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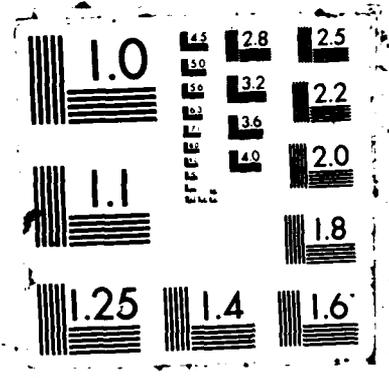
IN-SITU SURFACE EXAFS AT CHEMICALLY MODIFIED ELECTRODES 1/1
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Technical Report #7

In-Situ Surface EXAFS at
Chemically Modified Electrodes

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**IN-SITU SURFACE EXAFS AT
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Abstract:

The surface EXAFS and near edge structure of electropolymerized films of $[\text{Ru}(\nu\text{-bpy})_3]^{2+}$ on platinum electrodes have been studied as a function of surface coverage and applied potential by measuring the characteristic RuK_α fluorescence intensity. Spectra for electrodes modified with 1, 5 and 50 monolayers were obtained. Analysis and comparison of EXAFS and XANES features for these films with those of bulk $[\text{Ru}(\text{bpy})_3]^{+2}$ showed similar morphological and electronic characteristics in agreement with previous electrochemical studies showing that solution redox properties of monomer complexes can be transferred to electrode surfaces by electrodeposition as polymer films of varying thickness. Electrochemical oxidation of the films resulted in a shift of 2 eV in the edge position towards higher energy, consistent with the higher charge on the ruthenium centers. Other spectral features, however, remained essentially unchanged. The applicability of these studies to the in-situ investigation of electrocatalytic systems is discussed.

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Introduction:

Among the main goals of electrochemical research are the design, characterization and understanding of electrocatalytic systems, [1,2] both in solution and on electrode surfaces.[3] Of particular importance are the nature and structure of reactive intermediates involved in the electrocatalytic reactions.[4] The nature of an electrocatalytic system can be quite varied and can include activation of the electrode surface by specific pretreatments [5] to generate active sites, deposition or adsorption of metallic adlayers [6] or transition metal complexes. [7] In addition the electrode can act as a simple electron shuttle to an active species in solution such as a metallo-porphyrin or phthalocyanine.

Over the years, many systems have been investigated and a variety of experimental probes, both electrochemical and spectroscopic, have been used in their study and characterization. Thus, electrochemical techniques such as rotated-ring disk electrodes [8] and spectroscopic techniques such as Raman [9] (in its numerous variants) have provided much insight into the mechanisms of many of these processes. However, in-situ structural studies of such systems have, to date, proved very elusive to direct experimental probing.

The application of ultra-high vacuum surface spectroscopic methods coupled to electrochemical techniques [10] have provided valuable information on surface structure/reactivity correlations. However, the fact that these determinations are

performed ex-situ raise important concerns as to their applicability to electrocatalytic systems, especially when very active intermediates are involved.

An added difficulty that arises in the in-situ spectroscopic study of electrocatalytic systems in solution is that the active species will be located in the vicinity of the electrode so that the material in solution will generally represent a large background signal making the detection and identification of related species difficult. Thus, it would be ideal to be able to probe only that region proximal to the electrode surface and furthermore to be able to obtain structural information of the species involved.

A way to circumvent the first problem is to ensure that all of the active material is present at the electrode surface. That is, employ a chemically modified electrode where a precursor to the active electrocatalyst is incorporated. The field of chemically modified electrodes [3] is approaching a more mature state and there are now numerous methodologies for the incorporation of materials that exhibit electrocatalytic activity. Moreover, some of these synthetic procedures allow for the precise control of the coverage so that electrodes modified with a few monolayers of redox active material can be reproducibly prepared. [3]

The second problem of concern is being able to perform an in-situ structural characterization of the redox active catalyst incorporated on the electrode surface. For this application,

surface EXAFS is perhaps the only technique capable of yielding in-situ (that is with the electrode in contact with an electrolyte solution and under potentiostatic control) structural information on electrodeposited layers.

We have previously employed such a technique in the study of iodide adsorption onto Pt(111) electrodes [11] as well as in the in-situ structural characterization of underpotentially deposited copper on gold(111) electrodes. [12]

We now present an in-situ surface EXAFS study of electropolymerized films of $[\text{Ru}(\text{v-bpy})_3]^{2+}$ (v-bpy is 4-vinyl, 4'-methyl, 2,2' bipyridine) and on the applicability of this technique to follow the course of redox transformations.

This system has been the object of considerable study since the monomer complex and its analogues have been widely studied [13] and electropolymerization is readily accomplished at the vinyl substituent on the bipyridinyl ligand. [14] There are two aspects that we wish to address and these are the dependence of the structure of electrodeposited layers on coverage and the ability to follow redox transformations. The dependence of structure on surface coverage should indicate 1) the nature and strength of interaction of the electrodeposited film with the electrode surface and 2) the applicable range of surface coverages over which polymer local structure is similar to that of the monomeric parent complex in solution (and by inference, the range over which redox behavior is similar). In addition, the ability to follow redox transformations will be of great

utility in investigating electrocatalytic systems.

The information obtained from the previously described studies may thus be used to establish guideposts for the rational design and synthesis of electrochemical interfaces (in particular, of polymer modified electrodes), with high catalytic activity.

Experimental:

1. Reagents

$[\text{Ru}(\text{v-bpy})_3]^{2+}$ was prepared as previously described. [14] Acetonitrile (Burdick and Jackson distilled in glass) was dried over 4Å molecular sieves. Tetra n-butyl ammonium perchlorate (G.F. Smith) was recrystallized three times from ethyl acetate and dried under vacuum at 70° C for 72 hours.

2. Electrochemical Instrumentation

A 1 cm diameter platinum disk brazed onto a brass holder was used as a working electrode. It was masked with ChemGrip (a teflon based epoxy) except for the upper face. Prior to use, it was polished with 1 micron diamond paste (Buehler) and rinsed with water, acetone and methanol. The counter and reference electrodes were a platinum coil and a silver wire, respectively

Electropolymerization of $[\text{Ru}(\text{v-bpy})_3]^{2+}$ was carried out in acetonitrile/0.1M TBAP solution in a conventional three compartment electrochemical cell according to previously described procedures. [14]

The electrochemical cell for the EXAFS experiments was

machined from a teflon cylinder (6 cm diameter x 6 cm high) and was provided with contacts for all electrodes as well as teflon fittings for the injection of electrolyte. The electrode was placed flat on the top of the cell and seated with an O-ring. The cell cover consisted of a thin tefzel (E. I. DuPont de Nemours Inc.) film (12 μm) held in place with a viton O-ring placed 1 cm below the top and around the circumference of the cell. The surface of the platinum electrode was raised about 1 mm above the cell so as to allow near grazing incidence of the x-ray beam. The tefzel cover made effectively a thin layer cell whose thickness we estimate to be of the order of 20 μm . The cell was mounted on a plexiglass box with Kapton windows. The top of the box was provided with entrance and exit ports so that it could be constantly flushed with He. The box assembly was bolted on a Huber 410 goniometer stage providing very fine and reproducible rotation and translation. (Typically 4,000 steps/degree of rotation and 100 steps/ μm translation.)

3. X-ray Instrumentation

All experiments were performed at the Cornell High Energy Synchrotron Source (CHESS) operated at 5.8 GeV (Stations A-1 and C-2). Monochromatic radiation was obtained with a Si(220) double crystal monochromator. 50% detuning was typically employed in order to eliminate higher harmonics.

A Princeton Gamma Tech Si(Li) solid state detector in conjunction with an EG&G Ortec Model 673 Spectroscopy Amplifier and a Tennelec Model 450 Single Channel analyzer were employed to

detect the characteristic RuK_α fluorescence at 19.3 keV. Data were analyzed using a modified version of the EXAFS analysis program B.M. Kincaid (AT&T Bell Labs).

For $[\text{Ru}(\text{bpy})_3]^{2+}$, (employed as a model compound) acetonitrile solutions were evaporated on top of a platinum electrode and the EXAFS signal obtained. In this case, however, the electrode was in contact with a He atmosphere and not in solution.

Procedure:

The platinum electrode was modified as described in the experimental section. It was rinsed with acetone and placed in an acetonitrile/0.1M TBAP solution and a cyclic voltammogram of the $[\text{Ru}(\text{v-bpy})_3]^{2+/3+}$ wave obtained. From the charge consumed (i.e. by integration of the area under the voltammetric wave) the surface coverage (in equivalent number of monolayers) was determined. Samples with 1, 5, 12, 25 and 50 monolayers were prepared.

The electrode was mounted on the EXAFS cell and all the cell connections were made. The spectrum of the reduced form (i.e. $[\text{Ru}(\text{v-bpy})_3]^{2+}$) of the polymeric film was performed while the potential was held at 0.0 V. Afterwards, the potential was scanned to +1.6 V and held for 5 minutes (to ensure complete oxidation to $[\text{Ru}(\text{v-bpy})_3]^{3+}$) prior to obtaining the spectrum. After spectroscopic investigations the voltammetric behavior of the modified electrode in acetonitrile/0.1M TBAP was performed to

confirm that there was no loss of material.

Results and Discussion:

Figure 1 presents EXAFS spectra for bulk $[\text{Ru}(\text{bpy})_3]^{2+}$ (A) as well as for electrodes modified with 1 and 5 monolayers of poly- $[\text{Ru}(\text{v-bpy})_3]^{2+}$. The spectrum for bulk $[\text{Ru}(\text{bpy})_3]^{2+}$ shows a well defined edge at 22.18 keV with three well defined oscillations beyond the edge. Qualitatively similar spectra are obtained for electrodes modified with 1 (Fig. 1B) and 5 (Fig. 1C) monolayers of the polymer. Again a well defined edge is present and although the first oscillation is clearly defined in both cases, the second and third oscillations are difficult to discern in a spectrum for the electrode modified with a monolayer of polymer. However, for the electrode covered with 5 monolayers, the second and third oscillations are well defined. The appearance of oscillations at higher energies is more difficult to detect because of the rapid decrease in the backscattering amplitude for low Z scatterers (nitrogen in this case), in addition to the small amounts of material present on the modified electrode. A monolayer of complex on the electrode surface represents about 8×10^{-11} moles/cm² which is about 5% of a metal monolayer. Thus, even for very low coverages of ruthenium, clear signals can be obtained. For samples containing 25 or more monolayers, the spectrum obtained was indistinguishable from that obtained for the bulk material.

Figures 2A and B show the phase uncorrected radial

distribution functions for bulk $[\text{Ru}(\text{bpy})_3]^{2+}$ (Figure 2A) and an electrode modified with 50 monolayers of poly- $[\text{Ru}(\text{v-bpy})_3]^{2+}$ (Figure 2B) and both show a very prominent peak at a distance of about 1.5 Å. These peaks were fourier filtered (in the indicated regions) and back transformed (into k space) where they were fitted for amplitude and phase. Phase corrections were made employing the Ru-N distance reported by Rillema et al [15] for an x-ray diffraction study of $[\text{Ru}(\text{bpy})_3]^{2+}$. Figure 3 shows the k weighted experimental data and fit for an electrode modified with 50 monolayers of poly- $[\text{Ru}(\text{v-bpy})_3]^{2+}$. A very good fit is obtained for the first three oscillations although at higher wave vector the fit degrades somewhat due to the lower signal to noise ratio in this region of the spectrum.

Virtually identical results were obtained for bulk $[\text{Ru}(\text{bpy})_3]^{2+}$. Upon fitting the data to theoretical amplitudes and phase shifts, bond lengths of 1.9, 2.0, and 2.1 angstroms and coordination numbers of about 6 were found for 1, 5, and 50 monolayers respectively. There is doubtful statistical significance in the trend observed in the bondlengths. However, it appears that the similarity between the data for the samples is indicative of similar local structure at all stages of polymer deposition. These values correlate very well with the known coordination number of six and a Ru-N distance of 2.056 Å. [15]

In addition to the similarities aforementioned, it is also clear that there is little difference between the electrodeposited polymer and monomeric parent compound

$[\text{Ru}(\text{bpy})_3]^{2+}$ in terms of the near edge spectral features pointing to a similar geometric disposition of scatterers.

The results presented here seem to indicate that 1) the local order about ruthenium centers in the polymers is essentially unchanged from that in the monomer complex and 2) that the interaction with the electrode surface occurs without appreciable electronic and structural change. This spectroscopic information corroborates previous electrochemical results which showed that redox properties (e.g. as measured by formal potentials) of dissolved species could be transferred from solution to the electrode surface by electrodepositions as polymer films on the electrode. [3] Furthermore, it is apparent that the initiation of polymerization at these surfaces (i.e. growth of up to one monolayer of polymer) involves no gross structural change.

The results presented to this point were for films where the ruthenium was present in the 2+ oxidation state. Identical results were obtained for electrodes potentiostated at 0.0 V or at open circuit.

Having established that there were no significant structural perturbations in the coordination spheres of the ruthenium centers in the polymer films we investigated the effect of oxidation of the ruthenium to the 3+ oxidation state. This was performed in acetonitrile/0.1 M TBAP by holding the potential at +1.6 V for 5 minutes to ensure oxidation of the film. A clear indication that the film was indeed oxidized came from the fact

that the color of the polymeric deposit changed from orange (typical of $[\text{Ru}(\text{bpy})_3]^{2+}$) to green (typical of $[\text{Ru}(\text{bpy})_3]^{3+}$). The spectral features obtained in this case were essentially identical to those obtained for the film present in its reduced form (i.e. $[\text{Ru}(\text{bpy})_3]^{2+}$). This is not surprising, since the difference in metal/ligand (Ru/N) bond distance is estimated to be less than 0.01 Å. Upon oxidation from Ru^{2+} to Ru^{3+} there was, however, a well defined shift towards higher energies in the edge position. This is shown in Figure 4 which shows the edge regions for the films present in the reduced form $[\text{Ru}(\text{v-bpy})_3]^{2+}$ (Figure 4A) and in the oxidized form $[\text{Ru}(\text{v-bpy})_3]^{3+}$ (Figure 4B). The shift, taken at half the edge jump is of the order of 2 eV, consistent with the change in oxidation state of the metal centers. This was a reversible change as re-reduction of the film resulted in a shift of the edge back to lower energies.

There are two points from this study that need to be emphasized. First of all, it is possible to obtain good quality in-situ surface EXAFS spectra for electrodes modified with about one to five monolayers of a transition metal complex and in addition changes in oxidation state can also be monitored. There were also no significant changes in the structural features of the electropolymerized film as compared to bulk $[\text{Ru}(\text{bpy})_3]^{2+}$. Although in this specific system there were no changes in coordination or significant changes in metal/ligand bond distances as a function of the oxidation state of the metal center, it is clear that such determinations can be performed.

We are currently involved in a study of electropolymerized films of $[\text{Ru}(\text{CO})(\text{v-bpy})\text{Cl}]$ which, upon electrochemical reduction, form a metal-metal bonded dimer. [16] In addition, the monomer complex shows electrocatalytic activity towards the reduction of CO_2 [17] and we are assessing the possibility of performing an in-situ surface EXAFS study of a modified electrode under electrocatalytic conditions.

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Figure Legends:

Figure 1. EXAFS spectra for:

- a. $[\text{Ru}(\text{bpy})_3]^{+2}$
- b. platinum electrode modified with one monolayer of poly- $[\text{Ru}(\text{v-bpy})_3]^{+2}$
- c. same as b except the coverage was 5 monolayers

Figure 2. Phase uncorrected radial distribution functions for:

- a. $[\text{Ru}(\text{bpy})_3]^{+2}$
- b. electrode modified with 50 monolayers of poly- $[\text{Ru}(\text{v-bpy})_3]^{+2}$

Circles indicate the fourier window employed in peak isolation for fitting of phase and amplitude.

Figure 3. EXAFS as a function of wave vector for the fourier filtered peak for an electrode modified with 50 monolayers of poly- $[\text{Ru}(\text{v-bpy})_3]^{+2}$

- a. solid line: experimental
- b. dashed line: fit over entire range of k values
- c. circles: fit for k values from 3 to 12

Figure 4. Potential dependence of the edge region of the absorption spectrum for an electrode modified with 10 monolayers of poly- $[\text{Ru}(\text{v-bpy})_3]^{+2}$

- a. solid line: 0.0 Volts
- b. dotted line: +1.6 Volts

RU(BPY)3 2+ MODEL

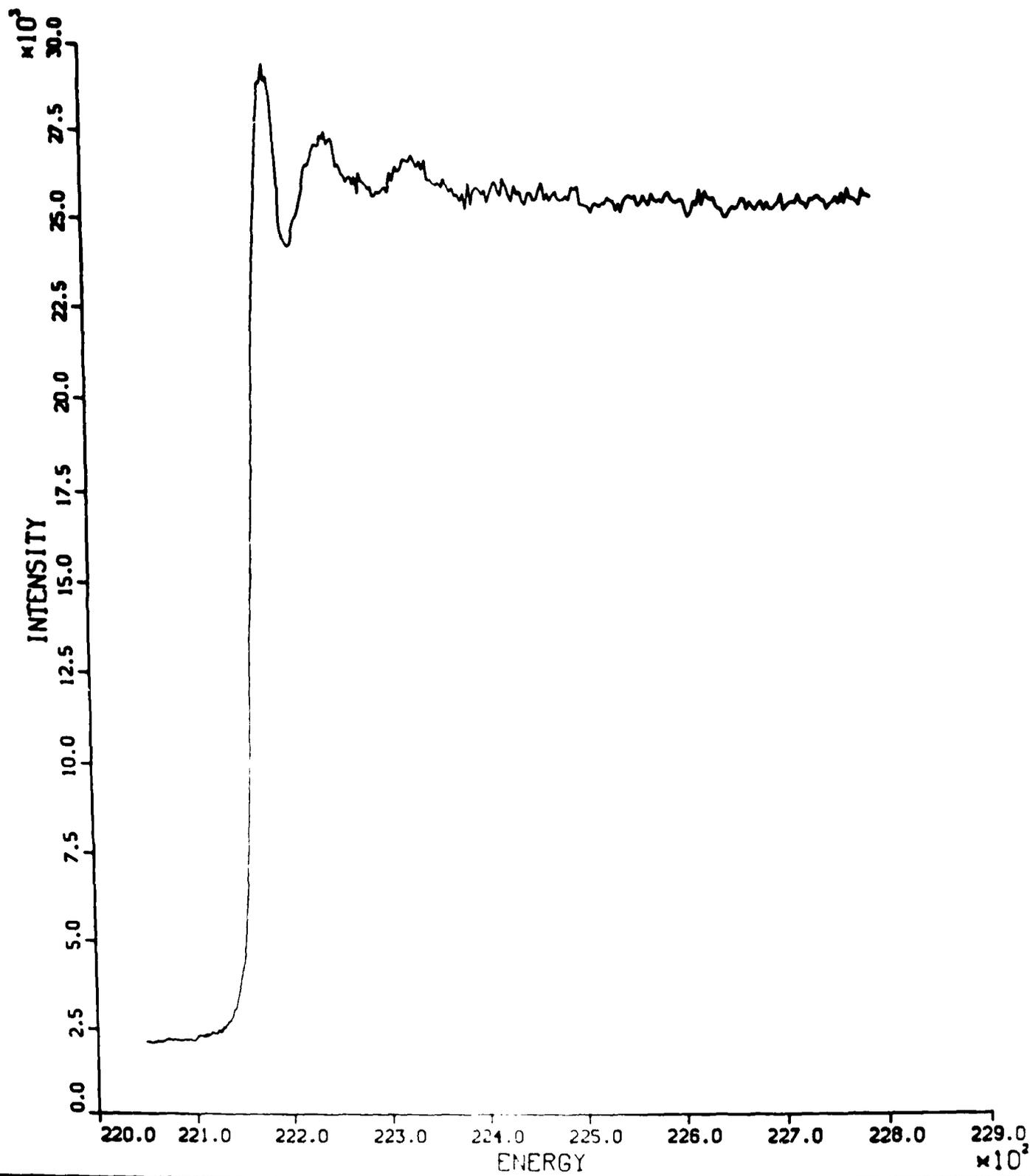
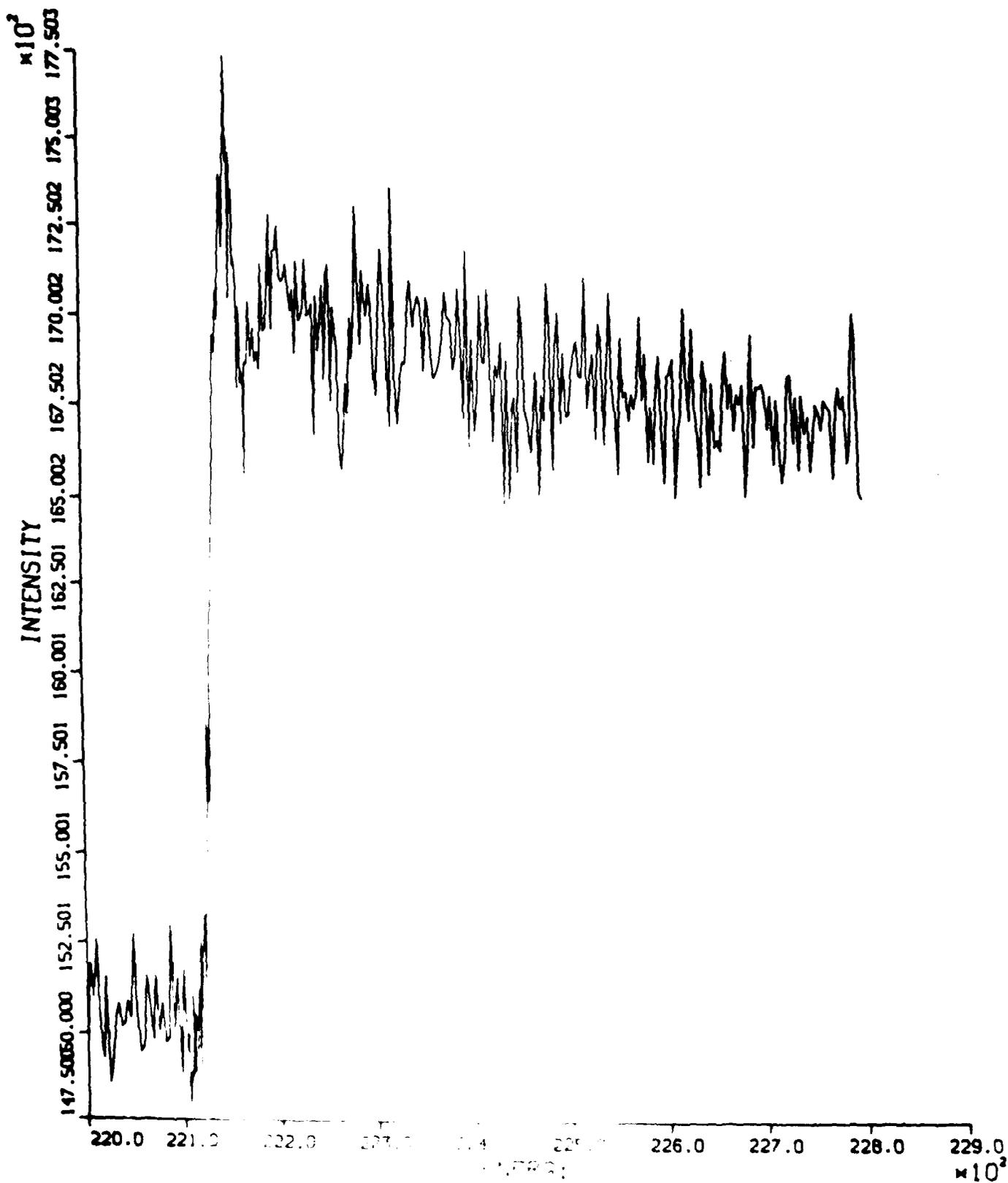


Figure 1A

1 mL RU(VBPY)3 2+ ON PT FOIL



5 ML RU(VBPY)3 2+ ON PT FOIL

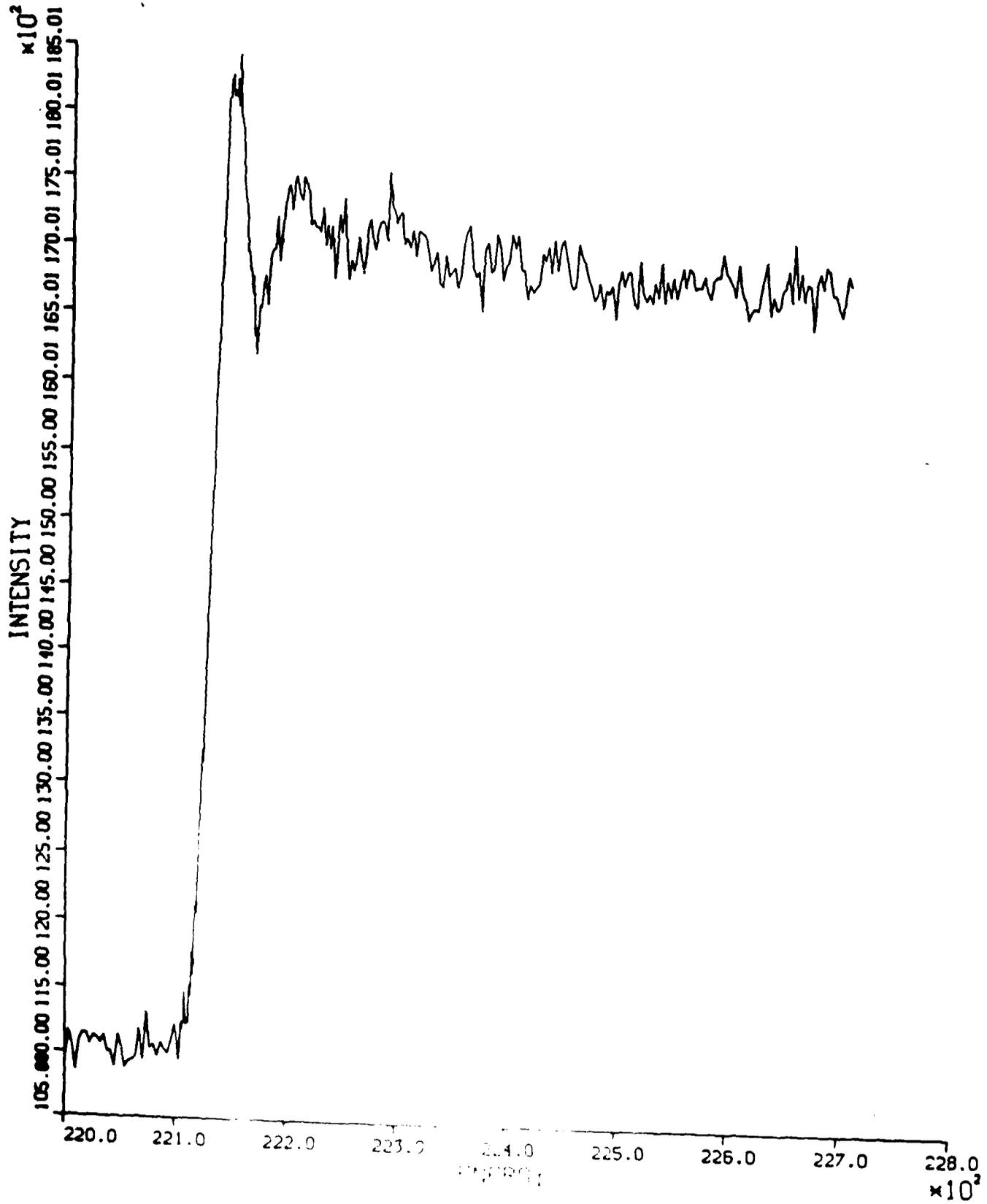


Figure 10

RU(BPY)3 2+ MODEL

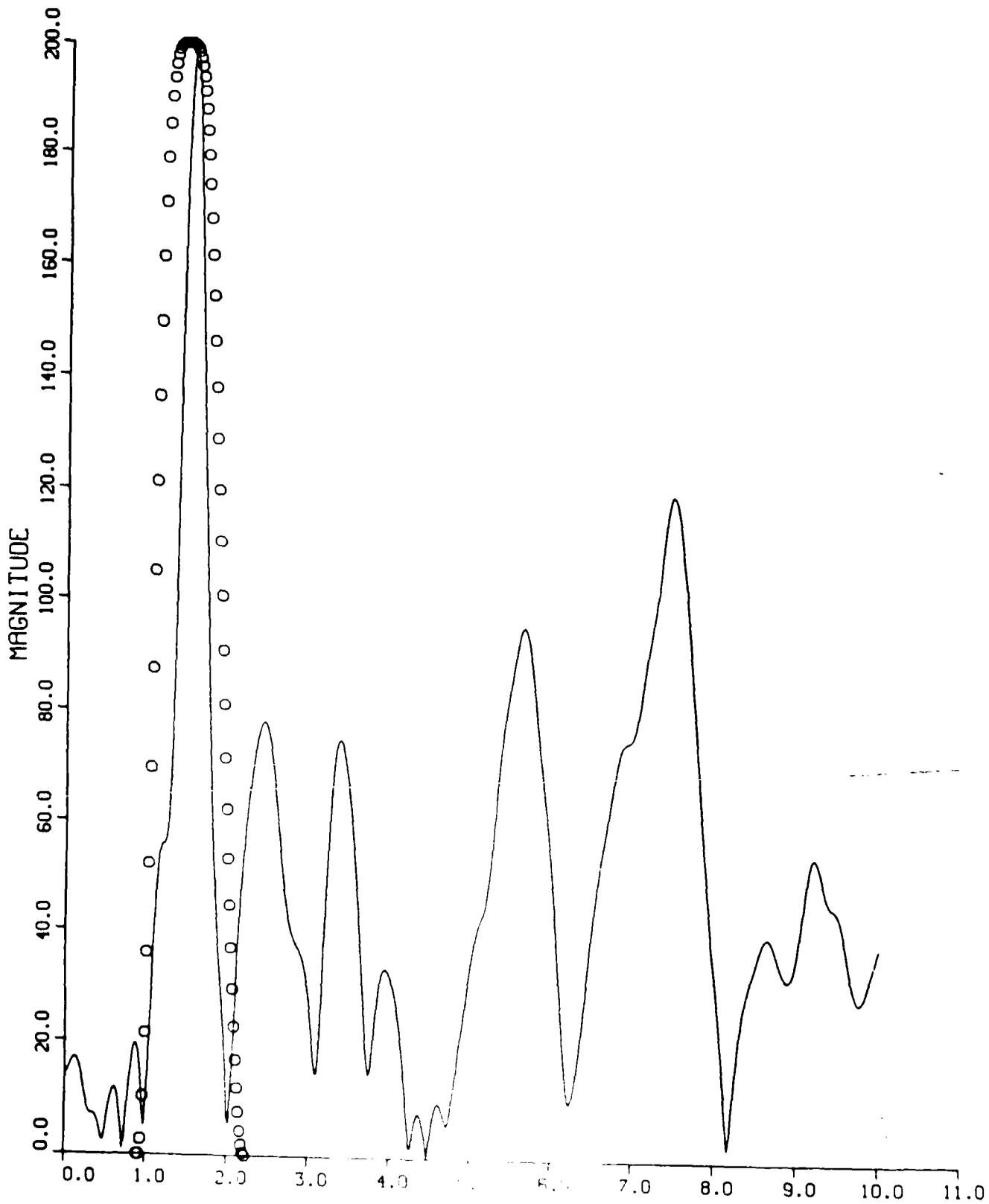


Figure 2A

50 ML RU(VBPY)3 2+ ON PT FOIL

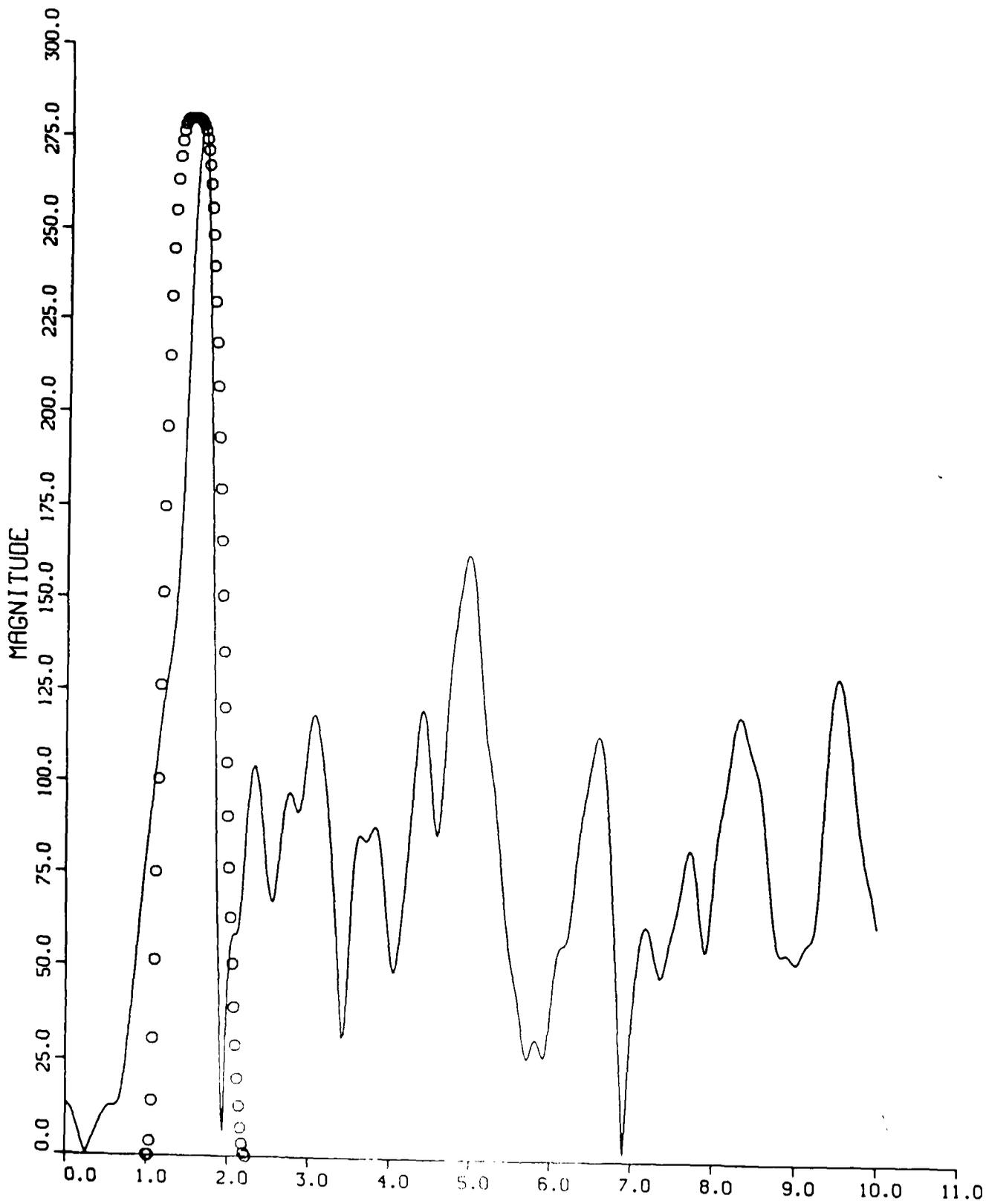


Figure 2B

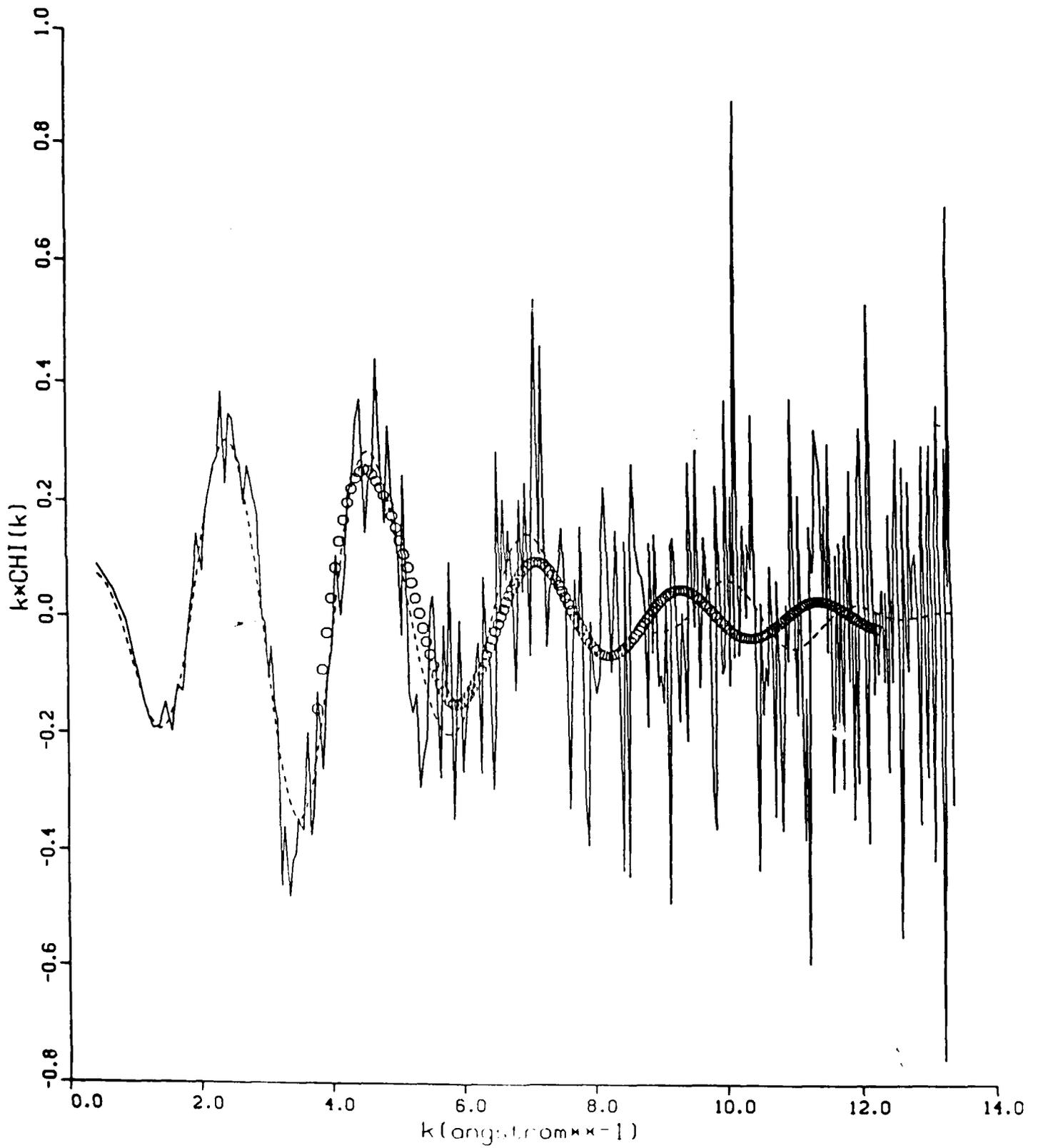


Figure 3

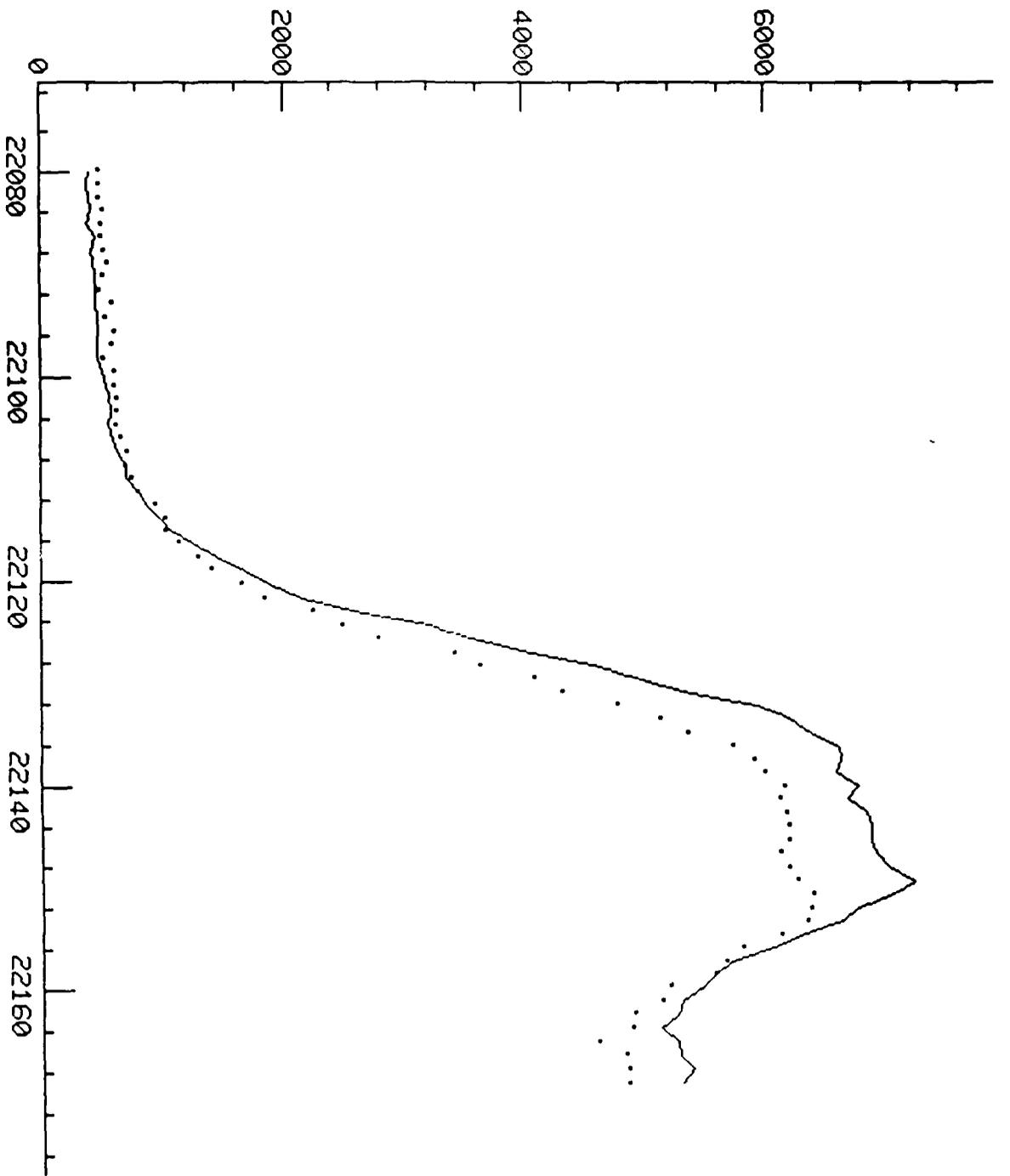


Figure 4

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