

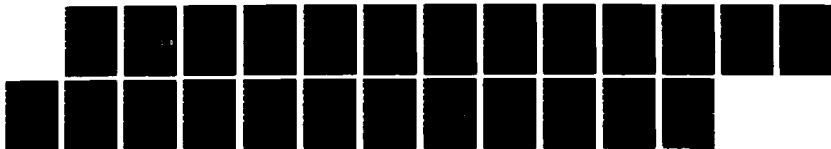
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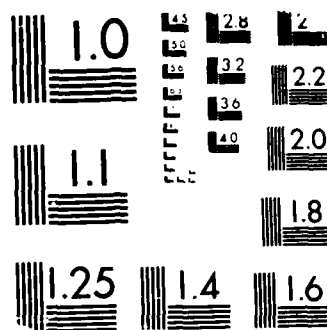
SURFACE EXAFS OF UNDERPOTENTIALLY DEPOSITED SILVER ON
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the silver atoms sit at three-fold sites on the gold surface
with water or perchlorate anion (from the electrolyte)
bonded at a well defined distance



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Surface EXAFS of Underpotentially Deposited Silver on
Au (111) Electrodes

by

J.H. White*, M.J. Albarelli*, H.D. Abruna*, Lesser Blum**, O.R.
Melroy***, M.G. Samant***, G.L. Borges*** and J.G. Gordon II***

*Department of Chemistry
Baker Laboratory
Cornell University
Ithaca, NY 14853

**Department of Physics, University of Puerto
Rico, Rio Piedras 00931

***IBM Almaden Research Laboratories
650 Harry Road, San Jose, CA 95120

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SURFACE EXAFS OF UNDERPOTENTIALLY DEPOSITED
SILVER ON Au (111) ELECTRODES

J.H.White, M.J. Albarelli, and H.D. Abruña *
Department of Chemistry
Baker Laboratory
Cornell University
Ithaca, NY 14853

L. Blum*
Department of Physics, College of Natural Sciences
University of Puerto Rico
P.O. Box AT, Rio Piedras, Puerto Rico 00931

O.R. Melroy *, M.G. Samant, G.L. Borges, and J.G. Gordon II
IBM Almaden Research Laboratories
650 Harry Road, San Jose, CA 95120

ABSTRACT

The fluorescence detected surface EXAFS of silver, underpotentially deposited from aqueous solutions of silver ion (HClO_4 electrolyte) on Au(111) electrodes was used to investigate the local structure of the adsorbate. Analysis of the data indicates that the silver atoms are bonded to three surface gold atoms at a distance of 2.75 ± 0.05 Å and to an oxygen atom (from solvent or electrolyte) at a distance of 2.42 ± 0.05 Å. These data suggest that the silver atoms sit at three-fold sites on the gold surface with water or perchlorate anion (from the electrolyte) bonded at a well defined distance.

INTRODUCTION

The electrode/electrolyte interface has heretofore been the object of much interest. The elucidation of interfacial structure has, however, been hampered by the lack of probes sensitive to microscopic structural features, particularly those on the atomic scale. The in-situ use of spectroscopies based on electromagnetic radiation of wavelengths from infrared to ultraviolet has provided interesting and extremely valuable information concerning vibrational modes and electronic energy levels at electrode surfaces.[1] The major limitation of these techniques is that the information extracted relates only indirectly to microscopic structural detail and hence, the accuracy of the conclusions rests on the appropriateness of the assumptions made in the models of particular interest.

The ex-situ use of electron spectroscopies and diffraction techniques has provided a wealth of information concerning structural detail.[2] However, the lack of control of electrode potential and the need to employ ultra-high vacuum (UHV) introduces questions about the relevance of that data to the structure actually present at the interface. The advent of synchrotron sources of x-rays of high intensity has provided an alternative to electron spectroscopy in structural studies of electrodes. In addition to the possibility of obtaining photoelectron spectra of high quality, the extended x-ray absorption fine structure is obtainable under a wide variety of

conditions.[3] The method of detection, however, determines the applicability of x-ray absorption spectroscopy to the in-situ characterization of electrode surfaces.[4] The fact that the fluorescence cross section is proportional to x-ray absorption cross section allows the detection of photons emitted upon relaxation of a core hole to be used as a measure of the post-edge x-ray absorption coefficient (EXAFS).[3]

The application of fluorescence detected surface EXAFS to the study of electrosorbed metal ions is of obvious interest, since 1) underpotential deposition (UPD) of metals on foreign metal substrates is clearly a process that would involve definite structures in various potential regimes, 2) some of these structures should be discernible by a short-range order technique such as EXAFS, and 3) UPD is an example of an important group of electrochemical processes involving specific adsorption of ions with subsequent and/or concomitant discharge of the ion. Reviews of UPD of metals have appeared previously. [5] We have also previously reported on surface EXAFS studies of Cu UPD on gold (111) as well as other systems.[6]

In this paper we present an in-situ surface EXAFS study of silver underpotentially deposited onto gold (111) electrodes.

The underpotential deposition of silver on gold substrates has been studied electrochemically [7] and by radiotracer techniques.[8] However, in these cases, definitive structural assignments were not made. The observation of the UPD was attributed to the variation of the activity coefficient of the

metal deposit with coverage below a monolayer. An expression for the UPD current, similar to that expected from calculations by Anson and Hubbard [9] for the reversible deposition of metals, was found to fit these equations.

Experimental

Gold (111) electrodes were prepared by epitaxially depositing 2500 Å of Au onto cleaved (in air) ruby mica surfaces (1 x 3 inches) which were maintained at 300 °C during the deposition.[10] Epitaxy was confirmed by Laue x-ray diffraction backscattering. The films were stored in an inert atmosphere prior to use in the electrochemical cell.

The electrochemical cell employed has been previously described.[6a] The reference electrode was a Ag/AgCl (3 M KCl) microelectrode, against which all potentials are reported. A Pt coil was used as the counter electrode. Solutions were deoxygenated with nitrogen and added (and removed) from the cell through teflon tubing connected to teflon syringes. The electrolyte was contained between a thin (0.5 mil) polypropylene film and the electrode. The electrochemical cell was continuously flushed with nitrogen to eliminate any problems from diffusion of oxygen through the thin polypropylene film. The electrolyte was 0.1 M perchloric acid (G.F. Smith double distilled) containing 5×10^{-5} M silver ions and was prepared from Aldrich Gold label reagents in pyrolytically distilled water.[11] Prior to deposition, solution was added to the cell so that the

polypropylene film distended somewhat, allowing the UPD layer to be deposited from bulk electrolyte. The monolayer was deposited from bulk electrolyte because of the low silver concentration. At this concentration approximately 10 minutes were required to form the monolayer, which was deposited at +0.60 V. All measurements were made at full monolayer coverage. After deposition, solution was removed, leaving only a thin layer of electrolyte between the electrode and polypropylene window. We estimate that the thickness of the electrolyte layer is of the order of 30 microns. In the thin layer configuration (at full monolayer coverage), we calculate that less than 5% of the absorbing silver atoms are present as ions in the electrolyte. As a result, the interference from silver in solution can be ignored. All experiments were conducted at room temperature.

Data were collected at the Cornell High Energy Synchrotron Source (CHESS) on beam line A-3. A Si (220) double crystal monochromator was used to select the incident wavelength. The absorption spectrum was measured about the Ag K edge, at 25.5 KeV by monitoring the Ag K_{α} fluorescence line at 22.1 KeV. This was detected with a 36 mm diameter high purity germanium solid state detector (Ortec GLP-36360/13-S) in conjunction with an Ortec model 673 spectroscopy amplifier and a single channel analyzer. The x-ray beam was incident on the sample at near grazing incidence (i.e., angle of incidence greater than 89°) although the actual angle was not measured. This geometry enhances the signal from the surface as the incident x-ray beam undergoes

total external reflection [12] thus increasing the local intensity of x-rays at the surface at least by a factor of 2. Furthermore, since the penetration depth of the x-rays in the sample is small in such a configuration, the scattered radiation (Compton and elastic) which represents the most significant source of background noise is greatly reduced. The angle of the sample was adjusted experimentally to minimize background scattering while maximizing the fluorescence peak. Soller slits were used to further reduce the background scattering incident on the detector.

Data were collected in scans of 20 to 30 minutes and typically about 35 scans were averaged to obtain a reasonable signal to noise ratio. These data were analyzed by employing a modified version of the program of B.M. Kincaid (AT&T Bell Labs.) The major inflection point in the edge jump was taken to be the position of the edge. Bond distances were obtained by fitting the oscillatory part of the EXAFS equation [13] to the experimental oscillations with the phase shift for the pair of interest being obtained experimentally from reference compounds.

DISCUSSION

The raw x-ray spectrum at the silver K edge for a silver UPD layer on a gold (111) electrode in contact with a 0.1M perchloric acid electrolyte solution and at an applied potential of +0.60 V is shown in Figure 1. A very well defined edge is present at about 25.5 keV. Pronounced edge features (e.g. XANES [14]) are

not readily visible and the EXAFS is somewhat weak. Such results are expected for adsorbed polarizable metals, since excitation of a bound electron to a conduction band would not be a process which would be resonant as is the case with semiconductors and certain metal ions which possess unfilled subshells at the valence level. The relatively weak EXAFS can be attributed to substantial inelastic scattering and large amplitude thermal vibrations and static disorder. (i.e. large Debye-Waller factors) [13] Such would be the case for a model consisting of a silver atom adsorbed on the gold substrate and possessing a large amplitude of vibration as would be expected for a relatively low melting metal or alloy. While one would anticipate the adsorbed silver layer to exhibit a certain degree of order, this would not necessarily be the case for adsorbed water or electrolyte (perchlorate) ions in the compact layer. However, as we previously reported there appears to be a considerable degree of order in the layer of sulfate ions adsorbed on UPD copper on gold (111) in sulfuric acid.[6a]

Upon stripping of the monolayer and flushing the thin layer cell volume, only background scattering was observed, indicating that the signal originates from the silver UPD layer.

As in our previous study of Cu UPD on Au [6a], we considered scattering by surface gold atoms and solvent or electrolyte. These were anticipated to represent the largest contributions to the scattering since the plane of polarization of the x-ray was normal to the electrode surface; thus minimizing the effects of

scattering by silver since in this case the polarization of the x-ray beam would be normal to the silver-silver bond vector. Figure 2 shows the k weighted EXAFS (raw (A), and smoothed (B)) as well as the fitting (C; open circles) obtained when considering only gold as a backscatterer. Although the fit is reasonable at low k values, there are gross deviations for k values larger than 5. Figure 3 shows the results obtained when considering only oxygen as a backscatterer. Clearly in this case the fit is greatly improved but again there are significant deviations; especially at intermediate values of k . Finally, Figure 4 shows the results obtained when backscattering by both oxygen and gold is taken into account. In this case an excellent fit of the data is obtained over the entire range of k values.

The fitted values of the uncorrected coordination numbers for oxygen and gold occur in a ratio of approximately one oxygen atom per three gold atoms. Based on this, we propose a model, shown in Figure 5, in which a silver atom sits in a three-fold site on the gold substrate and is bonded to an oxygen atom from water (Figure 5A) or perchlorate ion (Figure 5B). The accurate determination of coordination numbers here is not claimed, since inelastic scattering lengths and Debye-Waller factors are not known to a high degree of accuracy. However, it is sufficient to say that gold is the dominant backscatterer in the compact layer in terms of number.

The bond lengths obtained from least squares minimization were $2.75 \pm .05 \text{ \AA}$ and $2.42 \pm .05 \text{ \AA}$ for gold and silver backscatterers,

respectively. The first value is consistent with, although somewhat shorter than, the bond length anticipated for a Ag-Au alloy (2.88) angstroms).[15] This might be due to partial charge transfer (i.e. electrosorption valency less than 1) which would result in a smaller bondlength than that anticipated on the basis of the bulk alloy. In addition, a contraction of the bond length at the surface would not necessarily be unexpected. The silver oxygen distance of 2.42 Å is significantly longer than the anticipated value of about 2.30 Å. This was a rather surprising finding and we are not yet certain as to its origin.

The unambiguous assignment of structure in this system is contingent upon the availability of information related to the polarization dependence of the EXAFS signal. However, it may be stated that a glimpse into the composition of the compact layer may be inferred by the data presented here. Such information is valuable with regard to the system studied here since it is revealing in terms of the kind of interaction to be expected between substrate, adsorbate, and solvent.

The results presented here were analyzed on the basis of a single scattering plane wave formalism. It has been shown that atoms arranged in a colinear array should show rather pronounced multiple scattering effects.[13] The structural model proposed here would probably not give rise to pronounced multiple scattering effects although the structures inferred should be accessible using the single scattering formalism. A multiple scattering formalism analysis would, of course, provide more

detailed information about bond angles. However, the low signal to noise ratio obtained here would create considerable difficulty in the analysis of this data, since the analysis of higher coordination shells by fourier filtering is quite difficult. It has been shown that the width of the filter window is inversely proportional to the degrees of freedom allowable in the subsequent chi square minimization routine. Practically, then, one must perform the minimization on the unfiltered spectrum leading to the undesirable consequence of minimization in many parameters of a maximum likelihood estimator that is large and, hence, relatively insensitive to the small changes in parameters that would differentiate between models.

CONCLUSIONS

The surface EXAFS of underpotentially deposited silver on gold (111) films on mica was studied with the electrode under potential control. It was revealed that both gold and oxygen are present as backscatterers in the first coordination shell of silver. It was estimated that the bond length to gold and oxygen were $2.75 \pm .05$ and $2.42 \pm .05$ angstroms respectively, and the respective coordination numbers were 3 and 1. A model consistent with these findings is one where the silver atoms sit on three fold sites on the gold surface and have oxygen from water or electrolyte bound at a well defined distance. This model is qualitatively the same as that proposed for the Cu UPD layer on gold (111) electrodes.

Acknowledgements:

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Figure Legends

Figure 1. In-situ absorption spectrum around the silver K edge for an underpotentially deposited monolayer of silver on a gold (111) electrode in contact with a 0.1M perchloric acid solution and at an applied potential of +0.7 V.

Figure 2. K weighted raw (A) and smoothed (B) EXAFS for a silver UPD layer on a gold (111) electrode and fitting (C, open circles) when considering only gold as a backscatterer.

Figure 3. Same as Figure 2 but fitting with only oxygen as a backscatterer.

Figure 4. Same as Figure 2 but fitting with both gold and oxygen as backscatterers.

Figure 5. Model for the structure of an underpotentially deposited monolayer of silver on a gold (111) electrode with either water (A) or perchlorate (B) bonded through the oxygen.

AG UPD ON AU(111)

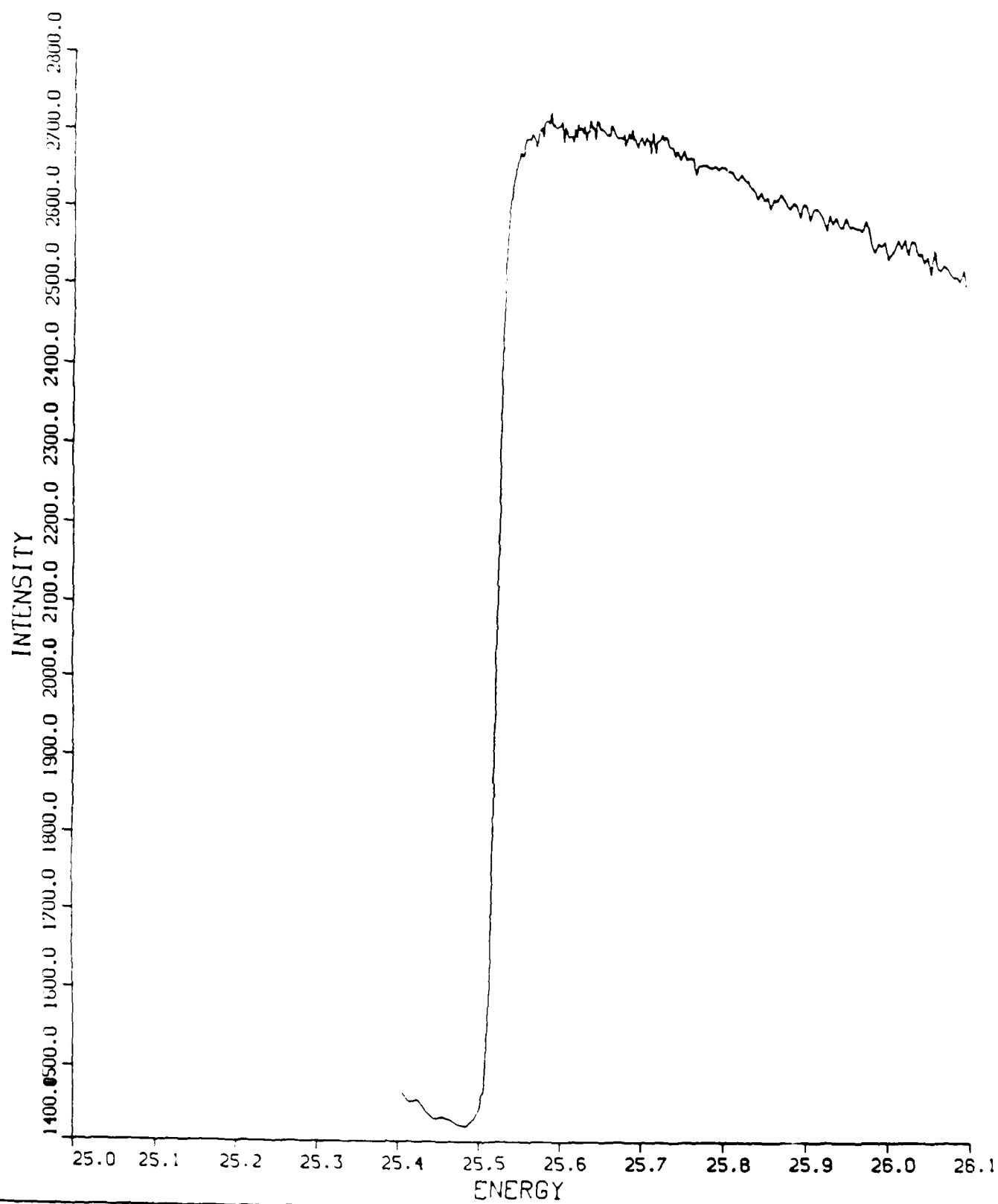


Figure 1

Ag UPD ON Au(111): Au ONLY

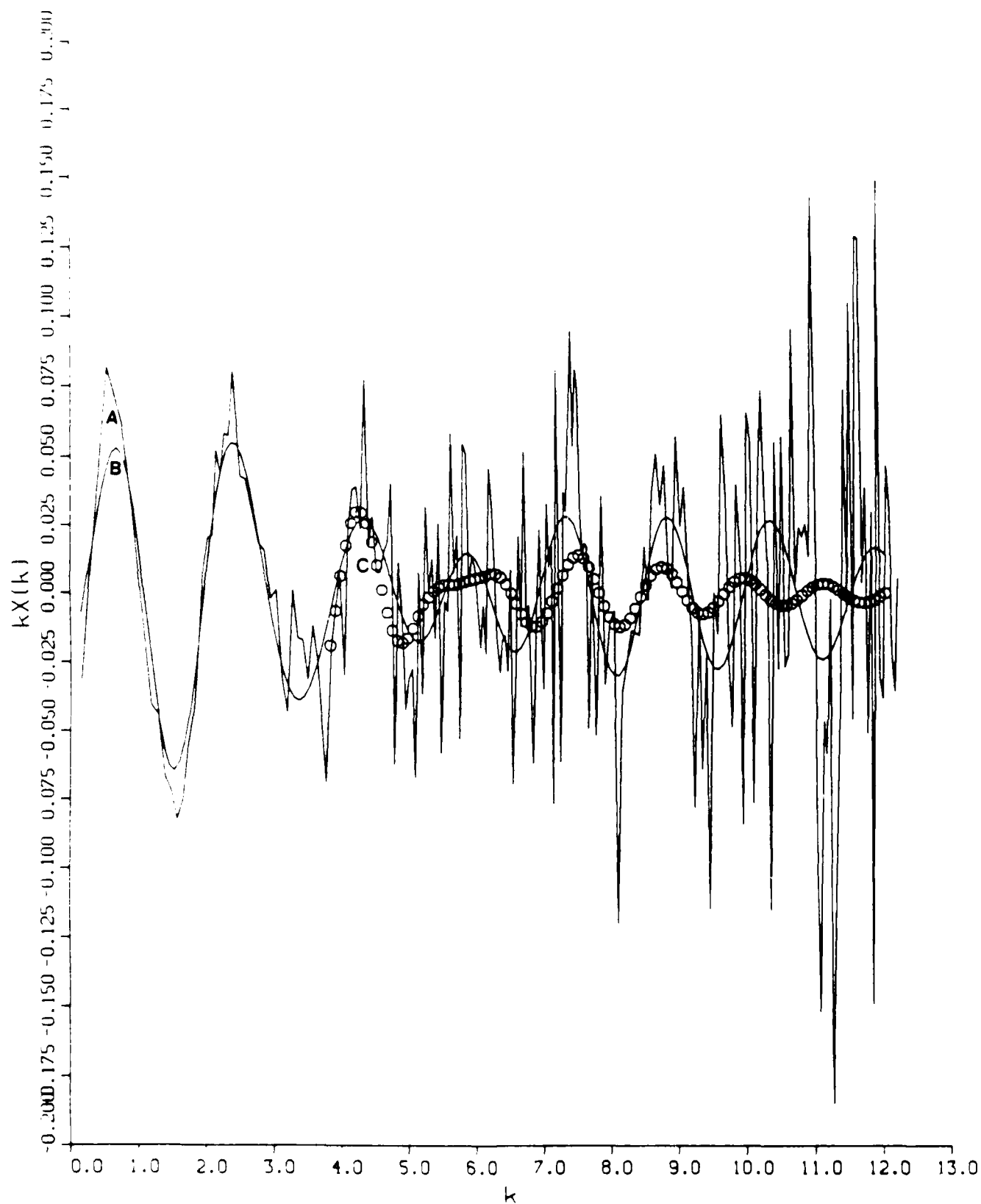


Figure 2

RG UPD ON AU(111): 0 ONLY

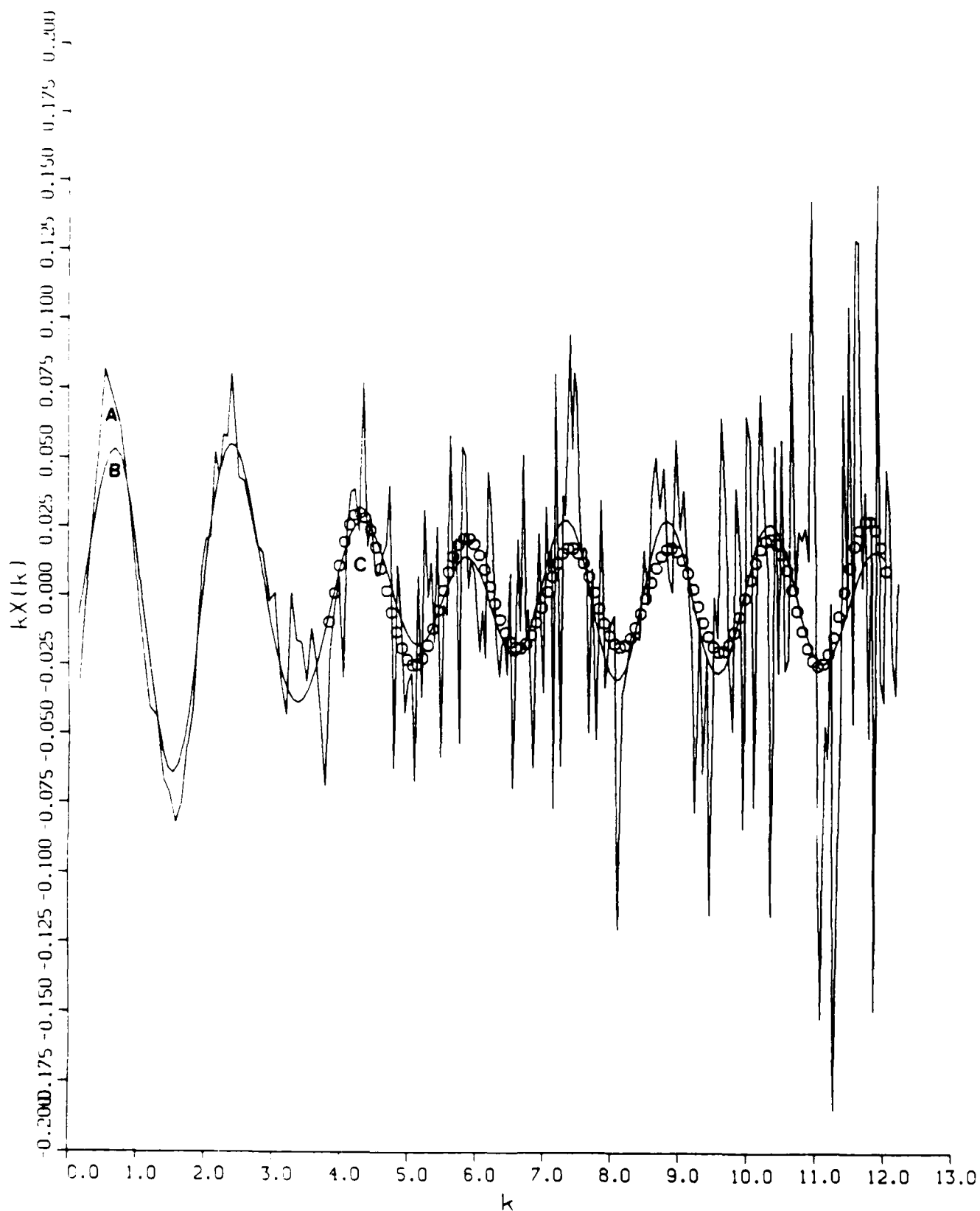


Figure 3

AG UPD ON AU(111): AU + O

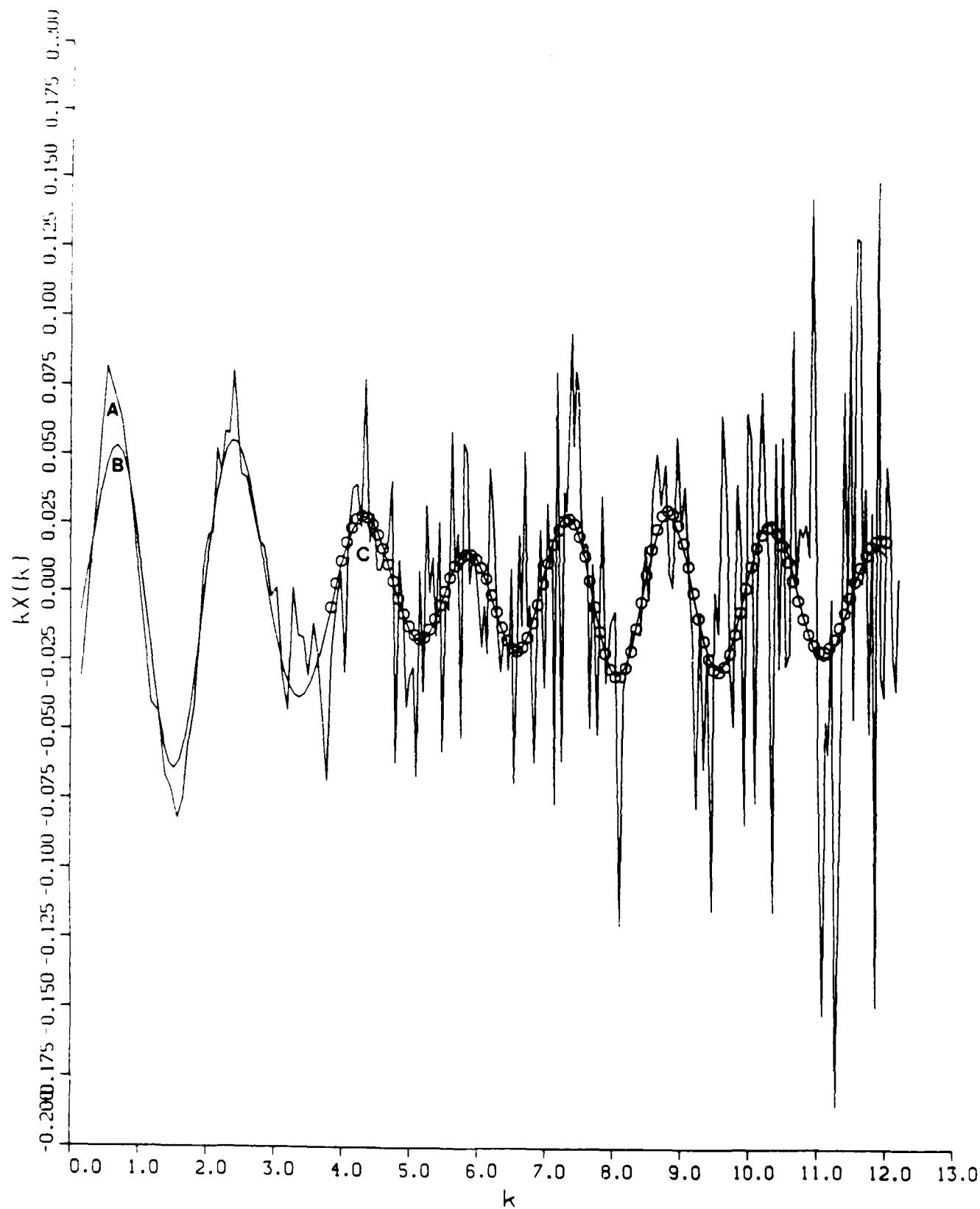


Figure 4

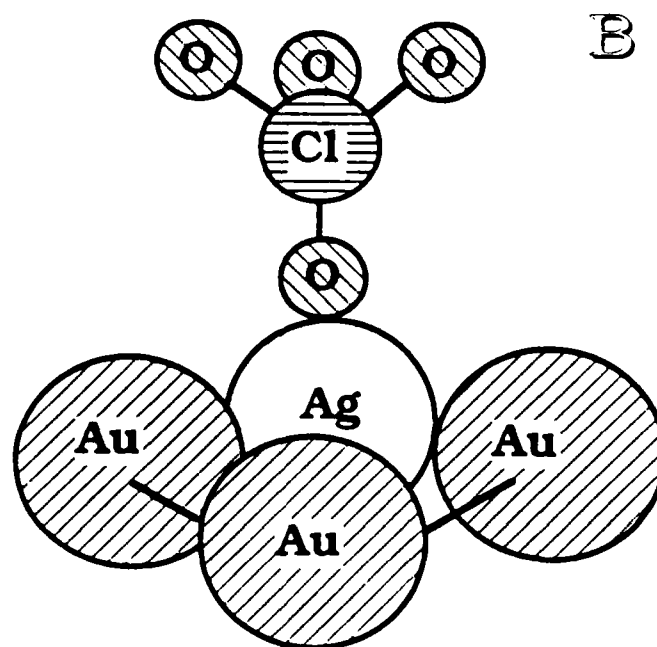
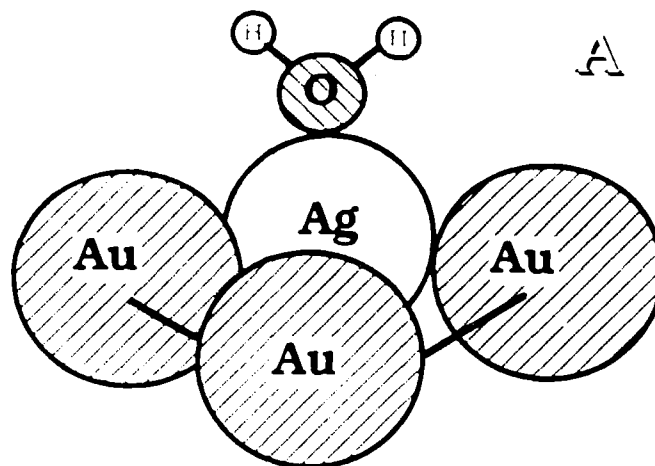


Figure 5

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