



Final Report  
 In-situ X-ray Analysis  
 of the Electrolyte-Solid Interface  
 ONR Grant Number N00014-90-J-1326

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Abstract

This project was undertaken to advance the experimental technology of x-ray absorption spectroscopy in the study of electrochemical interfaces. The objective was to establish the standard by which subsequent measurements would be evaluated. To this end we paid a great deal of attention to the details of the control of a large sample, the potential pitfalls related to artifacts in the data, and to high quality analyses of the results. These goals were met.

Extended x-ray absorption fine structure (EXAFS) is capable of revealing the near-neighbor environment of a specific element in a complicated system. By placing a monolayer of a foreign metal on an electrode, and studying this material, we hoped to reveal the geometry of the electrolyte in the first layer next to the sample. We chose Cu on Pt as the prototype, partly for its suitability regarding x-ray absorption edges, and also for its exemplary role as a strongly bound electrochemically controlled adsorption system. Our experimental design was based upon use of an unusually large sample (47 cm<sup>2</sup>) to obtain large signals. The sample was excited with grazing incidence x-rays, and the absorption structure associated with the Cu was monitored through the Cu K $\alpha$  emission. We used a specially designed sample and electrolyte control system that enabled experiments to be performed with both p- and s-polarized incident radiation. We discovered that this combination was essential for the unique determination of the coordination number of a given neighbor. The data are of exceptionally high quality with regard to the signal-to-noise ratio (S/N = ~ 5 in  $k\chi$  for a single 20 minute scan). When averaged and analyzed by state-of-the-art procedures we were able to identify the atomic environment of Cu in the stable layer. We found the following average characteristics: 2 O atoms at 1.04 Å, 4 Cu atoms at 2.62 Å, and 6 Pt atoms at 2.65 Å. This is consistent with an evolving consensus that oxygen plays a significant role in the structure of some metal electrodes that were previously thought to be completely reduced. The copper neighbors are not in a close-packed relationship to each other. On the contrary, the stable layer must be significantly open. Our model would place the copper in a three-fold hollow site on the Pt.

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In addition to the x-ray absorption experiments, we also conducted extensive testing using conventional electroanalysis, optical experiments on the Cu-covered electrodes, and more novel measurements based upon the quartz crystal microbalance. Through the latter technique we were able to show that the electroadsorption valence changes, as a function of copper coverage, from above 2 at low coverage to nearly zero for the stable layer. This information supports the x-ray experiments by showing that co-adsorption helps determine the structure of the final configuration.

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# 1 Introduction

With the availability of high intensity tunable x-ray sources associated with synchrotron radiation facilities it is now possible to perform structural studies on very dilute samples which would not have been possible only a few years ago. Attracted by this potential we undertook a program designed to reveal the identities and arrangements of atoms at the electrolyte-solid interface. When we began this effort six years ago there were only a few reports of the successful application of EXAFS in an electrochemical environment. We were convinced that the technique was being limited by the poor signal-to-noise (S/N) quality of those data. EXAFS analysis must be performed very carefully on clean data to avoid faulty conclusions. We adopted as our primary objective the goal of obtaining absorption spectra that were far better than had been achieved in the past. Therefore, our principle aim was to improve the methodology of electrochemical EXAFS experimentation and data analysis.

Since x-rays are not, by fundamental properties, particularly sensitive to the surface of a sample there are two important features that had to be introduced. First, the experiment had to be conducted at grazing incidence. Since the index of refraction for x-rays in matter is less than in air, one can achieve total reflection provided the incident angle is beyond the critical angle. For a material like Pt this means the x-rays could not make an angle larger than about 8 mrad with the surface. Second, we needed to mark the surface with a chemically distinct layer, different from the bulk metal of the electrode, since even at grazing incidence some x-ray energy penetrates into the substrate. Our choice was to use Pt as the electrode and Cu as the overlayer. Prior to 1989 this was thought to be a fairly well understood system—of the underpotential deposition (UPD) family. That is, the Cu is more strongly bound to the Pt than it is to itself. This makes it possible to electroplate one layer of Cu onto Pt using a control voltage which is more positive than that which would produce multilayer plating. Our long-term plan was to thoroughly characterize the Cu layer through surface EXAFS. Then, we would use this insight to study a variety of electrochemical phenomena, such as anion adsorption and adsorption of organic molecules.

As things turned out, we spent most of our time on the first step of the plan. We felt that it was more important to pay attention to all of the details of the experiment, explaining every artifact and anomaly, rather than to branch out with a set of measurements on many different systems. This was a wise choice. Through our project we have established a standard for future electrochemical EXAFS investigations.

The main design feature of our approach was to use a very large sample (an order of magnitude larger in surface area compared to prior efforts). This set the scale of everything. It produced several difficult problems which were eventually solved. However, it also led to the largest surface EXAFS signals that have ever been measured. Our data were so clean, in fact, that we were forced to deal with several subtle aspects of the x-ray detection, the electrochemistry and the interfacial system, which would not have otherwise been noticeable.

## 2 Chronology

### 2.1 Personnel

The experimental aspects of the project were designed by the partnership of Prof. Furtak with Prof. Tim Hayes. When the program was initially funded by the Office of Naval Research Hayes and Furtak were together at the Physics Department of the Colorado School of Mines (Grant Number N00014-87-K-0551). About three years into the project Prof. Hayes moved to RPI, but the collaboration continued. Most of the experimental aspects of the program were maintained at CSM, with the data analysis being conducted at RPI (under Grant Number N00014-90-J-1332). This report covers the overview of most of the accomplishments, with an emphasis on the CSM contributions. Additional information will be independently provided by the RPI group, emphasizing the data analysis aspects of the experiment.

The CSM group consisted of the following individuals:

- Prof. T. E. Furtak, Principal Investigator
- Dr. P. Samanta, Post-Doctoral Fellow (spring 1989 - winter 1991).
- Mr. N. Winjum, Technical Assistant (1988 - summer 1988)
- Ms. Edie Creek, Undergraduate Assistant (fall 1989 - spring 1990).
- Dr. Li Wang, Graduate Research Assistant (fall 1989 - fall 1993).

Li Wang's primary thesis research was dedicated to this program. She has passed all of the formal requirements for receipt of the Ph.D., which will be awarded at the end of the summer, 1994. The title of her thesis is "*In-Situ Studies of the Electrochemical Interface of Cu on Pt by Surface Extended X-ray Absorption Fine Structure*".

### 2.2 National Facility Visits

All of the x-ray experiments were conducted at national synchrotron radiation laboratories through awards of general user time by means of the normal competition. In general, our proposals received high ratings, enabling us to run nearly whenever it was needed. The data analysis efforts were very time consuming, taking several months for each run. So the duty cycle of one opportunity every four months was not a serious impediment to progress. Between trips to the synchrotron the CSM group was involved with sample handling, chamber improvement, electrochemical testing, and other auxiliary experiments designed to help in the interpretation of the x-ray results. Over the course of the project we made the following trips to national facilities:

1. March 1989 — Stanford Synchrotron Radiation Laboratory
2. April 1989 — National Synchrotron Light Source (NSLS)

3. October 1989 — NSLS
4. July 1990 — NSLS
5. November 1990 — NSLS
6. May 1991 — NSLS
7. December 1991 — NSLS
8. May 1992 — NSLS
9. November 1992 — NSLS
10. July 1993 — NSLS
11. November 1993— NSLS

Each trip consisted of five to seven days of 24 hr time as a general user. At NSLS we worked at beamline X9, which was built and is operated by the National Biostructures Primary Research Team.

## **3 Experimental Issues**

### **3.1 X-ray Experiment**

#### **3.1.1 Detectors**

A purchased intrinsic Ge energy dispersive detector was used in the initial stages of the project. It was very important to characterize the quality of the incident x-ray beam, since the design and maintenance of the monochromators were beyond our control. During a given trip to the light source we spent the initial hours setting the beamline optics for our special needs. This included tuning of the x-ray monochromator and, in the case of runs at NSLS, setting of the grazing incidence Ni harmonic-rejection mirror. The latter element was designed to exploit the energy dependence of the x-ray reflection coefficient—allowing near 100% efficiency for lower energy radiation, with the cutoff dependent on the angle of incidence. This was important to eliminate the third-harmonic of the fundamental (at about 27 keV). We used Si(111) crystals in the monochromator so that second harmonic radiation could not be Bragg reflected. These characteristics of the incident beam were checked by using the Ge-detector. In addition, it was important to verify that other sources of stray radiation were not entering the hutch.

In one configuration we could mount the Ge-detector above the sample to monitor the energy spectrum of the radiation which would be detected in the EXAFS experiment. Some groups have used energy dispersive detectors to perform the actual k-scan data acquisition. This was not possible in our case, since our large sample created such a large Compton scattered signal that the total flux exceeded the dose limit of the detector. Still, with a significantly reduced aperture, we were able to measure, not only the Compton scattering,

but also the fluorescence from a non-dilute copper layer. This enabled us to adjust the Ni-foil transmission filter in front of our principle ion-chamber detector, verifying that adequate Compton rejection was being accomplished.

Our main detector for this experiment was a specially built ion chamber that was aperture-matched to the size and shape of our sample. We built two Söller-slit assemblies, one for each polarization configuration, using thin tantalum. The detector contained five metal-wire electrodes. These were biased using a high-voltage battery. An integrated pre-amplifier was built into the detector. The entire assembly was housed in lead sheet to eliminate spurious radiation. The performance of this detector was outstanding. It was very quiet, and, when filled with argon or a quench-gas mixture, provided more than enough sensitivity, as well as the necessary dynamic range, to monitor the  $K\alpha$  emission from a Cu monolayer.

### 3.1.2 Samples

Our samples were constructed from 1"  $\times$  10"  $\times$  0.5" float-glass bars. These were checked for flatness by an optical interferometer and were found to have less than 2000 Å of large-scale height variation from one end to the other. Many of our Pt films were grown by the Stanford Synchrotron Radiation Laboratory. They perform a coating service for a fee using their large evaporation system which was designed to create x-ray mirrors. However, we determined that we needed to study the evaporation conditions with many different processing parameters. For this purpose we modified a UHV system at CSM to enable high-quality Pt evaporation to be performed. The system employed a multi-pocket electron-gun and standard UHV pumps, as well as a quartz-crystal thickness monitor. A unique characteristic of this system is a large sample containment chamber. This was necessary to make it possible for us to produce Pt films on our large substrates. Most of the samples were produced with 200 Å of Cr as an adhesion-promoting layer under 1000 Å of Pt.

We characterized the Pt films with x-ray diffraction, finding a preference for (111) orientation (approximately half of the area of the sample). The rest of the surface was equally shared by grains with (100) and (110) orientations. While the polycrystalline character of our starting material is a limitation when it comes to detailed modeling of the surface structure, it is not a significant problem where the goal is a study of the electrolyte. The polycrystalline distribution of orientations also helps us avoid complicating Bragg reflections which exhibit resonances throughout the EXAFS energy range.

### 3.1.3 Sample Chamber and Mount

The Pt-coated glass bars were held in a Teflon sample chamber which was fitted with a Kapton top window. Since Kapton is known to be permeable to oxygen, we employed a double window arrangement. The second window was about 3 mm above the primary window. Oxygen-free nitrogen was continuously passed through this gap to eliminate the question of dissolved oxygen in the electrolyte. This is an important issue, since our results confirm that covalently bound oxygen is present on these electrochemically controlled Cu layers. Other investigators have also detected oxygen but have, in some cases, attributed

this to the gas permeability of Kapton.

The primary window was sealed with a Viton o-ring. This seal turned out to be one of the biggest problems during the course of the project. Without accurate control of the pressure gradient across the window we were susceptible to loss of control of the thickness of our water layer. Many of the difficulties were connected to our large sample size and its rectangular shape. We built several sample chambers of different materials. We always returned to Teflon because of its superior chemical resistance. However, its tendency to relax after being machined made it difficult to establish perfect seals. Our typical failure mode would be under slight negative pressure, where air would leak into the electrolyte chamber in the form of a slowly growing bubble. Our best data were obtained under conditions where the leak was extremely small or absent. We considered altering the basic decision to use a large sample. However, in the interests of accomplishing one of our main goals, to obtain large S/N ratios, we stayed with our first choice throughout the project.

The sample chamber was mounted on a tilt-translation stage for control of the incident angle. The latter was remotely operated by a portable computer which we brought to the synchrotron. The two degrees of freedom made it possible to accurately rotate the sample about its center with better than 0.2 mrad of precision. The ion chamber was held at a fixed position above the sample. However, the entire assembly could be rotated about an axis along the incident x-ray beam to allow changing between s-polarization and p-polarization without removing the electrochemical control. In addition to the large sample, this aspect of our experimental design was unique among electrochemical EXAFS efforts.

### 3.1.4 Electrochemical System

The electrochemical control was established with wire electrodes that penetrated the sample chamber through gas-tight seals. The counter electrode was a Pt wire coil. The reference electrode was a pure Cu wire. The latter established an exchange reaction with the Cu ions in solution, thus defining a reversible condition. This technique has the advantage of providing a positive identification of the Cu plating voltage. We were very careful to avoid bulk Cu deposition and its possible restructuring influence on the first layers. It is also known that Cu can diffuse into Pt under multilayer deposition.

The electrolyte, which was externally purged with oxygen-free nitrogen, was introduced into the sample chamber by means of a liquid delivery system. The latter was also used to control the pressure in the chamber. With a slight positive pressure, excess liquid forced the Kapton window away from the sample. This facilitated electrochemical control and was the condition under which all Cu deposition and stripping was conducted. With a slight negative pressure, the Kapton window was pressed against the sample, trapping a thin layer of electrolyte against the metal. Under this condition we could still control the surface by the conductivity made possible by an acid electrolyte. The electrolyte was sufficiently thin to enable the x-rays to reach the sample with significant intensity, even at grazing incidence.

The electrochemical control electronics followed conventional practice. We chose compact units that could be easily transported. However, these same instruments were heavily used at CSM for testing and improvement of the sample control practice.

### 3.1.5 Alignment Procedures

Our long sample geometry enabled us to establish reproducible positioning in the x-ray beam. The method was based on use of a narrow slit, beyond the sample, which allowed only the unobstructed beam to pass through to a following detector. With this setup, we could move and rock the sample until it was parallel to the beam. However, prior to this step, we needed a way to establish rough alignment. For this purpose we designed a laser-based device. Using x-ray sensitive photographic paper we identified the location of the beam at the hut aperture, and again at the back wall of the hutch. Using a micrometer adjustment we introduced a thin mirror into the beam to direct a He-Ne laser along the same two points. The mirror could be kinematically lowered and raised to allow rechecking of the sample positioning and also the positioning of the other detectors in the experiment. Our use of the laser was apparently a unique idea, particularly for the beamline personnel on X-9. They have indicated a desire to incorporate this feature into a new beamline that has just recently been completed.

### 3.1.6 X-ray Spectroscopy

In the standard EXAFS experiment for dilute samples at least two detectors are used, one at the hutch aperture to monitor the incident flux, and a second to detect the fluorescence efficiency. In addition, for a transparent sample, it is also desirable to have a third detector to monitor the transmitted intensity. In our case this corresponds to the x-ray reflectivity. We always used this extra detector, but also added a fourth. Between the third and fourth detectors we placed a thin Cu foil. We could perform conventional transmission EXAFS by this means. More importantly, this extra data gave us a continual calibration for the energy of the incident x-rays. We found, as is commonly the case, that the mechanical linkages in the x-ray monochromator were unreproducible. This led to as much as 3 eV of shift in the apparent x-ray energies. Experiments which are performed without this feature, particularly high resolution near-edge studies, are subject to this uncertainty.

The RPI group established the means to perform the entire data analysis sequence using computer equipment which they brought to the light source each time we ran the experiment. Although the precise details of this procedure took several months to complete for each run, this on-site capability enabled us to evaluate and modify our experiment during the course of the week. This was an important advance, since many subtleties of the data can only be appreciated in the results of multiple scans, after Fourier transformation.

## 3.2 Reflectivity Modulation

Early in our project we became concerned about the stability of the Cu layer under the thin electrolyte under the Kapton window. It was not clear that we were holding the system stable during the several hours required to perform all of the scans of an EXAFS run. To answer this question we sought independent evidence that the Cu was not changing under these conditions. We assembled an optical reflection experiment which used polychromatic visible light. The system used sensitive photodiode detectors, one to monitor light from an

"inert" mirror, and the other monitoring the reflected light from the sample.

One immediate discovery, which we had not anticipated, was that this set-up was extremely sensitive to the thickness of the water layer. We were not able to quantitatively measure the water layer thickness. However, we could follow its relaxation after we established the pressure gradient across the Kapton window. Our reflectometer helped us to determine that the system needed at least 15 minutes to reach its final equilibrium. This information saved us a great deal of valuable x-ray time at the synchrotron, since equivalent tests did not have to be repeated.

The principle experiment which we performed with the reflectometer involved the change (about 0.0004) in the reflectivity of Pt when the Cu layer was deposited. Our precision was in excess of 0.00004 in this measurement, so we could easily determine if the Cu was leaving over a long elapsed time. The results showed that there was no detectable difference if the Cu layer was maintained for 20 minutes or for 2 hours. Throughout the waiting period, in each case, the electrolyte layer was no more than 20 microns in thickness. This is an important experimental verification that is of widespread interest among the electrochemical community. A manuscript covering these results is currently under preparation for submission as an apparatus note.

### 3.3 Quartz Crystal Microbalance

By 1991 we had independently established the capability to detect mass changes on electrodes using high precision frequency measurements. The concept is based on an AT-cut thin quartz crystal that is driven at its third harmonic (15 MHz) shear mode through metal contacts evaporated on opposing faces. If one of these contacts is also facing an electrolyte solution, it can act as an electrode on which adsorption and desorption can be monitored. As it applies to Cu on Pt, we could follow the accumulation of the Cu as the resonant frequency of the quartz crystal changed. Our sensitivity allowed 0.05 ML to be easily detected.

Of primary interest was the issue related to the charge state of the Cu on the Pt, under electrochemical control. Although one can monitor the reduction (or oxidation) currents associated with the deposition (or stripping) of the Cu, this is not a direct measure of the charge used by a Faradaic process. Particularly when the possibility of co-adsorption exists (as was the case in our system) charge re-arrangement in the double layer and/or charge transfer involving species other than Cu can invalidate conclusions drawn from the electrochemical experiment alone. The results of our study are outlined below.

## 4 Progress

### 4.1 Advances in the State-of-the-Art

#### 4.1.1 X-Ray Reflectivity

Largely through the efforts of Dr. Larry Lurio, with the group at RPI, we were able to establish a detailed model for the behavior of the x-ray reflectivity in our system. This used the materials properties of all of the components in the beam, including the water layer. The model incorporates possible roughness in the sample. It is very sensitive to the incident energy. In fact, we were able to use these results to verify that we had established the correct incident angle by measuring the x-ray reflectivity in a coarse interval energy scan. The information was also used to provide accurate numbers for the water thickness (about 13 microns) and the sample roughness (about 15 Å ).

This is a valuable contribution to the technology of interfacial x-ray spectroscopy, and will be published by the RPI group in a separate manuscript.

#### 4.1.2 Cu and Electrolyte Layer Stabilities

Through the differential optical reflectivity experiment, and by means of the x-ray reflectivity model, we verified that, under ideal conditions, the water layer was essentially identical through the time necessary to complete a 10 hour experiment. Our sensitivity and awareness of this issue contributes to the overall quality of our data, and has provided a guide for future electrochemical EXAFS projects.

We have verified that the Cu does not evolve with time under electrochemical control. Changes which may be observed are, by contrast, associated with changes in the thickness of the water layer (when pressure control was lost) and with changes in the background concentration of Cu ions. The latter was an undesirable side effect of the Cu-wire reference electrode. The problem was avoided by reducing the exposed area of this electrode to a minimum, so as to reduce the total amount of dissolved Cu.

#### 4.1.3 Ni Filter Artifacts

In early analyses of the data we detected a long-period oscillation which, in the r-space results, gave rise to a neighbor at a very small distance from the central Cu. We made exhaustive attempts to identify the origin of this effect by considering many experimental problems. Our data were sufficiently noise free that we could examine the EXAFS to unusually large k-values. The extra oscillations were particularly prominent in that region. It was only recently that we identified the source of this effect. This was accomplished by modeling studies at RPI. In our experiment the Compton scattered x-rays, which are coupled in energy to the incident x-ray energy, were exhibiting EXAFS in the Ni transmission filter in front of the ion-chamber fluorescence detector. The unanticipated feature of these oscillations is that they grew stronger, not weaker as we had expected, as the energy increased. This was particularly prominent in our s-polarized data, where the Compton scattering was higher in

intensity. By correctly understanding this effect we were able to remove its influence from the data. This has brought the s- and p-polarized results into excellent agreement, and has eliminated the spurious neighbor in the model for Cu on Pt.

#### 4.1.4 Polarization Combination

In our experiment we were the first to measure the EXAFS from a single layer with both s- and p-polarization. This is important since, for K-shell EXAFS, there is a simple relationship between the orientation of the electric field of the x-rays and the angular orientation of the sampling efficiency. This has been used in the past to aid model development as surface EXAFS data have been interpreted. An important insight, provided by the RPI group, is that it is possible to combine the data from both polarizations to obtain a model-independent measure of the coordination number for a particular neighbor. One must weight the s-polarized data by a factor of 2. It can then be arithmetically combined with the p-polarized data. We have pointed out this insight in the manuscript which is now in press at the Journal of the Electrochemical Society.

## 4.2 Cu on Pt

### 4.2.1 EXAFS

Our final model for the Cu/Pt system has not yet been set. We are still finishing the details of the analysis on the last few runs, incorporating all of our accumulated insight. The preliminary results are as follows. The environment of an average Cu atom is 2 O atoms at 2.04 Å, 4 Cu atoms at 2.62 Å, and 6 Pt atoms at 2.65 Å. This amounts to a total number of 12, a reasonable number for dense packing. The Cu distance is larger than fcc Cu (which is 2.55 Å), but consistent with the strained-layer picture which could be expected in the strong bonding scenario between Cu and Pt. The Pt distance is also consistent with a model based upon the sum of metallic radii of Cu and Pt (2.66 Å). The oxygen distance is larger than is commonly found in copper oxides, however its origin in our system is not clear. The distance appears too small for it to be adsorbed water (which would be about 3 Å). We also do not think that we are seeing adsorbed sulfate. We could not distinguish any sulfur signatures in our data (although that possibility is not excluded by the EXAFS). It is not expected that sulfate oxygens could be so close. It is most likely that the oxygen is an essential feature of the layer. The fact that there are so few Cu atoms leads one to speculate that the layer is actually quite complex. This interpretation is consistent with the only other detailed EXAFS data which have been published on this system.

Our earlier perspective is represented by the analysis presented in the Journal of the Electrochemical Society manuscript (now in press). We will continue to finalize our interpretation during the summer of 1994.

#### 4.2.2 Electrosorption Valence of Cu on Pt

The results of our near-edge data are consistent with completely reduced Cu. A widely publicized near-edge study of this system (although under very different conditions) concluded that the Cu singly ionized, due to interaction with a co-adsorbate. Our structural analysis seems to confirm the co-adsorbate model. However, we are unable to extract a similar picture from the near edge feature. It is worth pointing out that near-edge analyses are subject to problems because of the complicated nature of multiple scattering in this region. For a proper fit, one needs a complete model for the phenomenon. This has not been attempted on this system as of yet.

Our quartz crystal microbalance experiments are more conclusive. By comparing the mass accumulation with the charge transfer, as a function of the coverage of Cu, we were able to extract the electrosorption valence. With no adjustable parameters we find that this is two, to within experimental error, except for the very low and the very high coverage. That is, Cu atoms that are initially deposited require more charge than is necessary to neutralize a Cu(II) ion, and those which finish the layer come down with nearly no charge transfer. Most of the Cu is deposited through a Faradaic transfer of two electrons per atom. These data are consistent with recently published information in which the coverage was measured through *ex situ* Auger analysis on the Cu signature.

## 5 Reports

### 5.1 Refereed Publications

- "Surface Extended X-ray Absorption Fine Structure of Copper on a Platinum Electrode", T. E. Furtak, L. Wang, E. A. Creek, P. Samanta, T. M. Hayes, G. Kendall, W. Li, and C. M. Lo, *Electrochim. Acta* **36**, 1869 (1991).
- "Underpotential-Deposited Cu Monolayer on Pt", T.M. Hayes, W. Li, G. Liang, C.M. Lo, T.E. Furtak, E.A. Creek, P. Samanta, and L. Wang, in *X-ray Absorption Fine Structure*, ed. by S.S. Hasnain (Ellis Norwood, New York, 1991), 229-231.
- "Structure of the Copper Monolayer/Platinum Electrode Interface as Measured by In Situ X-Ray Absorption Spectroscopy", T. E. Furtak, L. Wang, J. Pant, K. Pansewicz, and T. M. Hayes, *Proceedings of the Symposium on X-Ray Methods in Corrosion and Interfacial Electrochemistry*, Phoenix, AZ (The Electrochemical Society, 1991).
- "Structure of the Copper-Monolayer/Platinum-Electrode Interface as Measured by In Situ X-ray Absorption Spectroscopy", T. E. Furtak, L. Wang, J. Pant, K. Pansewicz, and T. M. Hayes, *Journal of the Electrochemical Society* (in press 1994).
- "Electrosorption Valency of a Cu Monolayer on Pt", T. E. Furtak and L. Wang, *Chem. Phys. Letters*, (to be submitted 1994)
- "In Situ EXAFS of Cu on Pt Under Electrochemical Control", L. Wang, T. E. Furtak, L. B. Lurio, J. Pant, and T. M. Hayes, *Journal of the American Vacuum Society*, (to be submitted 1994)

### 5.2 Presentations

- "Underpotential Deposited Cu Monolayer on Pt", T. M. Hayes, L. Hwang, W. Li, G. Liang, T. E. Furtak, E. A. Creek, P. Samanta, and L. Wang, March Meeting of the American Physical Society, Anaheim (1990).
- "Underpotential Deposited Cu Monolayer on Pt", T. M. Hayes, G. Kendall, W. Li, G. Liang, C. M. Lo, T. E. Furtak, E. A. Creek, P. Samanta, and L. Wang, EXAFS-VI, York, United Kingdom, (August, 1990).
- "Surface Extended X-Ray Absorption Fine Structure of Copper on a Platinum Electrode", T. E. Furtak, L. Wang, E. A. Creek, P. Samanta, T. M. Hayes, G. Kendall., W. Li, G. Liang, and C. M. Lo, Interdisciplinary Conference on Electrified Interfaces, Asilomar CA, (Sept. 1990).
- "Underpotential Deposited Cu Monolayer on Pt", T. M. Hayes, W. Li, G. Liang, A. Rahimi, H. Su, T. E. Furtak, L. Wang, E. A. Creek, and P. Samanta, March Meeting of the American Physical Society, Cincinnati (1991).

- "In Situ EXAFS of Copper on Platinum", J. Pant, K. Ponsewicz, T. M. Hayes, L. Wang, and T. E. Furtak, 38th Annual American Vacuum Society Symposium, Seattle, (November 1991).
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## 6 Summary

This project has helped pioneer the development of electrochemical EXAFS as a more routine tool for study of buried interfaces. We achieved the best signal-to-noise quality in a system of this type. This enabled us to concentrate on experimental artifacts which are usually unobservable in electrochemical EXAFS. As a result, we perfected several procedures which are necessary to reach high precision. Our prototype, Cu on Pt, proved to be more complicated than we had anticipated. However, our data were sufficiently clean that we could adopt a "blind perspective" regarding our approach to their interpretation. Although our best model is still being finalized we are confident that our experiment will resolve some inconsistencies created by earlier authors regarding this specific system. More importantly, we have established a standard of quality for subsequent projects of this type, and have helped demonstrate that EXAFS can be successfully applied to electrochemical phenomena.

## 7 Appendix: Manuscript in Press

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### Structure of the copper-monolayer/platinum-electrode interface as measured by in situ x-ray absorption spectroscopy

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#### ABSTRACT

Using a large polycrystalline Pt film electrode with one layer of electrochemically adsorbed Cu, we have measured the EXAFS of Cu at the K edge through a grazing-incidence, fluorescence-detection experiment while the sample was under electrochemical control. The quality of the data permit reliable analysis of the  $k\chi$  spectrum up to 800 eV above the K edge. Measurements with x-ray electric field vector parallel and perpendicular to the surface were made on the same monolayer. The results indicate that the neighbors of Cu are: O at 2.06 Å, Pt at 2.58 Å, and Cu at 2.62 Å. These are similar to what would be expected from considerations of metallic or covalent radii.

#### INTRODUCTION

We have applied extended x-ray absorption fine structure (EXAFS) spectroscopy [1] to the determination of the structure of a metal monolayer at the interface between a metal electrode and an aqueous electrolyte. The x-ray absorption cross section for an atom displays oscillations as a function of the energy above the threshold for excitation of a K- or L-shell electron. These oscillations are caused by interference between wavefunctions which describe the outgoing electron and the electrons scattered back from the atom's neighbors. Standard methods exist for analyzing an EXAFS spectrum to provide precise information about the type and number of the neighboring atoms and their distances from the excited atom. Since x rays do not interact as strongly with matter as do electrons or ions, it is possible to design an experiment in which a metal buried under a thin layer of water and a thin

plastic membrane can be probed by a high intensity x-ray beam. Relaxation of an excited atom in the sample gives rise to fluorescence at a characteristic energy which is below the absorption edge, the intensity of which is proportional to the absorption cross section. Therefore, by monitoring the fluorescence intensity as a function of the energy of the incident x rays, one can record an EXAFS spectrum even on a sample which is under water, as in an electrochemical environment. To provide surface specificity in experiments of this type, it is essential to exploit total external reflection of the x rays. If the incident x-ray beam makes a very small angle with the plane of the surface,  $0.5^\circ$  or less depending on the material, then the x rays are totally reflected. This condition is referred to as grazing incidence. The electric field of the x rays penetrates only 20 Å or so into the surface, enabling a surface sensitive x-ray experiment.

The x rays from the synchrotron are polarized. Moreover, the excited electron is emitted preferentially parallel to the electric field vector. So, with the x-ray electric field vector oriented parallel to the surface, we obtain information about the adsorbed monolayer in the plane of the surface. With the electric vector perpendicular to the surface we get information preferentially about the substrate and about the electrolyte in the region of the interface. In analogy with visible light we call these two polarizations s and p, respectively.

We recognized that undesirable scattering from the substrate and the liquid and window layers would lead to appreciable background and its associated noise. To improve the signal-to-noise ratio it is necessary to create as large a signal as possible. This led to our choice of an unusually big sample,  $1 \times 10$ ". It also dictated other features of the experiment. The form of the sample was a polycrystalline Pt film. The detector was a high-flux ion chamber. These and other aspects of our design have led to unprecedented signal-to-noise quality in the EXAFS from a foreign metal monolayer, in this case Cu. This enabled our analyses to be carried out over a larger range of energy above the edge than has previously been possible. Through some special aspects of our cell design we have been able to maintain one state of adsorption, at monolayer coverage, for more than 30 hrs. This was enough time to acquire a statistically significant collection of EXAFS spectra.

*In situ* EXAFS on electrochemical systems was pioneered by the groups at IBM and Cornell in the late 1980's [2-4]. They studied Cu on Au(111) in the underpotential adsorption condition with a relatively small sample and a solid state detector. They concluded that the Cu-Cu spacing was the same as that expected for Au-Au, implying an epitaxial, strained-layer structure. They also identified a near neighbor oxygen in p polarization. However, in a separate s-polarization measurement the oxygen could not be found. This led

them to propose that co-adsorbed water or sulfate was on top of the Cu atoms. This system has recently been re-examined by a group in France (using a scintillation detector) [5,6]. With s polarization they identified oxygen as the nearest neighbor to Cu and agreed that the Cu is epitaxially aligned with the substrate. On Au(100) they concluded that Cu atoms in the monolayer have spacing intermediate between that of fcc Au and fcc Cu. *In situ* STM and AFM have now been applied to Cu on Au(111) [7,8]. These reports also indicate that, for this system, at full ML coverage, Cu is associated with Au in a (1x1) surface structure.

We chose Cu on Pt for our experiments because it was our perception that this combination was relatively well understood. In UHV, Cu grows to 1 ML on Pt(111) through the expansion of p(1x1) two-dimensional islands [9-11]. There is some indication that three-dimensional growth begins prior to the completion of the first ML [11]. However, this was not thought to involve more than 10% of the surface. Some differences were noted in the electrochemical environment. Optical reflectance spectroscopy on polycrystalline Pt indicated a significant modification of the electronic structure of the Cu at 0.6 ML [12]. This was interpreted as a disorder-order transition which was not observed for Cu on Pt in UHV. Later this electronic effect was shown to be primarily associated with the Pt(111) orientation [13]. There is also some evidence in the electrochemical data that multilayer formation precedes the completion of the first ML, but only by a small amount [14]. In the most recent study of Cu on Pt(111) it has been shown that Cu grows epitaxially in a (1x1) arrangement, covering the Pt sites uniformly without cluster formation [15].

White and Abruña have reported measurements of fluorescence EXAFS from a ML of Cu adsorbed at underpotential on Pt(111)-I with a surface area of 1.2 cm<sup>2</sup> [16]. The iodine was used to stabilize the surface through a preparation method which involves high temperature annealing. Their data, recorded with a small solid-state detector, are quite noisy. As a result, they were only able to analyze a range of the spectrum 50-300 eV above the edge. Their results, in s polarization, indicate that the Cu-Cu spacing is 2.88 Å, larger than the Pt-Pt distance of 2.77 Å. Because of the strong influence of the co-adsorbed iodine in their experiment it is unclear if our results, where there was no iodine present, should be directly compared to theirs. Recently *in situ* EXAFS was measured from Cu adsorbed on carbon supported Pt clusters [17]. In that experiment the surface was randomly oriented with respect to the x-ray electric field. The near-edge features reported in that study, although averaged over all polarizations, are consistent with the results we are reporting here. In a recent EXAFS study of Cu on Pt(100), the stable phase is proposed to be a c(2x2) bilayer in which O is intermixed with the Cu [17a].

The data on which those conclusions are based extend to only 450 eV above the Cu K edge and consequently are of significantly lower quality than the data reported here.

#### EXPERIMENTAL METHOD

The substrate for the sample was a 12.5 mm thick bar of float glass with a surface area of 55 cm<sup>2</sup>. Interferometry tests showed that typical bars were flat to within 1 μm across the entire surface. The bars were cleaned with acetone and methanol, then heated to 200°C in a stainless steel vacuum system at 10<sup>-10</sup> torr. An underlayer of 200 Å of Cr was evaporated first. This was followed by 1000 Å of Pt without breaking the vacuum. Both materials were deposited from an electron beam heated source. After the samples were allowed to cool to room temperature they were stored in a diffusion-limited container, but were not isolated from atmospheric contact.

The cell was built from Teflon and was designed to accommodate the sample with a minimum of excess fluid volume. The bar was glued to an Al plate on the side opposite the Pt film. This was used to pull the glass against the open bottom of the cell to make a water-tight seal. The open top of the cell was closed with 0.5 mil Kapton. This was sealed to the Teflon with a flange whose top surface was slightly below the surface of the sample. This provided unobstructed access to the sample, through the Kapton window, in the grazing incidence geometry. To aid the sealing of the cell openings, quick-set epoxy was used on the gaskets. Pure Pt and Cu wires were positioned parallel to the long axis of the substrate and on either of its sides. These served as the counter electrode and the reference electrode respectively. A third wire, of varnished Cu, was used to contact the Pt surface through a soldered connection which was masked with several layers of lacquer. The wires were brought out of the cell through sealed fittings, as were 2 mm Teflon tubes. The latter enabled the electrolyte to be supplied and withdrawn using an external solution reservoir and a dual pumping arrangement. The solution was prepared from Millipore 18 MΩ water with glass-distilled H<sub>2</sub>SO<sub>4</sub> (0.5 M) and Reagent-grade CuSO<sub>4</sub> (0.2 mM). In this electrolyte the reference electrode was defined by the Cu/Cu<sup>++</sup> equilibrium, a convenient aspect of the underpotential deposition procedure. We also found that the Cu wire yielded a reproducible reference in the absence of specifically added Cu ions, presumably through a similar exchange reaction involving Cu and H<sub>2</sub>SO<sub>4</sub>.

The experiment was performed on beamline X-9A at the National Synchrotron Light Source. Typical storage ring characteristics were electron currents of 190 mA with a lifetime of 40 hrs. The x-ray monochromator used Si(111) crystals. This was followed by a large Ni mirror, set at an angle of 5 mrad with respect to the beam. Through the energy dependent reflectivity under

these conditions, higher harmonics of the primary energy were greatly reduced. This was checked with a solid state detector. Because of our large sample we were able to define the size of the beam at 1.9 mm(V) x 19 mm(H). The entire cross-section of that beam was used in the excitation. The cell was mounted on a tilt stage for control of the incident x-ray angle. This was accomplished by obscuration of the nearly collimated beam and detection of the transmitted residual through a slit beyond the sample whose size was the same as that of the beam. By this method we could set the angle at 8 mrad (1.4 mrad below the critical angle for Pt) with a precision and reproducibility of 0.5 mrad. Beyond the slit we set up a separate Cu absorption experiment using a 2.5  $\mu\text{m}$  foil and an extra set of transmission ion chambers. This provided an absolute energy calibration for each individual scan, thus removing any uncertainty in the identification of the position of the edge in our fluorescence data due to beam fluctuations.

Our principal detector is a specially designed 5-electrode ion chamber with a rectangular window whose size is 240  $\text{cm}^2$ . This was filled with Ar and activated with high-voltage batteries. A ultra low noise pre-amplifier is built into the device. To provide some discrimination against scattered primary radiation a 0.5 mil thick Ni foil filter was placed over the detector window at a distance of 2 in. The intervening space was filled by Ta Söller slits, designed to reduce secondary fluorescence from the Ni. Other aspects of the x-ray experiment followed standard EXAFS practice. Materials of known structure were also measured to help calibrate the phase shifts of the backscattered electrons from the possible Cu neighbors. In addition to our monolayer sample, we measured spectra from a Pt:Cu(1%) alloy by fluorescence. Conventional transmission techniques were applied to the other standards, Cu foil and  $\text{Cu}_2\text{O}$  powder.

Using the electrolyte plumbing system we introduced pure 0.5 M  $\text{H}_2\text{SO}_4$  in an amount sufficient to distend the Kapton window several mm above the surface of the Pt. In this expanded-window configuration we electrochemically cleaned the surface with a periodic triangular potential ramp between -0.25 V and +0.65 V at 80 mV/s for 30-60 min. The resulting development of hydrogen and the negative potential led to reducing conditions which removed atmospheric oxides from the Pt. In earlier experiments we had varied the potential over a much larger range, encompassing the oxide formation and reduction region. This followed accepted practice for preparing Pt electrodes [18]. While more distinct hydrogen adsorption-desorption peaks were achieved with the latter procedure, we found that these surfaces were very unstable. This was initially discovered through the time-evolution of the EXAFS spectrum. Similar evidence has been reported by Itaya et al. [19], and at least one experiment showed accelerated reconstruction which was induced by adsorbed Cu

[20]. The data reported upon here were recorded under conditions where there were no observable changes for nearly 30 hrs. After the *in situ* cleaning step, more pure 0.5 M H<sub>2</sub>SO<sub>4</sub> was flushed through the cell while the cell potential was maintained at 0.6 V. Then the Cu<sup>++</sup>-containing solution was introduced through continual flushing. With the window still distended the adsorption-desorption of Cu was monitored through the current vs. potential behavior between 0 V and 0.6 V with a ramp speed of 20 mV/s. The adsorption step was found to be poorly defined, but the Cu desorption followed the expected behavior for polycrystalline Pt. A single ML was bound between 0 and 0.1 V, while a generally broad desorption signature was observed between 0.1 V and 0.4 V, involving 340  $\mu\text{C}/\text{cm}^2$ . While this is less than expected for a simple close-packed layer, co-adsorbed anions are known to affect the apparent charge flow in stripping adsorbed layers [15]. Our record did not contain sharp desorption peaks frequently associated with unique sites on single crystal electrodes. However, the dominant surface orientation of our electrode should still have been Pt(111), since this is the low energy growth mode of vapor-deposited polycrystalline fcc metals.

After the system reached reversible behavior we fixed the potential at 0 V. After 5 min. to allow the formation of a complete monolayer, the excess liquid was withdrawn so as to contract the window into intimate contact with the sample. A continual application of negative pressure ensured that the water layer between the window and the electrode had a constant thickness. This was determined to be  $\sim 13 \mu\text{m}$  in x-ray absorption tests of the residual amount of non-deposited Cu<sup>++</sup> (which was about 10% of the amount of Cu in the adsorbed ML). The stability of this setup was tested in a separate experiment involving differential optical reflection [21]. We verified that the Cu remains bound to the Pt, providing exactly the same optical reflectance change upon immediate stripping or after a waiting period of up to 12 hrs.

The near edge spectra (XANES) were recorded with higher resolution than the pre-edge and post-edge regions. This enabled some diagnosis to be performed on the chemical state of the Cu. We could verify that the Cu was removed from the ML condition in the state Cu<sup>++</sup>, since these edges are significantly different (e.g., see ref. 5). Data were recorded from -700 eV to 800 eV surrounding the Cu K edge at 8979 eV. Individual scans lasted approximately 30 min. The entire sample mount with the attached detector could be rotated by 90° to arrange for s or p polarized incident x rays. In the p polarization orientation the incident beam was reduced in size to 3 mm(V) x 1.9 mm(H), limited in the vertical direction by the extent of the beam.

## RESULTS

Evidence of the quality of our data is presented in Fig. 1. Here we see a fluorescence spectrum recorded from the Cu ML at 0 V in s polarization. The signal-to-noise ratio decreases with increasing energy (typical of EXAFS data). However, it is still larger than 5 at  $E_{\text{edge}} + 800$  eV. These data were handled as follows. Each individual spectrum was analyzed to yield the height, shape, and energy position of the edge. The height of the edge is proportional to the amount of Cu in the x-ray beam (this was used as a normalization parameter to allow different experimental trials to be compared with each other) while the shape and position are related to the state of the Cu. These features also display some dependence on the angle of incidence. We have found that, particularly in our earlier experiments, there was appreciable variation in these parameters depending on the history of the sample. With our recent improved sample control these variations have been significantly reduced. The individual spectra were shifted in energy so that the Cu-foil references coincided. (This adjustment was justified because, according to the monochromator setting, the Cu-foil edge was also subject to some variation--an indication that the energy calibration of the monochromator was unstable.) We accumulated 20 s polarization and 14 p polarization individual scans, adding those for each polarization to average out random fluctuations. In Fig. 2 we display the near-edge region of summed spectra corresponding to the two different polarizations in our experiment. We can immediately conclude several things from this figure. The two polarizations give rise to different edge shapes and positions. This demonstrates that we have a well-defined surface plane. If an appreciable amount of the Pt or the Cu existed in 3-d clusters, then we would not see much difference between the two orientations. We can also comment on the position of the edge. In s polarization, the edge appears at approximately the same energy as the edge in metallic copper. The edge in the case of p polarization is shifted by approximately 1 eV toward higher energy. There is an evident shoulder on the edge in s polarization, weaker but still reminiscent of that on the Cu metal K edge. The "white line" at the edge is larger for the p polarization data, while the first positive oscillation above that is clearly smaller. These differences are evident in Fig. 3 also.

The portion of the summed spectrum above the edge was fitted to a 5th- or 6th-order polynomial in  $(E - E_{\text{edge}})^{\frac{1}{2}}$ . The EXAFS oscillations  $\chi$  were extracted by subtracting this polynomial from the summed spectrum and converting the abscissa from energy  $E$  to final-state electron momentum  $k$ , which is given approximately by  $(\hbar k / 2\pi)^2 / 2m = (E - E_{\text{edge}})$ . The resulting  $k\chi$  is shown in Figs. 3a and 3b for s and p polarization respectively. These were multiplied by a window function and Fourier transformed into  $r$  space, where the complementary

variables are  $k$  and  $2r$ . The window function was a unit amplitude step between  $2.8 \text{ \AA}^{-1}$  and  $14 \text{ \AA}^{-1}$  broadened with a Gaussian of half-width  $0.5 \text{ \AA}^{-1}$ . The real part of the resulting function,  $\phi(r)$ , is plotted in Figs. 4a and 4b, together with its amplitude (envelope). To extract structural information from these data we used the algorithm developed by Rehr et al. [22] to generate the  $k\chi(k)$  expected for backscattering from a single atom of, for example, Pt at some specific appropriate distance from the excited Cu atom. This spectrum was Fourier transformed into  $r$  space using the same window function applied to the data. Let's refer to this model spectrum as  $\phi_{\text{Cu-Pt}}$ . This theoretical model was calibrated by fitting an experimental spectrum from the Pt-Cu alloy standard with known structure. This was repeated for other potential neighbors to create  $\phi_{\text{Cu-X}}$ , where X is Cu, O, Pt, or S. Then the spectrum from the Cu ML was modeled as a linear superposition of  $\phi_{\text{Cu-X}}$ . The number and positions of the atoms in the superposition were treated as variables in the fitting process, constrained only by physical "common sense". Because the backscattering phase shift contains some  $k$  dependence, the "features" in  $\phi(r)$  appear at values of  $r$  which are not the same as the associated interatomic separation. In addition, each feature in the real part of the unknown spectrum might well include contributions from several atoms at different positions. Also, each atom has one to three substantial peaks. We must include all overlapping contributions in order to arrive at a meaningful fit to any portion of  $\phi(r)$ .

We label the features in  $\phi(r)$  A-D as shown in Fig. 4. These features appear in both spectra but are not identical. The contribution of a neighboring atom to  $\phi(r)$  is proportional to  $\cos^2\theta$ , where  $\theta$  is the angle between the x-ray electric field and a vector from the emitting atom to the neighboring atom. Differences between polarizations are associated with the angular orientations of the atoms.

Features B, C, and D are all at the correct distances for Pt atoms at a distance of  $2.58 \text{ \AA}$  from the excited Cu atom. The model spectrum has, however, different relative amplitudes for the peaks in this region. It is therefore necessary to add a Cu-Cu contribution. Feature A can be explained through oxygen neighbors. The average of the nearest neighbor distances determined in the two polarizations is given in Table I. The Cu-Cu spacing is larger than that in bulk fcc Cu ( $2.55 \text{ \AA}$ ), but substantially less than the Pt-Pt distance in bulk fcc Pt ( $2.77 \text{ \AA}$ ). The sum of the metallic radii of Cu and Pt is  $2.66 \text{ \AA}$ , somewhat larger than the average distance in our system. The Cu-O distance is larger than that in  $\text{Cu}_2\text{O}$  ( $1.84 \text{ \AA}$ ) or  $\text{CuO}$  ( $1.95 \text{ \AA}$ ).

revised 

Table I. Average distances of Cu nearest neighbors (Å).

Cu-O	2.06
Cu-Pt	2.58
Cu-Cu	2.62

## DISCUSSION

Our signal-to-noise ratio is higher than that which has been achieved before in an electrochemically controlled metal monolayer. This was accomplished under some constraints. Our sample is not a single crystal. However, this should not be a serious problem. Near neighbor distances in the substrate are independent of crystal orientation. It is also true that, on a polycrystalline sample, Bragg diffraction resonances are averaged out. If these exist in the EXAFS raw data then the analysis is difficult or impossible. The fact that the s- and p-polarization data are significantly different in the near edge region gives evidence that we have reasonably flat samples, not reconstructed through electrochemical contact. We have avoided the Pt oxidation conditions in the surface preparation method. These were associated with time-dependent, unreproducible EXAFS spectra. This evidence is also an indication that the Cu is not found in 3-dimensional clusters.

Our observation of O, Pt, and Cu contributions in both polarizations is not surprising. It is expected if the bond between the Cu atom and its nearest neighbor is in any direction other than parallel or perpendicular to the surface normal.

The Cu coverage determined from the electrochemical stripping measurement is less than that expected for a close-packed monolayer. However, recent coupled UHV-electrochemical experiments have suggested that the Cu is found in a state of partial discharge, induced by coadsorbed anions [23]. This would lead to incorrect coverage estimates based upon charge measurement alone [8]. It also implies that anions, in our case  $\text{SO}_4^{--}$ , must be strongly coordinated with the Cu. This is consistent with recent evidence that metal monolayers are generally associated with coadsorbed anions [24]. Coadsorption causes a shift, toward more negative potential, of the metal stripping peak in the current vs. potential record [25]. This explains our electrochemical results and provides understanding to the origin of the O neighbors found in our x-ray data. The oxygen would be associated with the  $\text{SO}_4^{--}$  and this would need to be very close to the Cu, perhaps in the hollow site of a close-packed layer.

Near neighbor oxygen was identified in the first successful electrochemical EXAFS report [2]. In that series the oxygen was found at 2.91 Å, far outside of our result. In a more recent report for the same system (Cu on Au) [6], oxygen appeared at 1.95 Å, similar to our finding. It was easier to model the early data with weak physisorption. Now we must seriously consider chemical bonding between the Cu and the O.

Evidence for the partially charged form of Cu cannot be derived from our near edge data at this time. The edge positions for Cu and Cu<sup>+</sup> are only ~1 eV apart. In the monolayer the Cu may be partially charged, yet closer to neutral than to the full ionic form. In their edge analyses the French group concluded that Cu on Au is actually Cu<sup>+</sup>. This would be more consistent with an XPS study of electrochemically deposited Cu on Pt in which the Cu 2p<sub>3/2</sub> core level in the ML was found 0.95 eV below the same state in Cu [26]. These comparisons are made more complicated by the growing realization that coadsorption plays a major role in these systems.

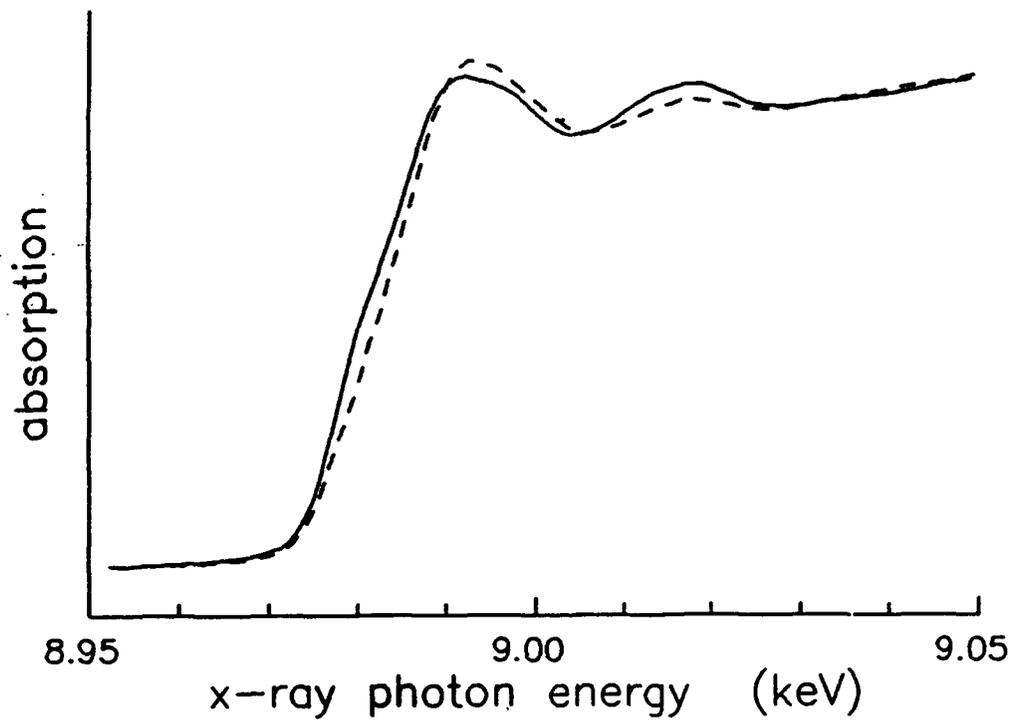
In this regard it is hard to evaluate the results of White and Abruña because of the presence of strongly adsorbed iodine in their experiment [16]. They found that the Cu-Cu spacing in the ML on Pt(111) was 2.88 Å. This would have to be associated with an incomplete ML in a strained structure. X-ray reflectance measurements on the same system indicated that the iodine "floats" on top of the Cu upon deposition of the metal [27]. Nonetheless, the presence of the iodine must be a significant influence to the structure.

The reflectance experiment [27] also showed that the average Cu height above the Pt was only 0.7 Å. This implies that some intermixing between the Cu and the Pt must be occurring. With this insight it is easier to understand why we see substantial Cu-Pt backscattering, even in the s polarization case. The Cu-Cu distance which we find is somewhat larger than that in bulk Cu. We do not know if, at lower coverage, larger distances will be measured (as was the case for Cu on Au [6]). Those experiments are now in progress. At least for the full monolayer we can say that there is no apparent epitaxy, unlike the situation in UHV [10, 11]. This is difficult to reconcile with the possibility that the Pt and Cu are mixed. It may mean that, in this case, we have something which is more like a random surface alloy.

Our results are different from those reported by Durand et al. for Pt(100) [17a]. They concluded that there are two Cu distances, 3.09 and 3.93 Å. Since the latter distance is the same as the Pt-Pt spacing on that face, there may be a special structure induced by that sample orientation. On the other hand, their observation of O at 1.97 Å is consistent with our result.

In conclusion, we have reported in this paper measurements made, for the first time, in both s and p polarizations on a single monolayer. The edge as well as the EXAFS spectra of both the s and p data are clearly different, confirming that the surface has not reconstructed to the extent of eliminating the original surface plane. We have strong evidence for oxygen, copper, and platinum neighboring atoms at reasonable distances from copper in both polarizations. Also, these contributions have differing amplitudes in the two cases due to their different angular orientations relative to the surface plane. The Cu-Cu distance of 2.62 Å suggests that copper does not form an epitaxial layer. The Cu-Pt distance is somewhat less than the sum of the metallic radii. Finally, the Cu-O distance of 2.06 Å is sufficiently short to suggest chemisorption, not simple physisorption.

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Revised Fig 2

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## FIGURE CAPTIONS

Fig. 1 The fluorescence from a single Cu monolayer on a Pt substrate in the presence of the electrolyte is shown in s polarization as a function of the incident x-ray energy. The background has been approximated by a low order polynomial and subtracted, leaving behind principally the fluorescence associated with Cu  $K_{\alpha}$  radiation. These data resulted from a single scan which took approximately 30 min.

Fig. 2 The edge region of the fluorescence spectra in s polarization (solid) and in p polarization (dashed) as a function of incident x-ray energy. The background has been subtracted as in Fig. 1. The resulting spectra were then normalized to unity at the arbitrary energy of 9030 eV to facilitate comparison of the shapes.

Fig. 3 The EXAFS oscillations  $k\chi(k)$  on the Cu K shell fluorescence in (a) s polarization and (b) p polarization, in units of  $\text{\AA}^{-1}$  as a function of the photoelectron momentum  $k$ .

Fig. 4 The real part (solid) and the magnitude (dashed) of the Fourier transform  $\phi(r)$  of the EXAFS on the Cu K shell fluorescence in (a) s polarization and (b) p polarization data in units of  $\text{\AA}^{-2}$ .

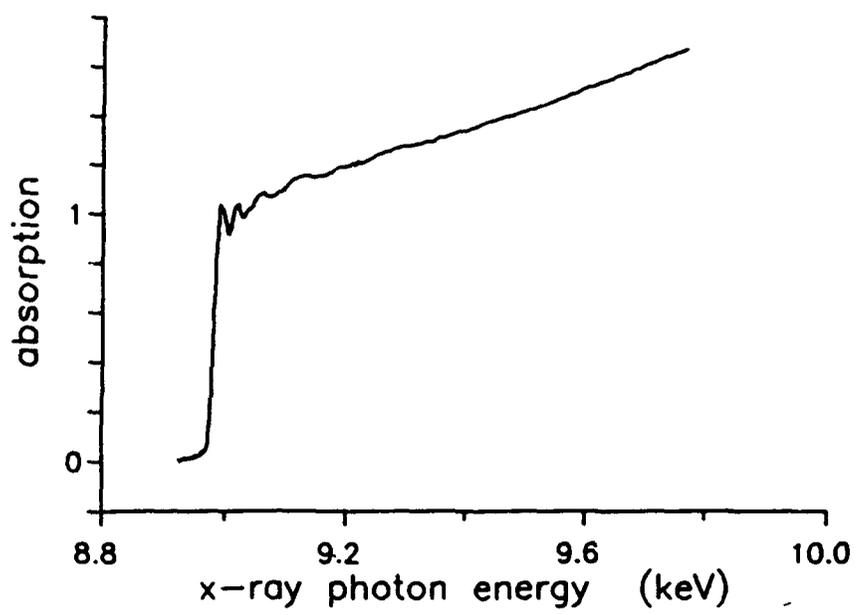


Fig. 1

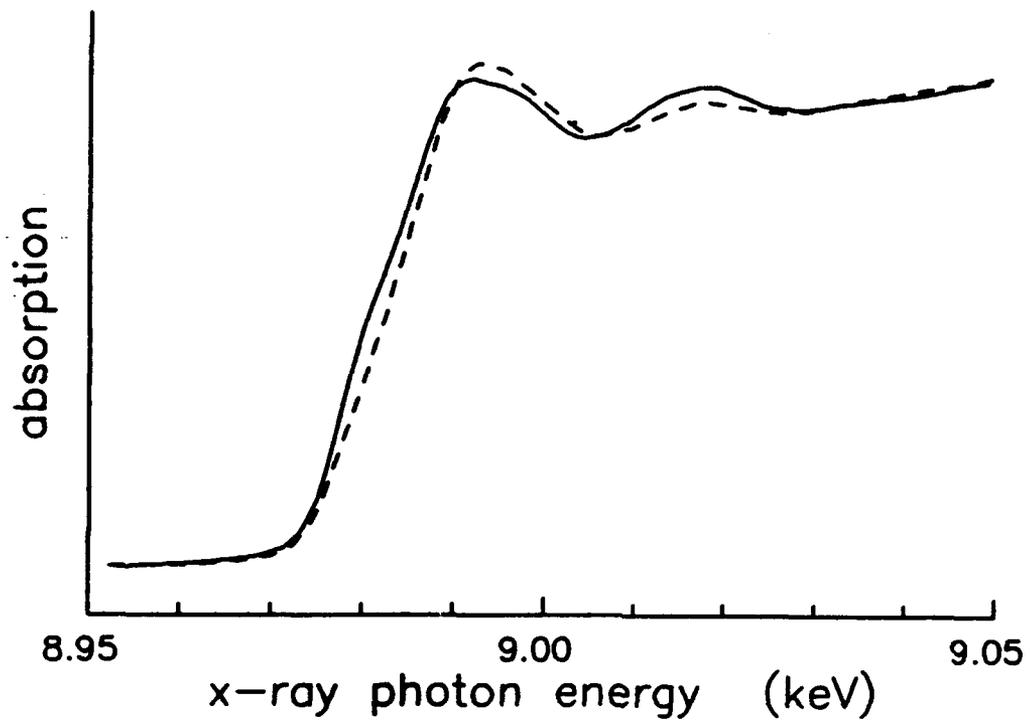


Fig 2

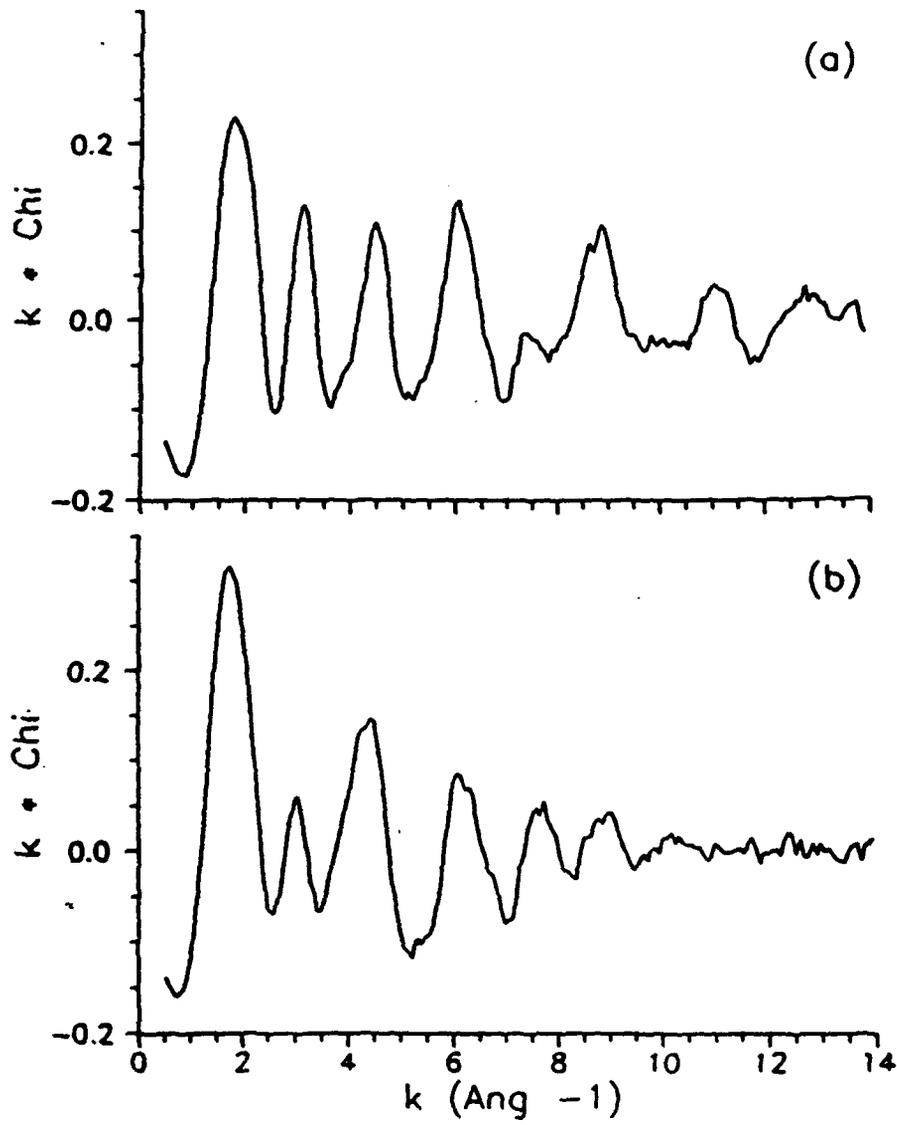


Fig. 3

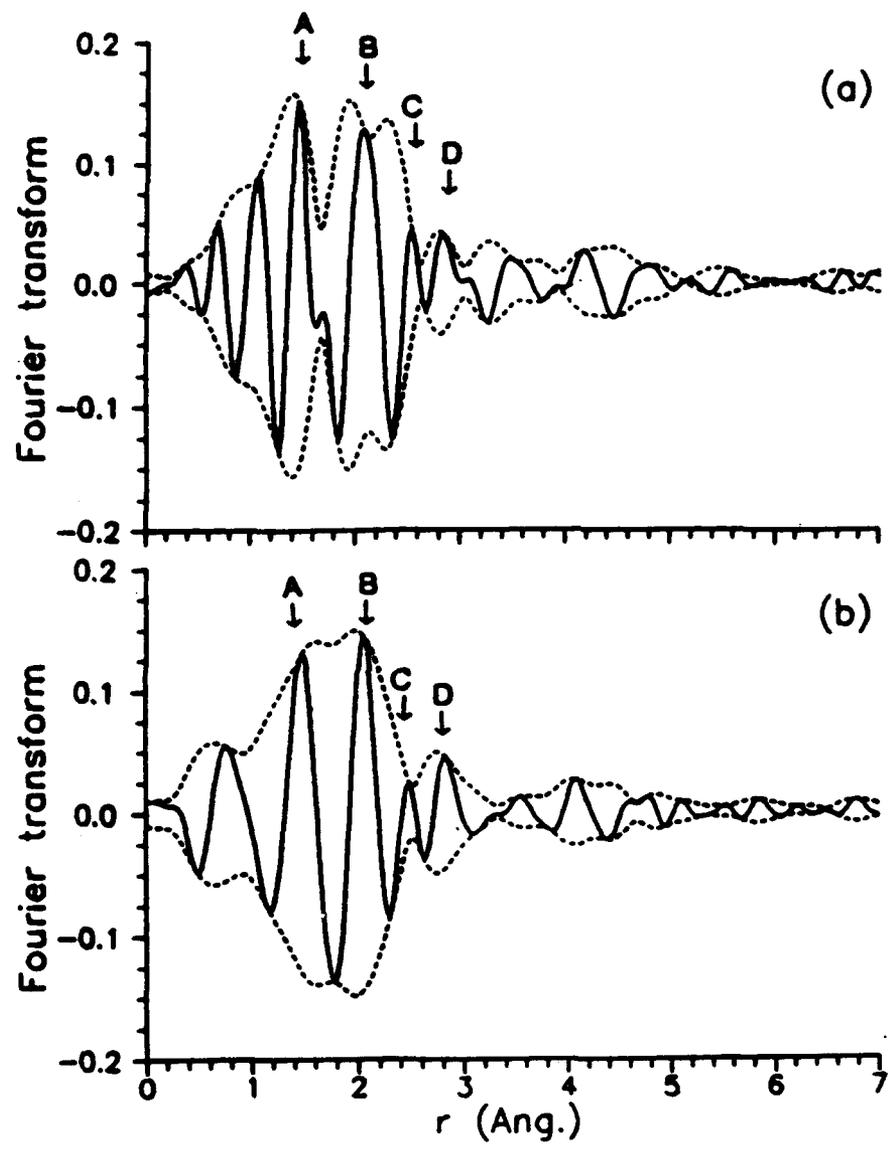


Fig. 4