbed 1-alkenes at Pt(111):

- | | | | |
|----|-----|----|-----|
| A. | ETE | D. | PTE |
| B. | PPE | E. | XHE |
| C. | BTE | F. | OCE |
| | | G. | DCE |



P. Comparison of EELS and IR Spectra:

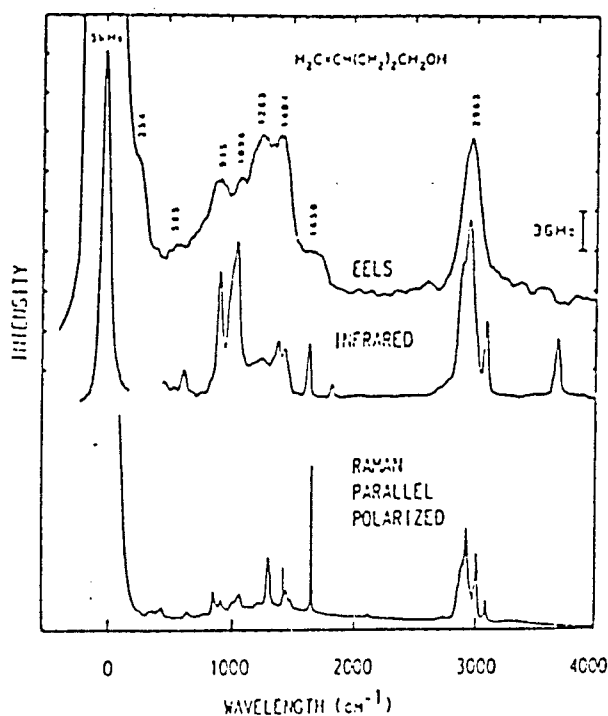
EELS spectra obtained for the adsorbed species formed from aqueous electrolytes at Pt(111) electrode surfaces have been compared with the IR and Raman spectra of the unadsorbed compounds in order to reveal the changes in vibrational spectra resulting from chemisorption of various important functional groups, and to explore the differences in vibrational absorptivities between EELS spectra of adsorbed species and IR and Raman spectra of the corresponding unadsorbed compounds (146). Of particular interest are the variations in EELS vibrational frequency, band width and absorptivity due to bonding with the surface, intermolecular interactions of adsorbed molecules and changes in adsorbate molecular orientation. The influence of surface bonding on the EELS spectrum of a functional group was explored through studies of phenol (PL), phenol- d_6 (PLD6), benzyl alcohol (BZOH), catechol (CT), benzoic acid (BA), 2-picolinic acid (PA), 2,6-pyridine dicarboxylic acid (26PDCA), and propenoic acid (PPEA). The aromatic ring of adsorbed PL, POD6, BZA, CT, BA, PA and 26PDCA is oriented parallel to the Pt(111) surface. The resulting strong interactions affect the frequencies and relative intensities of the EELS bands: weak CH stretching modes; a large CC stretching band (1600–1650 cm^{-1}), and weak CH bending (700–800 cm^{-1}).

The carboxylic acid moieties of BA and PA interact strongly with the Pt surface, while those of 26PDCA do so only when adsorbed at relatively positive electrode potentials. O–H stretching and bending are absent from the EELS spectra of adsorbed PL, BZOH and CT, perhaps due to dissociation of the hydroxyl hydrogen during adsorption of the molecule. Adsorption of alkenes at Pt(111) from solution preserves the characteristic C=C stretching band near 1650 cm^{-1} ; examples are: PPEA; 1-hexene (HXE); propenol (PPEOH); 4-pentenol (PTEOH), Figure 10; and *cis*-2-butene-1,4-diol (CBED); adsorption of ethene, propene and butene from vacuum at room temperature has been reported to result in loss of double-bond character. Adsorption of propynol (PPYOH) lowers the frequency of the C \equiv C triple-bond to approximately that of a double-bond. EELS spectra of adsorbed pyridine (PY), 2-methylpyridine (2MPY) and 2,6-dimethylpyridine (26DMPY) were examined in order to contrast the vibrational behavior of adsorbates having the aromatic ring perpendicular to the Pt surface (PY and 2MPY), giving rise to strong perturbation of the vibrational spectra or parallel (26DMPY), leading to limited perturbation of the vibrational spectra. Compounds for which the

surface interaction is limited primarily to bonding of a single sulfur atom were studied in order to observe the vibrational behavior of a comparatively unperturbed pendant ring or chain: thiophenol (TP); benzylmercaptan (BM); cysteine (CYS); and thiophene (TPE). The expected lack of perturbation was found, making TP, BM and CYS particularly suitable reference compounds for surface vibrational studies of aromatic rings and amino acids.

In contrast, L-phenylalanine (PHE) interacts with the Pt(111) surface through the phenyl ring as well as the amino acid functionality. In general, chemisorption and intra-layer intermolecular interaction both lower the surface vibrational frequencies (EELS) and incidentally affect peak amplitudes. Orientation affects peak amplitudes and incidentally affects frequencies insofar as a change in orientation is accompanied by a change in mode of surface bonding. Surface roughness leads to a scrambling of adsorbed states which affects bandwidths, chemical/electrochemical reactivities, and in turn the frequencies and amplitudes of EELS peaks. Specific findings and conclusions are presented for each compound and correlated.

Figure 10: EELS, IR and Raman spectra of 4-pentene-1-ol (PTEOH). EELS: PTEOH adsorbed at Pt(111) from 1 mM aqueous PTEOH in 10 mM KF (pH 3) at -0.1 V (141). IR: PTEOH vapor at 200°C (Sadtler standard spectrum). Raman: PTEOH liquid (Thermodynamics Res. Center Spectra Data, Texas A&M University).



Q. Imaging Metal Surface Atomic Structure (135,140,154).

Measurements of the complete angular distributions of low energy Auger electrons emitted from well-defined single-crystal surfaces, as illustrated in Figure 11, have led to

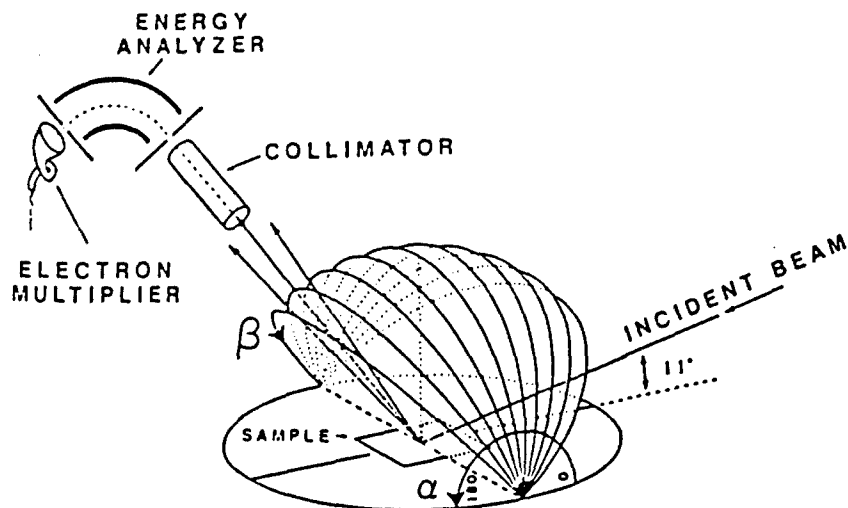


Figure 11 ADAM angular distributions are measured vs. the angular coordinates of the detector (α and β). Auger electron emission is stimulated by a fixed grazing incidence electron gun. Auger electrons emitted from the sample (also fixed) along trajectories selected by the moving analyzer must pass through angle- and energy-resolving optics before being amplified, counted, and recorded.

the discovery that the distributions contain silhouettes of surface atoms backlit by emission from atoms deeper in the solid. Theoretical simulations of Auger electron angular distributions based upon atomic point emitters and spherical atomic scatterers are in close agreement with these experimental results. In view of the definitive results obtained and the straightforward agreement between theory and experiment, angular distribution Auger microscopy (ADAM) is useful for direct imaging of atomic structure, and for fundamental studies of the interaction of electrons with matter. Usefulness of ADAM has been demonstrated by studies of Pt and Ag single crystals, and of thin films of Ag produced by electro-deposition (135,154).

R. Some Implications of These Results

Let us now spend a few moments to consider some of the theoretical and practical implications of the results which have been gathered.

Of course, a very useful implication of the remarkable lack of influence of vacuum and the weak electron beams employed in our electron spectroscopy experiments is that such surface analysis procedures are demonstrated to be applicable to analysis of electrode surfaces. These UHV techniques offer enormous advantages of sensitivity, generality, directness, accuracy, definitiveness, and so forth. This does not mean that we are turning away from the "wet" methods such as thin-layer electrochemistry, voltammetry, coulometry, impedance and so on, which continue to be essential, nor have we ever done so in the past. The success of these techniques also allows study for the first time at electrode surfaces of the behavior of compounds which do not have any particular electrochemical reactivity. We are now prepared to study any chemisorbed compound in any practical amount. Weakly adsorbed compounds of course require other methods.

A benefit of the observed similarity between EELS spectra of adsorbed compounds and IR spectra of unadsorbed compounds is that the extensive IR literature will greatly facilitate assignment of the EELS spectra and identification of adsorbed species. EELS has produced definitive spectra of all of the chemisorbed compounds we have studied thus far. Sensitivity is excellent, although resolution is moderate. The full frequency range is covered from far IR to near IR. Beam damage is generally negligible. Reproducibility in our experiments is excellent. The correlation between EELS spectra and electrochemical conditions is remarkably close. Nevertheless, EELS is not a stand-alone technique; its usefulness increases when it is combined with other definitive techniques and with reproducibly prepared samples.

Confirmation of the thin-layer electrochemical measurements of hydroquinone and related packing densities by Auger spectroscopy has the advantage of strengthening confidence in electrochemical and vacuum measurements. Comparison of data can also test the accuracy of calibration of the various methods. Differences between polycrystalline TLE results and single-crystal UHV results are useful in understanding the role of surface structure in catalytic processes. UHV studies of polycrystalline surfaces also contribute to understanding of this matter.

Comparison of electrochemical reactivity, packing density, stoichiometry and vibrational spectroscopy at electrochemically-cycled surfaces versus UHV annealed surfaces under otherwise identical conditions consistently reveals major differences in behavior. Such information is a valuable source of clues as to the role of surface structure and of adsorbed species in surface chemistry, catalysis and materials behavior. It is also a warning concerning the risks of surface spectroscopy and chemistry projects which ignore surface characterization.

Comparisons such as the amino acid studies at Pt(111) and Pt(100) of the influence of crystal planes on adsorption and electrochemical reactivity are a source of previously unavailable, essential information concerning the nature of adsorbed intermediates and the factors controlling reaction rates and product distribution.

Investigations of NA under conditions of potential-dependent and pH-dependent adsorption have yielded a remarkably definitive and unusual look into the interactions between a surface, an adsorbed layer and a solution. These observations are proving to be general, as noted from the trends consistently displayed by a variety of compounds. Surface electrochemistry and acid-base chemistry will never be the same again. LEED studies of PYR and other organic adsorbates at electrodes reveal some intriguing characteristics of the close-packed, oriented but incommensurate and presumably undulating layers. The cyclic voltammetry of adsorbed pyridine and benzoic acid reveals the remarkable differences in electrochemical reactivity of the N-bonded pyridine molecule and the pi-bonded benzoic acid (or other horizontally oriented benzene derivatives).

Studies of the layers formed by adsorption from ionic solutions such as sulfide are an essential part of the understanding of electrodes and electrical double-layers. They are also of importance in connection with passivation, metal coating and electroplating behavior. Surface structure studies and theories of surface valency will benefit from this new knowledge.

Alcohols are of great interest in connection with fuel cell behavior. Unsaturated alcohols readily provide insights into the behavior of aqueous organic solutions. Electro-oxidation rates, mechanisms and products are accessible for alcohol solutions. Studies of the neat alcohols are one of the first instances of study of pure liquids in contact with well-defined metallic surfaces.

Electropolymerization studies at well-defined surfaces by use of the techniques employed in our work will add a useful bit of information concerning the nature of the films: stoichiometry, mode of attachment, and molecular structure from Auger, EELS and surface infrared spectroscopy.

Studies of non-noble metals, whether silver, ferrous alloys, or virtually any other element or combination, often much easier to achieve than those of the difficult metal platinum, will broaden and deepen the understanding gained from such experiments. Electrodeposition studies at the level of atoms and molecules are vital to microcircuit fabrication and preparation of metal doped catalysts.

While many of our recent studies have focused on a few compounds, we note that there is also theoretical and practical benefit in studying families of compounds spanning the various possible chemical characteristics, thus allowing the opportunity to discover phenomena and trends which might be missed by investigations of only a small set of similar compounds.

Clearly, the measurement of low-energy Auger electron angular distributions (the ADAM method) will yield valuable evidence regarding the structures of crystalline surfaces, atomic layers, ionic layers, molecular layers, alloys and thin-films of importance in the entire range of chemical, physical and biological sciences and engineering.

III. PUBLICATIONS

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anal. Chem.*
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IV. SCIENTIFIC PERSONNEL

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James White. Postdoctoral Research Chemist. BS, 1982, California Polytechnic State University; Ph.D., 1986, University of California Santa Barbara.

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V. CURRENT SUPPORT —ARTHUR T. HUBBARD

Gas Research Institute.

"Electrocatalyst Surfaces".

December, 1986 — November, 1989	\$359,500
January, 1990 — December, 1991	\$423,807

Air Force Office of Scientific Research, SR86-0200.

"Electrochemistry of Molecules Attached to Metal Surfaces".

May, 1987 — April, 1988	\$148,994
May, 1988 — April, 1989	\$156,443
May, 1989 — April, 1990	\$171,414
May, 1990 — April, 1991	\$120,649

Department of Energy.

"Surface Chemistry of Electrocatalysts".

July, 1986 — July, 1988	\$167,670
August, 1988 — July, 1989	\$112,955
August, 1989 — July, 1990	\$ 60,000

National Institutes of Health. 5 R01 GM38311

"Interfacial Electrochemistry of Biomolecules".

January — December, 1987.	\$101,727
January — December, 1988.	\$104,546
January — December, 1989	\$108,573
January — December, 1990	\$112,203

National Science Foundation

"Electrochemistry at Well-Defined Surfaces"

June, 1987 — May, 1988	\$145,000
June, 1988 — May, 1989	\$145,000
June, 1989 — May, 1990	\$225,000
June, 1990 — May, 1991	\$151,900

United Technologies Pratt & Whitney (Lehr Precision)

"Titanium Alloy Study"

December, 1988 — March, 1989	\$ 30,000
January, 1990 — December, 1991	\$320,000