



Lawrence Berkeley Laboratory

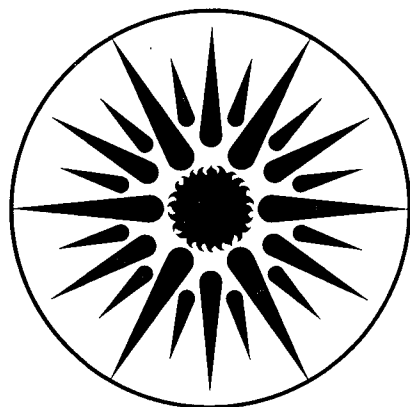
UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

Ex-Situ and *In-Situ* Spectroscopic Studies of the Passive Film on Lithium in Non-Aqueous Solvents

D.A. Scherson and G.S. Chottiner

October 1990



APPLIED SCIENCE
DIVISION

1 LOAN COPY 1
1 Circulates 1
1 for 2 weeks 1

Bldg. 50 Library.
COPY 2

LBL-29697

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

EX-SITU AND IN-SITU SPECTROSCOPIC STUDIES
OF THE PASSIVE FILM ON LITHIUM
IN NON-AQUEOUS SOLVENTS

Final Report

October 1990

by

Daniel A. Scherson
Gary S. Chottiner

Case Center for Electrochemical Sciences
and the Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106-2099

for

Technology Base Research Project
Applied Science Division
Lawrence Berkeley Laboratory
Berkeley, California 94720

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Deputy Assistant Secretary for Utility Technologies, Office of Energy Management, Advanced Utility Concepts Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098, Subcontract No. 4550010 with the Lawrence Berkeley Laboratory.

TABLE OF CONTENTS

I.	INTRODUCTION.....	1
II.	EXPERIMENTAL METHODOLOGY	
	A. Assembly and Characterization of Lithium/Non-aqueous Solvent Passive Films Under Ultra High Vacuum Conditions.....	1
	B. Ultra High Vacuum-Fourier Transform Infrared Reflection Absorption Spectroscopy.....	3
III.	RESULTS AND DISCUSSION.....	5
	1. Ex-situ Spectroscopic Characterization of the Li-THF System....	5
	A. THF/Ag(111).....	5
	B. Li/Ag(111).....	6
	C. THF/Li/Ag(111).....	6
	a. Thermal Desorption Spectroscopy.....	6
	b. X-ray Photoelectron Spectroscopy.....	6
	2. UHV-FTIRRAS.....	8
	3. In-situ FTIRRAS.....	8
VI.	REFERENCES.....	9
VII.	FIGURE CAPTIONS.....	9

I. INTRODUCTION

The presence of a passive layer formed upon exposure of metallic lithium to various non-aqueous solvents is essential to the operation of lithium electrodes in battery applications.¹ Specifically,

- i) it provides a protective barrier that hinders the corrosion of the metal beneath and,
- ii) it serves as a medium for the conduction of Li^+ -ions.

Two main models have been described in the literature to account for the structure and properties of these passive films. The first is based on the formation of an inorganic surface layer in which the transport is described by solid electrolyte theory,² whereas the second assumes that the film has both a compact and porous layer with polymer-like characteristics.³

The main aim of this research is to elucidate the structure and composition of lithium-non-aqueous solvent passive films by using an array of ex-situ and in-situ spectroscopic techniques including Auger Electron and X-ray Photoelectron Spectroscopies (AES and XPS, respectively), temperature programmed desorption (TPD), and Fourier Transform Reflection Absorption Infrared Spectroscopy (FTIRRAS). Attention during this past year has been focused on the reaction of tetrahydrofuran (THF) with lithium.

II. EXPERIMENTAL METHODOLOGY

A. Assembly and Spectroscopic Characterization of Lithium-Non-Aqueous Solvent Passive Films in Ultra High Vacuum

Special techniques have been developed in this laboratory over the past few years for the adsorption of non-aqueous solvents on alkali metal films in ultra high vacuum (UHV). The steps involved in the preparation and characterization of these layers are summarized as follows:

- a) A host, non-reactive metal substrate, such as Ag(111), is cleaned in UHV by conventional Ar^+ -sputtering/thermal-annealing cycles and subsequently

placed in front of a thoroughly degassed lithium metal source (SAES Getters).

- b) The desired amount of lithium is then evaporated on the Ag(111) surface by controlling the current and time of operation of the source. To the level of sensitivity of AES and XPS (ca. 1%), clean lithium films of a thickness ranging from submonolayer up to several layers have been routinely obtained by this method.
- c) The lithium-non-aqueous solvent passive film is then assembled by adsorbing ultra purified solvents from the gas phase onto the freshly prepared lithium film. This is effected by backfilling the chamber to a certain partial pressure (e.g. $5 \cdot 10^{-8}$ torr) for a prescribed period of time so as to achieve the desired exposure. Alternatively, the gas may be dosed through a multi-capillary array directly onto the freshly prepared film. The latter approach is particularly advantageous as the total amount of solvent introduced into the chamber is only a fraction of that required with the backfilling method to attain the same exposure.
- d) The assembled passive film is moved in front of the analyzer for the acquisition of AES and XPS spectra, and subsequently in front of the mass spectrometer for TPD measurements. The use of isotopically labelled compounds in TPD is of great value as the identity of the various thermally desorbed fragments can, in many instances be unambiguously determined.

With the exception of TPD, all measurements were performed in a UHV system with AES, UPS, XPS, and LEED capabilities using a Ag(111) single crystal surface as the host substrate.

B. Ultra High Vacuum-Fourier Transform Infrared Reflection Absorption Spectroscopy (UHV-FTIRRAS)

A very similar technique to that described in the previous section has been implemented to obtain Fourier Transform Infrared Reflection Absorption (FTIRRAS) spectra of Li/THF films under UHV conditions. For these experiments, a separate UHV chamber consisting of two interconnected crosses which house all the necessary components involved in the assembly of the lithium-non-aqueous solvent passive films was designed and constructed. The chamber is evacuated by means of a conventional sorption-ion pump system. Two differentially pumped, Viton O-ring sealed, highly polished NaCl disks installed in opposite flanges of one of the crosses, serve as windows for the infrared radiation.

Metal films are vapor deposited from a Getters source onto a flat substrate that is covered partially by a quartz crystal microbalance. This permits measurement of the weight uptake during metal deposition and subsequent exposure of the films to the non-aqueous solvent. In this fashion, estimates can be made of the approximate thickness of the alkali metal deposits, assuming the film is uniform, and also of the stoichiometry of the reacted layer.

Gases are introduced into the chamber through a doser aimed directly at the surface of the quartz crystal. The gas doser, the electrical feedthroughs involved in the resistive heating of the Li, as well as a gold source (*vide infra*), and an observation port are attached via individual mini-flanges to one of the flanges in the cross. The evaporation-doser assembly is surrounded inside the chamber by a thin stainless steel shroud in the form of a truncated cone to restrict the area of deposition to that probed by the infrared beam (see Figure 1).

The sample substrate is attached to the end of a liquid He cryostat

mounted vertically on the cross. The temperature of the sample can be raised by resistively heating a nichrome-coated sapphire substrate mounted on one of the sides of the copper holder, and monitored with a Pt thermometer inserted into an orifice drilled in one of the sides of the copper holder. An additional quartz crystal has been attached to the back of the copper holder. This allows frequency (or period) measurements to be conducted in a differential mode, which increases the sensitivity in the weight determination by about two orders of magnitude. An additional port in one of the crosses is used to house an ionization gauge for pressure measurements.

The reflection-absorption optical attachment for FTIRRAS experiments consists of two gold-plated mirrors mounted on a stainless steel rail inside the UHV chamber, which redirect the IR beam into the detector chamber.

In a typical experiment, a thick layer of Au is evaporated onto the substrate and quartz crystal to cover the film formed during the prior run. Subsequently, a film of alkali metal is deposited onto the gold layer and an FTIRRAS spectrum (referred to as R_{ref}) is recorded. The gas of interest is then admitted into the chamber in an amount sufficient to form sub-, mono- or multilayers while monitoring the weight uptake with the quartz crystal microbalance, and a new spectrum denoted as R is recorded. The actual spectrum of the Li/gas film is obtained in the form of $\Delta R/R_{ref}$ where $\Delta R = R - R_{ref}$.

As evidenced by the results obtained, the sensitivity of the UHV-FTIR assembly is high enough to detect adsorbed species even at submonolayer coverages.

III. RESULTS AND DISCUSSION

1. Ex-situ Spectroscopic Characterization of the Li-THF System.

Before any measurements involving coadsorbed Li and THF were attempted, a series of experiments were conducted to establish the cleanliness of the Li deposits and to examine possible interactions between THF and bare, well-defined Ag(111) surfaces.

A. THF/Ag(111)

The XPS spectrum of THF adsorbed (and/or condensed) on bare Ag(111) at 130 K exhibits two C(1s) peaks at 286.6 and 285.4 eV (see A, Fig. 2) of approximately the same area, ascribed to carbons in the α and β positions (with respect to the oxygen), respectively, and an O(1s) peak at 533 eV, (see B, Fig. 2) which is characteristic of compounds containing ether-type ($\text{CH}_x\text{-O-CH}_x$) functionalities. These observations are in agreement with those expected from the stoichiometry and molecular structure of THF. No evidence for adsorption of THF on Ag(111) at room temperature could be obtained from either AES and XPS, indicating that the interactions between THF and silver are rather weak.

B. Li/Ag(111)

The XPS spectrum of 87% Li on Ag(111) deposited at room temperature (see A, Fig. 3) is characterized by one prominent peak at a binding energy of 54.71 eV. This value is lower than that reported in the literature for lithium in ionic compounds such as LiBr and may thus be attributed to Li in metallic form.

No carbon or oxygen could be detected by XPS for freshly prepared Li/Ag(111) surfaces. A number of additional peaks could be observed, however, upon exposure of a freshly prepared Li layer to background gases in the UHV chamber for 17 hours (see B, Fig. 3), which can most certainly be

attributed to interactions between residual gases and the lithium layer.

C. THF/Li/Ag(111)

a. Temperature Programmed Desorption

The cracking pattern of THF was found to display in addition to the parent peak at $m/e = 72$ a number of other features. An unambiguous assignment of these species was performed based on a comparison with similar data obtained for perdeuterated THF.

The TPD for $m/e = 27$ ($C_2H_2^+$), 29 (HCO^+) and 42 ($C_3H_6^+$) obtained upon exposing a Ag(111) surface covered by a layer equivalent to 60% Li by AES to 200-L THF is given in Fig. 4. In these experiments, the Li deposition as well as THF exposure were performed while the substrate was kept at 200 K. Marked differences in the relative ratios of the 27 (and 29) peaks with respect to the 42 peak were observed for the features centered at around 290 and 530 K. Although it is certain that these peaks correspond to the thermal decomposition of different chemical species, it is not possible to conclude, based on TPD alone, that the low-temperature peak corresponds to the desorption of intact THF. In fact evidence to the contrary to be presented later in this report has been obtained by XPS.

b. X-ray Photoelectron Spectroscopy

A spectral deconvolution of the C(1s) (see left panel Fig. 5) and O(1s) (see right panel in the same figure) XPS regions for a 87%Li/Ag(111) surface exposed to 1-L THF at ca. 200 K yielded peaks centered at 292.0, 289.0, 287.8 and 284.0 eV, for carbon and 535.0, 532.5 and 529.9 eV for oxygen (see B, Fig. 5). None of these features corresponds to condensed THF as evidenced by a comparison between these spectra and those of pure THF in A in the same figure. This indicates that Li profoundly affects the bonding and/or

reactivity of THF on the bare Ag(111) surface.

As indicated in C, Fig. 5, further exposure of this specimen to 100-L THF at the same temperature leads to the disappearance of the 292.0 eV peak and an increase in the relative areas of the 287.5 eV compared to the 289.0 eV peak. Also noteworthy is the appearance of prominent O(1s) peaks at 533.0 and 530.2 eV.

Similar C and O peaks, albeit with different relative areas, were observed upon subsequent exposure of the specimen to 300-L THF at the same temperature (see D, Fig. 5). One of the most surprising observations for this set of data is that, despite the fact that the temperature was low enough for THF to condense, no such species could be observed in the spectra even after the highest THF exposure. This is clearly evidenced by the lack of a C(1s) peak at 286 eV and suggests that the amount of Li on the surface was sufficient to react with all of the adsorbed and/or condensed THF.

An increase in the temperature to about 270 K leads to the disappearance of the small peak at 535.5 eV with no other significant spectral changes (see B, Fig 6). Drastic modifications could be observed, however, when the sample was heated to ca. 500 K, which corresponds to the onset temperature for the second peak in the TPD spectra. These are shown in C, Fig. 6. Particularly noticeable is the decrease in the relative areas of the high, compared to the low binding energy peaks both for carbon and oxygen. In fact both high binding energy peaks disappeared when the sample was heated to 870 K as indicated in D, Fig. 6, with the integrated area under the carbon peaks undergoing a large decrease. This is in agreement with the results from the TPD which indicate a much larger desorption of carbon- than oxygen-containing species. Also in support of this view is the decrease in the C/O ratio as the exposure to THF increased, which provided evidence that the layer becomes progressively richer in oxygen. In fact, a

more quantitative analysis of the absolute areas indicated that the amount of oxygen remains essentially the same as the temperature of the specimen is increased. This strongly suggests that the thermal decomposition gives rise to the formation of alkanes (or other carbon-hydrogen chain compounds) for which the desorption temperatures are very low.

Exposure of a Li layer on Ag(111) left in the UHV chamber for 17 h to THF yielded much more prominent C(1s) 284 eV and O(1s) 530 eV peaks than those obtained for the freshly exposed Li (see Fig. 7), indicating that the reactivity of the surface is modified by the presence of contaminants.

2. UHV-FTIRAS

Preliminary measurements involving the newly developed reflection-absorption mirror arrangement have yielded encouraging results. As a means of illustration, Fig. 8 shows the spectra obtained for less than ten monolayers of phenol red deposited on the surface of a copper substrate. The high quality of these spectra is evidenced by the fact that the signal-to-noise ratio for C-H stretching at 2900 cm^{-1} is greater than ten. Both mirrors and the sample holder have now been coated with a thick layer of electrodeposited gold, an approach that is expected to increase even further the overall sensitivity of the reflection absorption system.

3. In-situ FTIRAS

The construction of an in-situ FTIRAS cell for use with non-aqueous solvents has been completed. Unlike other cells developed in this laboratory, the new design enables complete isolation of the main compartment from the atmosphere. This is achieved by a Kalrez O-ring connected to the solid Kel-F plunger that holds the Kel-F cast electrode (see Fig. 9). In this fashion it will be possible to assemble the cell inside a Vacuum Atmosphere glove box and subsequently to transfer it through

air to the FTIR spectrometer without any danger of contamination with atmospheric gases. The optical performance of a cell developed for use with aqueous electrolytes of essentially identical geometry has enabled detection of changes in the oxidation state of submonolayer coverages of irreversibly adsorbed species.⁵

It is expected that a continuation of these efforts will result in a much better understanding of the nature of the passive film on lithium in non-aqueous electrolytes and from which insight will be gained into the factors that control the rechargeability and shelf-life of actual lithium-based devices.

VI. REFERENCES

1. For a series of articles on lithium electrodes see: "Lithium Batteries", J. P. Gabano, Ed., Academic Press, New York (1983).
2. D. Aurbach, M. L. Daroux, P. W. Faguy and E. Yeager, J. Electrochem. Soc., 135, 1863 (1988), and references therein.
3. E. Peled, J. Electrochem. Soc., 126, 357 (1981).
4. J. Thevenin and R. Muller, J. Electrochem. Soc., 134, 273 (1987).
5. T. Sasaki, I. T. Bae, D. Scherson, B. Bravo and M. Soriaga, Langmuir, 6, 1234 (1990).

VII. FIGURE CAPTIONS

Fig. 1. Schematic diagram of the UHV chamber for FTIRRAS measurements.

Fig. 2. C(1s) and O(1s) XPS spectra of THF condensed on bare Ag(111) at 130 K.

Fig. 3. XPS spectra of 87 % Li (ca. 12 monolayers) before (A) and after (B) exposure to background gases in the UHV chamber for 17 h.

Fig. 4. Temperature Programmed Desorption TPD, spectra of A. m/e = 27, B. m/e = 29 and C. m/e = 42 for 60%Li/Ag(111) (by AES) exposed to 200-L THF at 260 K.

Fig. 5. C(1s) (left panel) and O(1s) (right panel) XPS spectra of freshly deposited 87%Li/Ag(111) at 200 K exposed to B. 1-L THF, C. 100-L THF and D. 300-L THF. The corresponding spectra of condensed THF in the

absence of Li (see caption Fig. 2 above) are shown in A.

Fig. 6. C(1s) (left panel) and O(1s) (right panel) XPS spectra of freshly deposited $87\%Li/Ag(111)$ exposed to 300-L THF at A. 200K, B. 270K, C. 500K and D. 870 K. The results in A are the same as those given in D. Fig 5.

Fig. 7. C(1s) and O(1s) XPS spectra of freshly deposited $87\%Li/Ag(111)$ which had been exposed to background gases in the chamber for 17 h before exposure to 300-L THF.

Fig. 8. FTIRRAS spectra of about 10 monolayers of phenol red dispersed on the surface of a copper substrate before (lower curve) and after smoothing (upper curve).

Fig. 9. Schematic diagram of the in situ electrochemical cell for FTIRRAS studies involving non-aqueous solvents.

UHV-FTIR CHAMBER
(TOP VIEW)

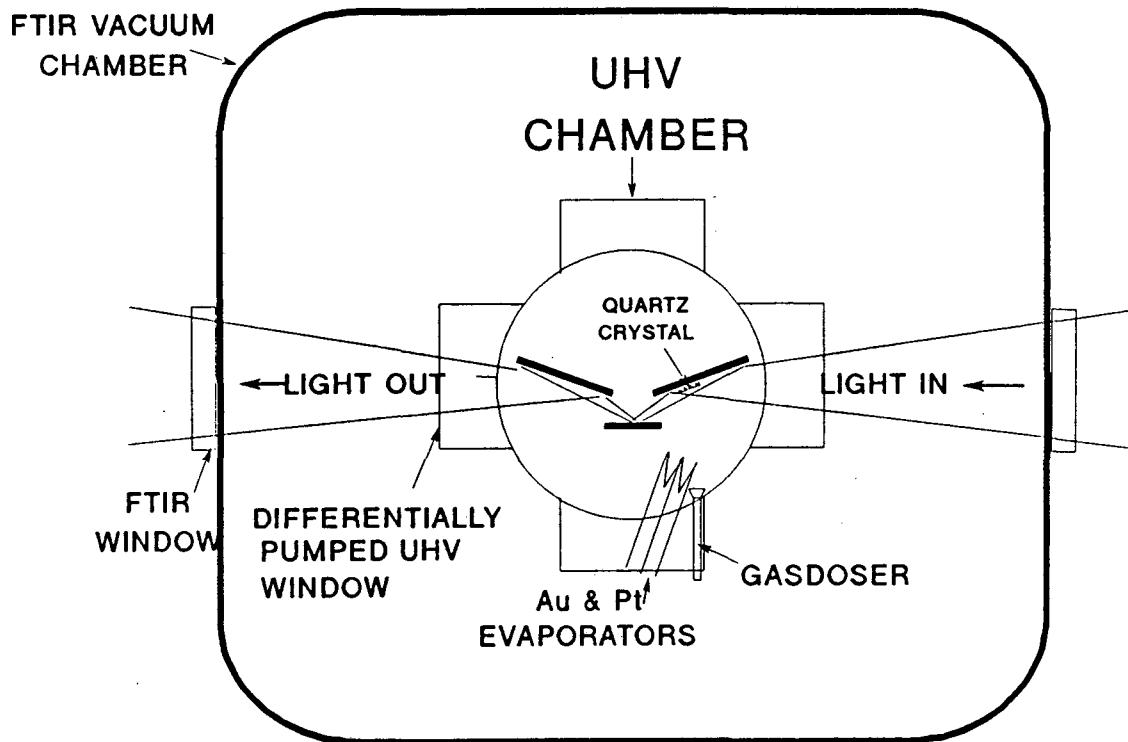


FIGURE 1

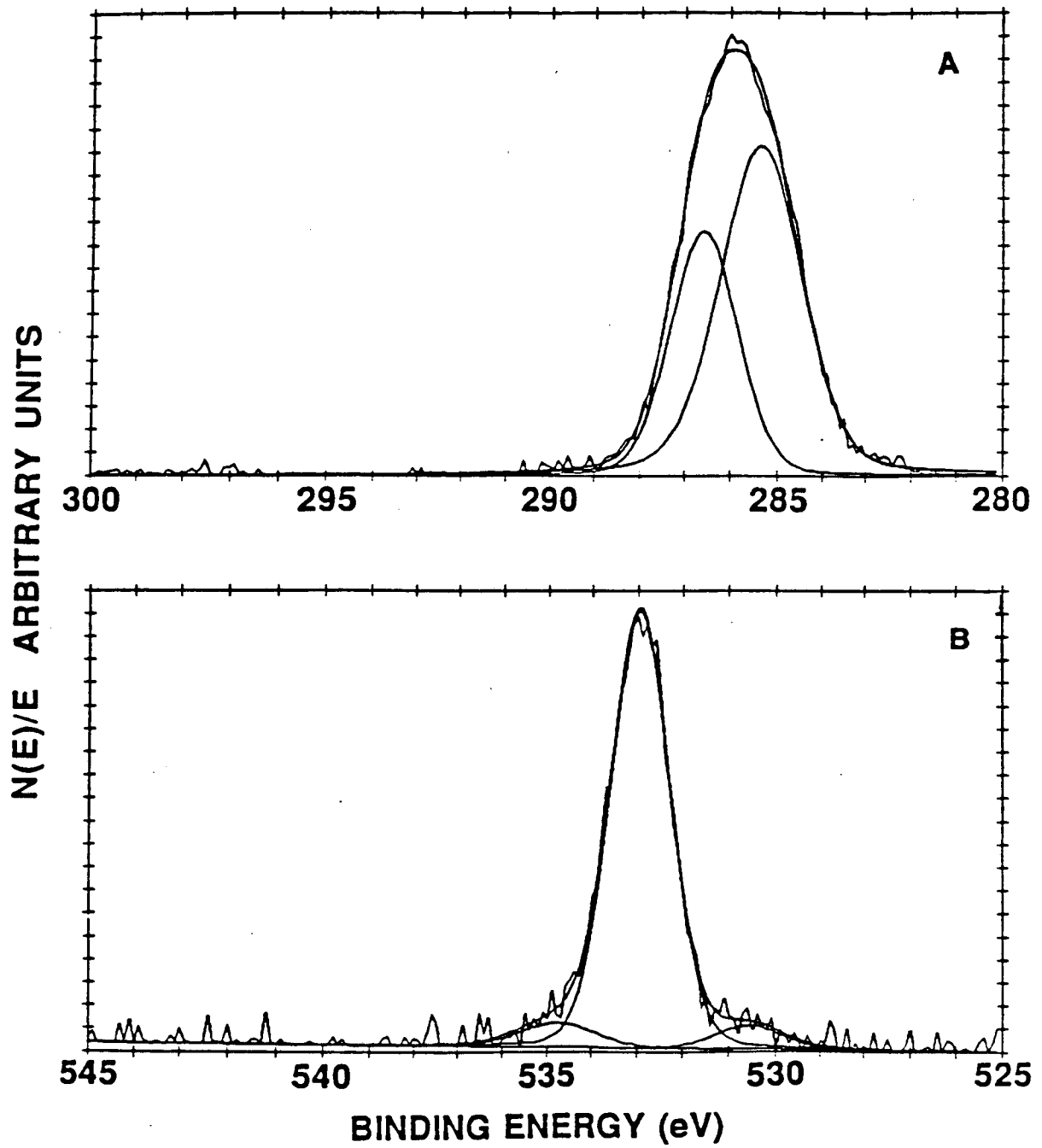


FIGURE 2

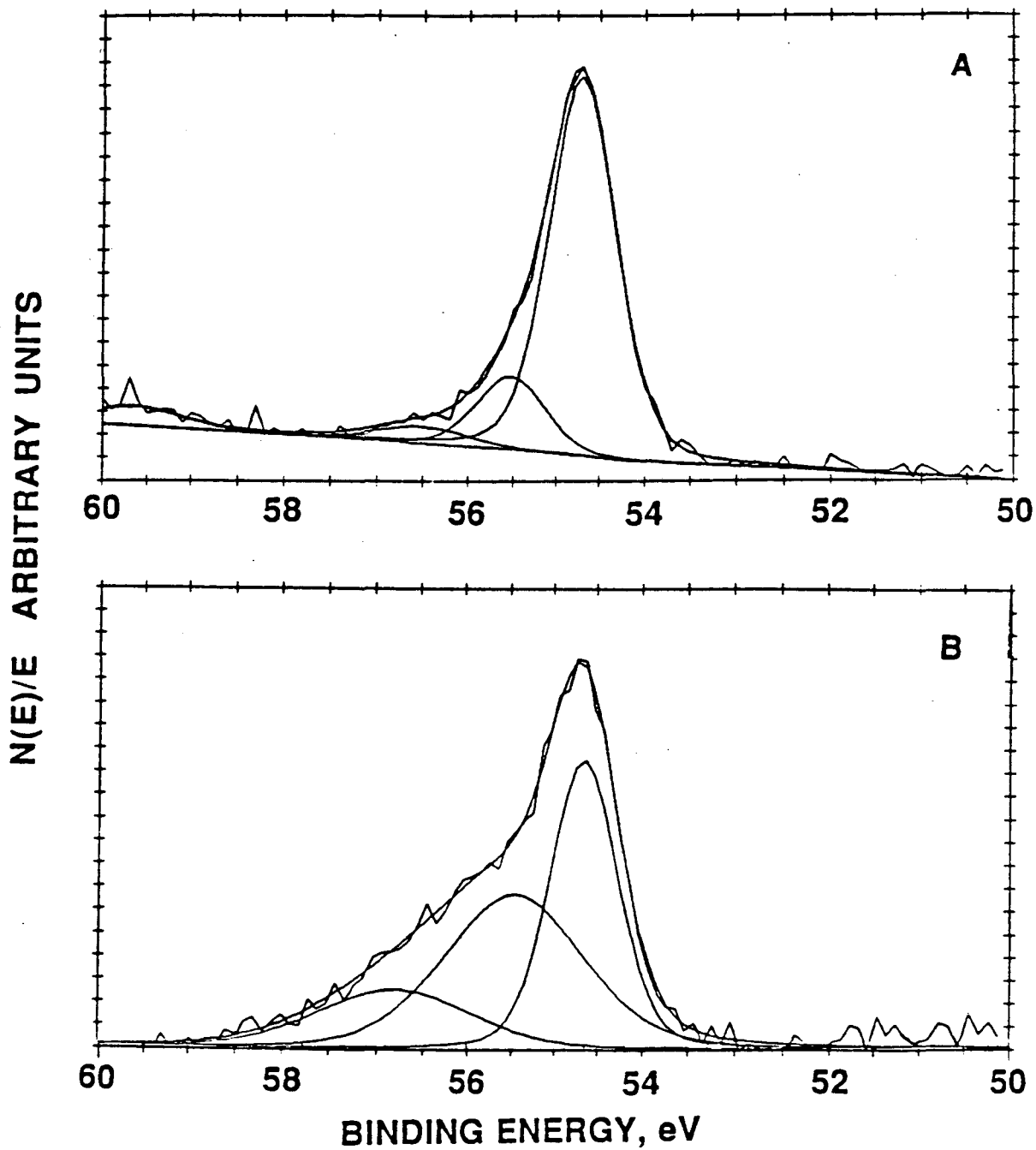


FIGURE 3

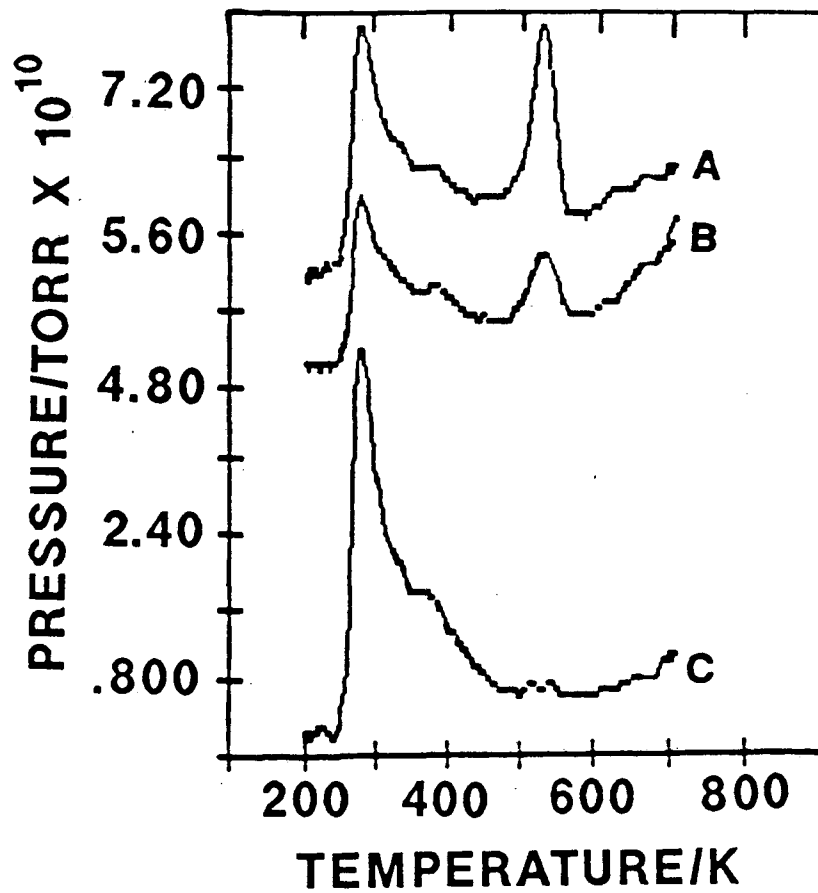


FIGURE 4

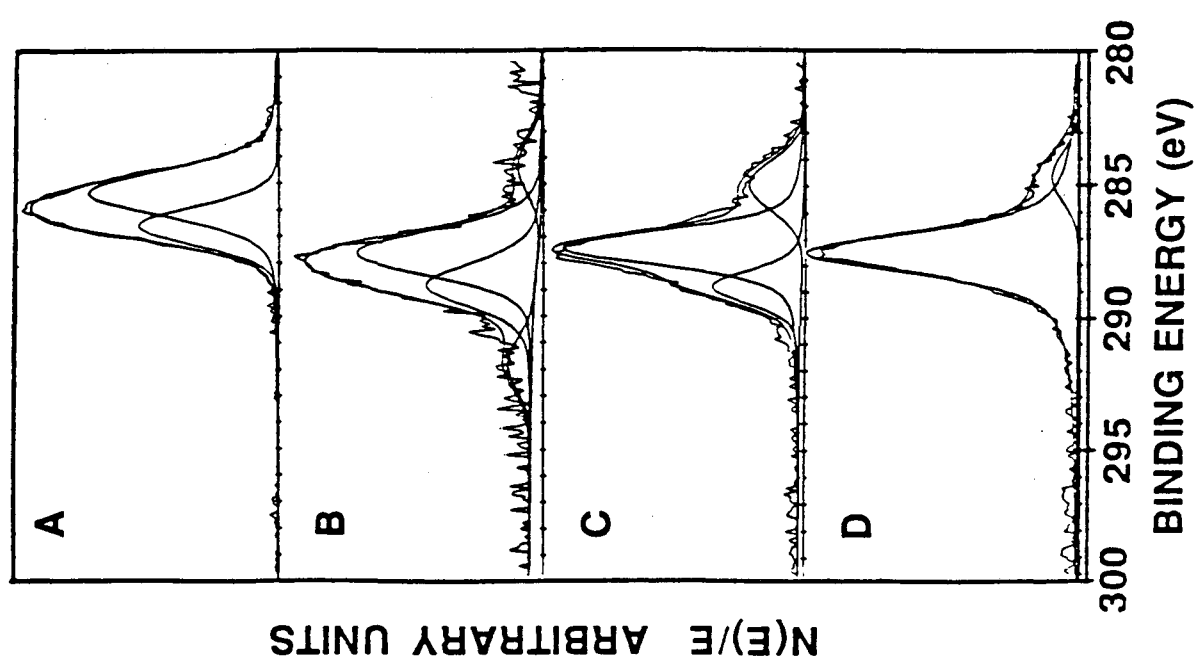
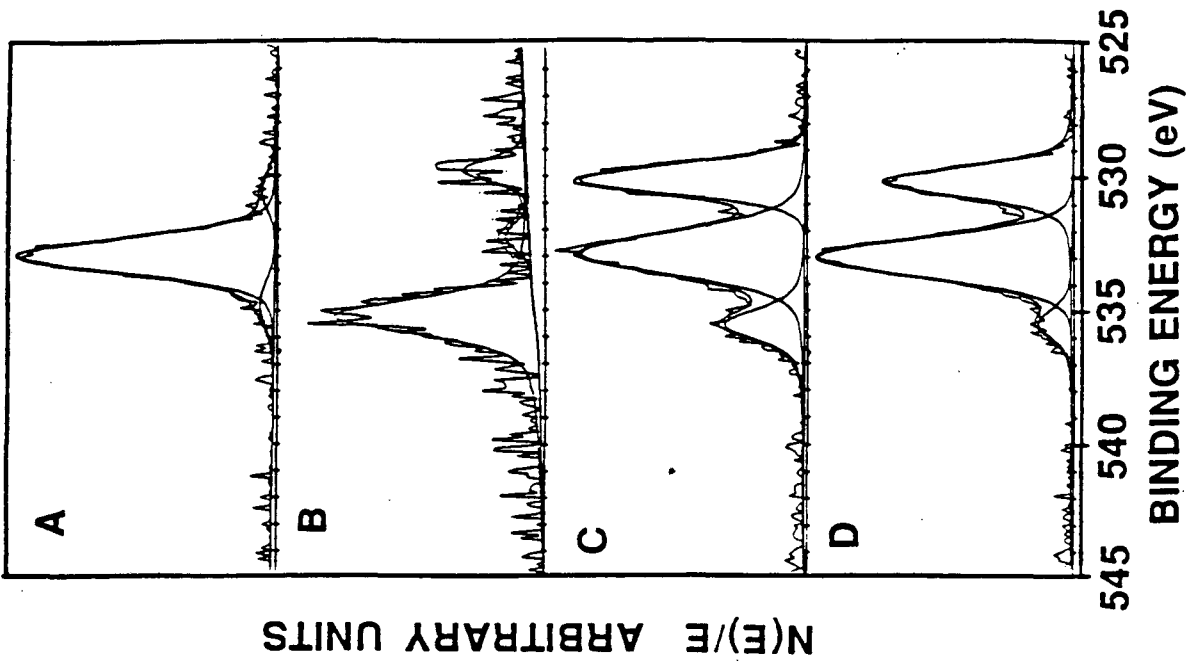


FIGURE 5

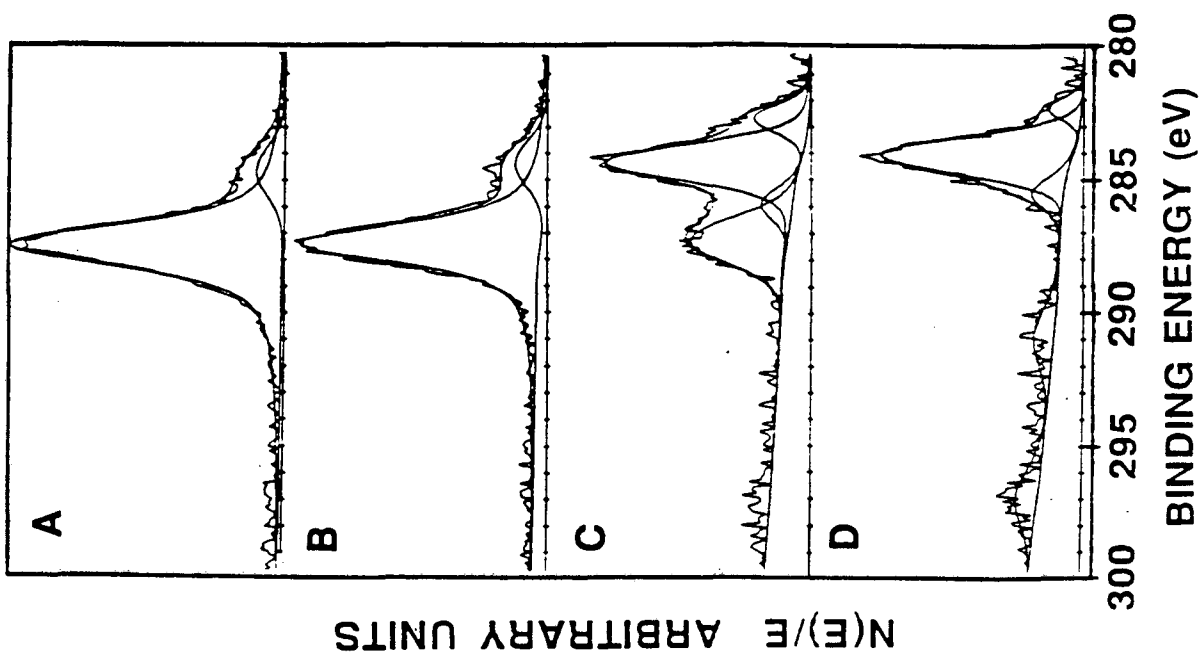
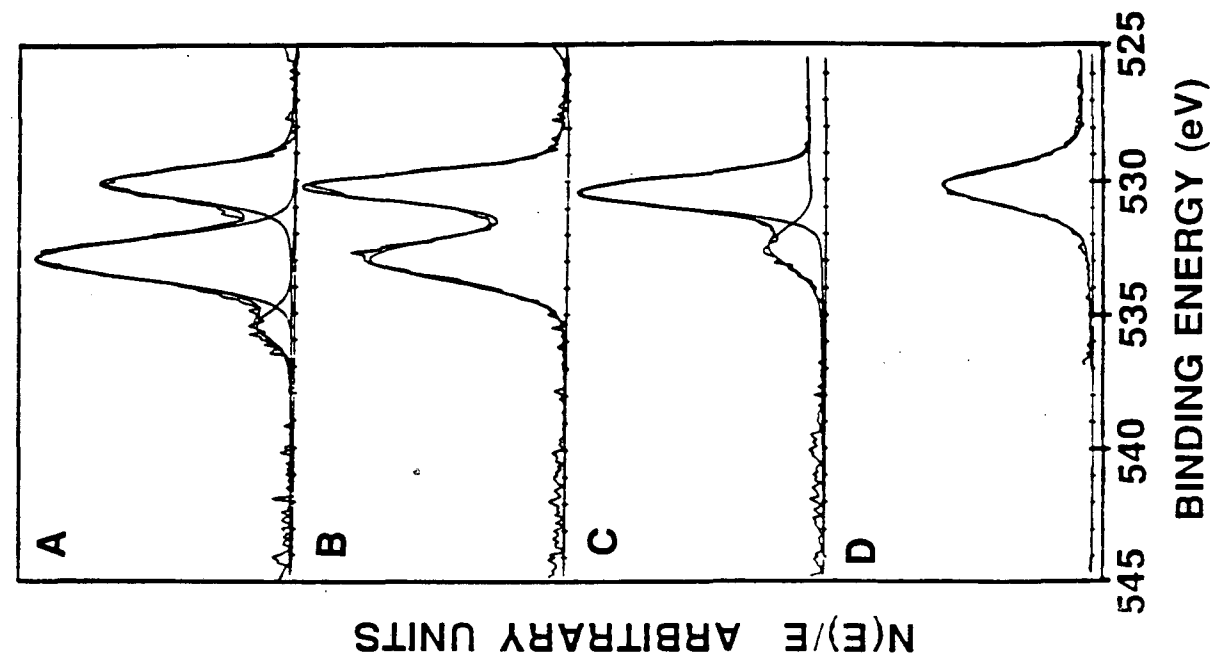


FIGURE 6

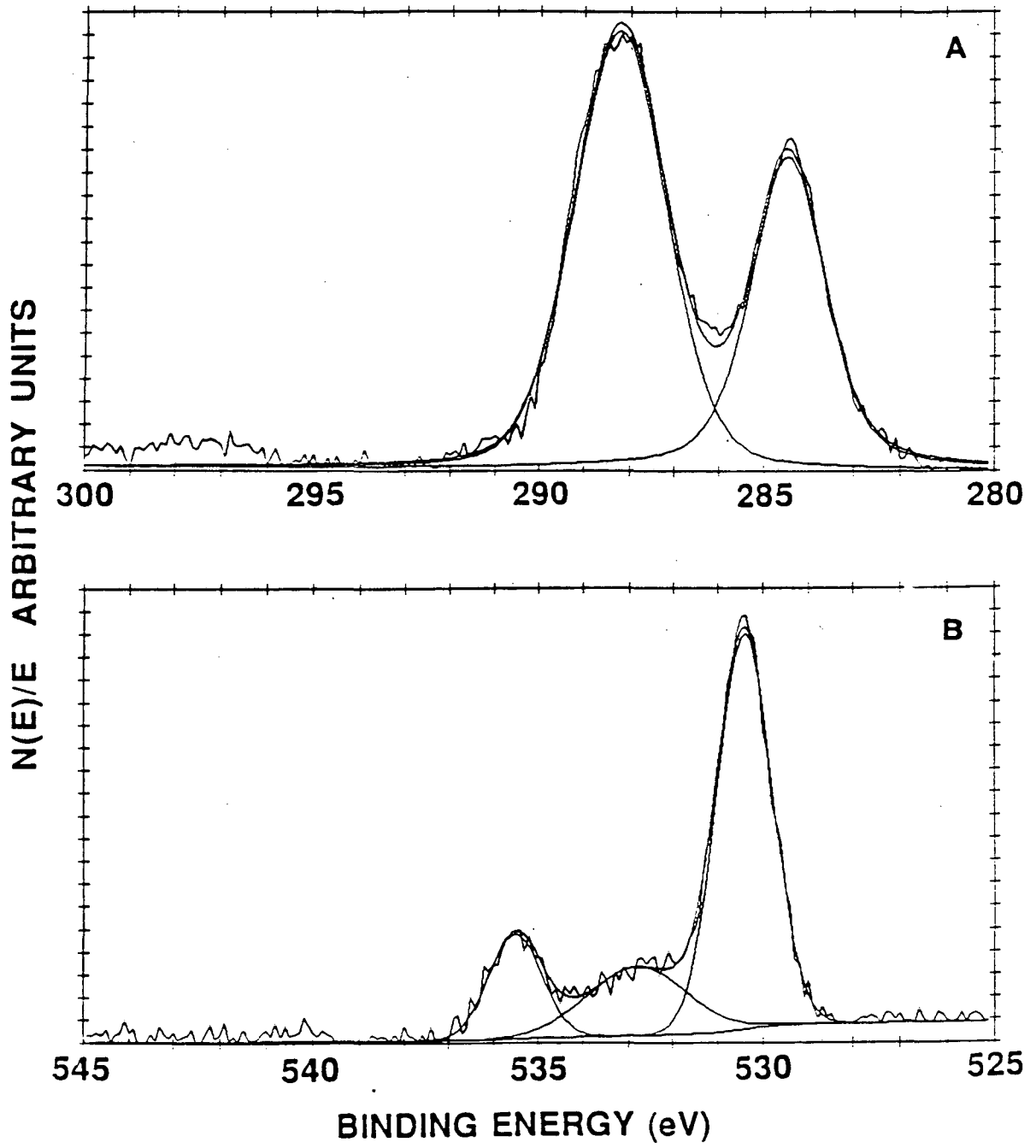


FIGURE 7

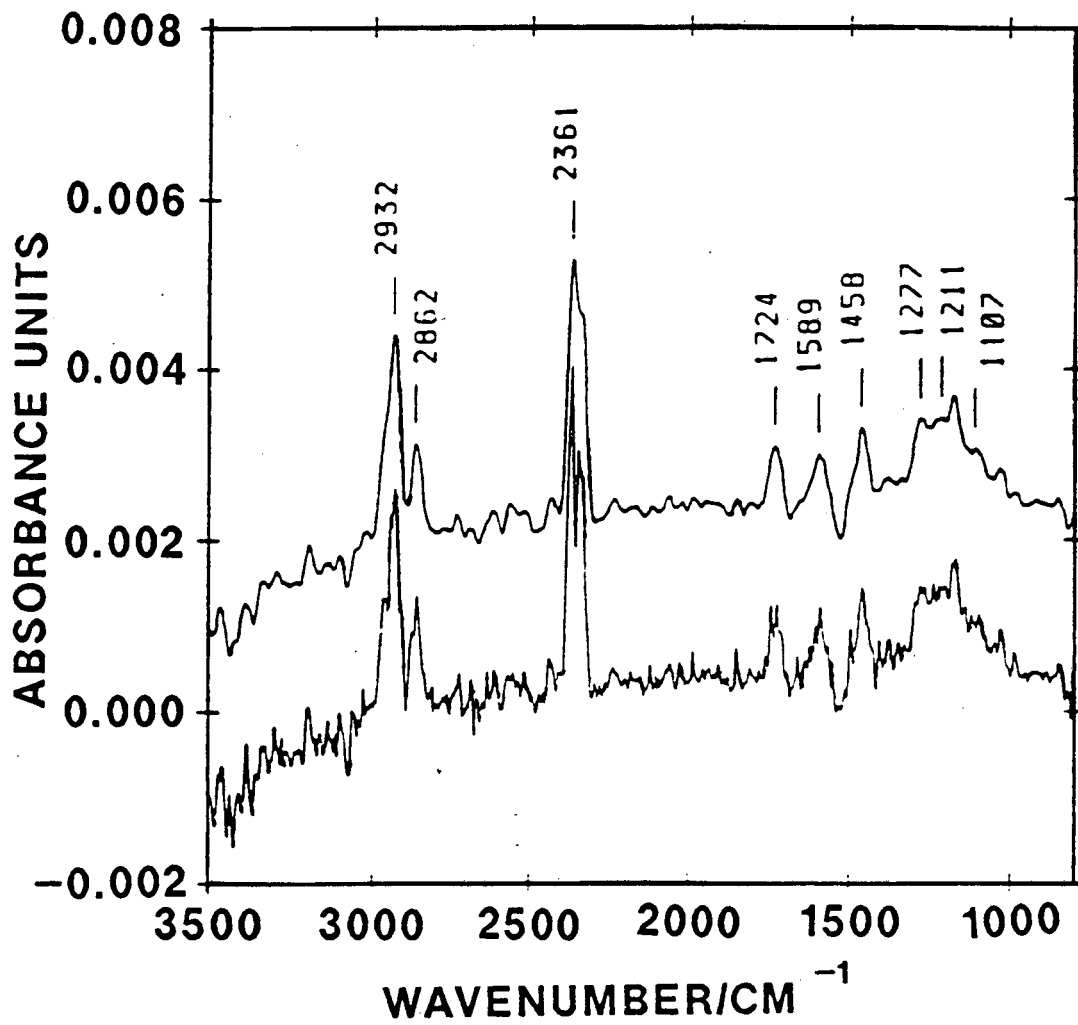


FIGURE 8

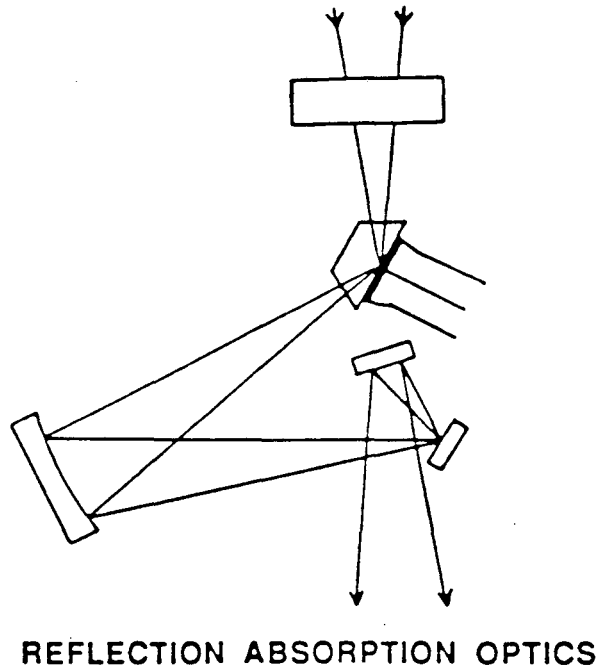
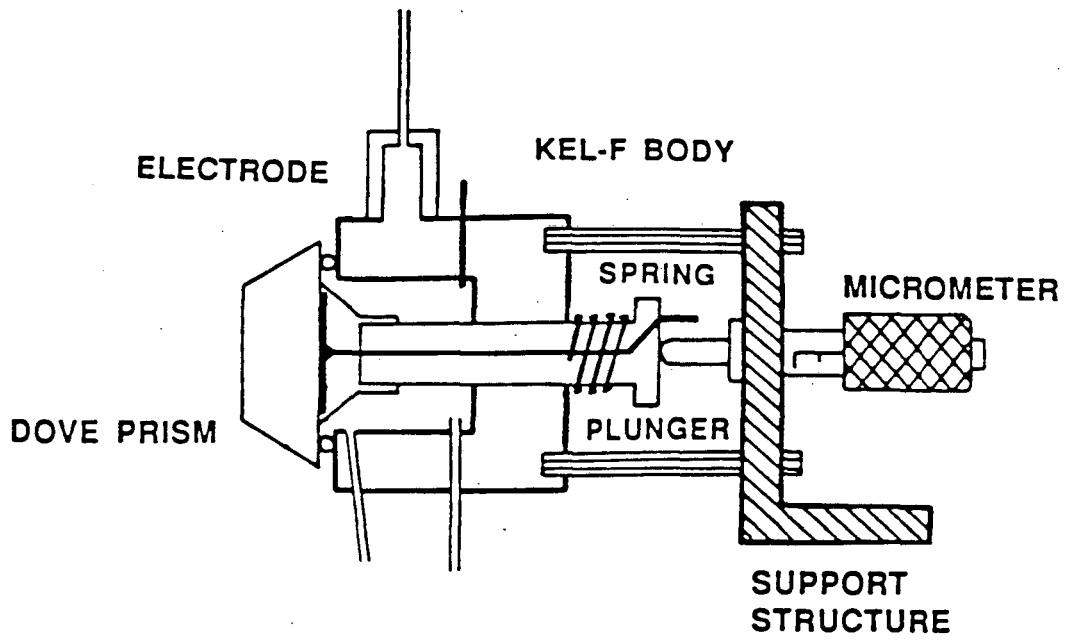


FIGURE 9

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720