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**CHEMICAL BONDING INFORMATION FROM  
PHOTOELECTRON SPECTROSCOPY**

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Chemical Bonding Information from Photoelectron Spectroscopy

Techniques of general applicability are demonstrated on iodine and europium compounds.

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## Introduction

A major source of our information about atoms, molecules, and solids comes from the study of spectra, whether they be of emitted or absorbed electromagnetic radiation or of particles such as electrons. After new spectroscopic techniques have been introduced they have generally been refined to the point of being sensitive to the chemical environment of a given atom. In this way a good deal of information has been obtained about the nature of chemical bonding.

In recent years, a new spectroscopic tool has been added to the repertoire, that of photoelectron spectroscopy (1). This technique also has been shown to be sensitive to chemical effects and considerable work has already been done on investigations of this type by K. Siegbahn and co-workers in Uppsala (2). The principle of the technique is to deduce the binding energies of the inner core electrons of an atom from very accurate measurements of X-ray produced photoelectron spectra. The precision of these measurements is sufficient to allow detection of shifts of the order of 1 eV in these binding energies. Since shifts due to changes in the chemical environment have been found to be several eV in some cases (2), they are easily detected. The versatility of the method arises from the fact that the core levels of virtually all atoms can be investigated. By contrast, most other spectroscopic methods are restricted to particular types of quantum mechanical systems or are governed by more restrictive selection rules. For example, nuclear magnetic resonance requires a reasonably abundant

isotope with a nuclear magnetic moment, and for work at highest resolution a nuclear spin of  $1/2$  is requisite. The Mössbauer effect, although exquisitely sensitive, is restricted to nuclei with an appropriate gamma ray transition. Unfortunately, no such nuclei are available for  $Z < 19$  nor are they uniformly distributed over the periodic table. The photoelectron method has an additional advantage for the interpretation of results. That is, the core level shifts can be related directly to the principal forces operating in atoms, molecules and solids--namely, those due to the Coulomb and exchange interactions.

In this paper we report some observations on the chemical shifts of core electron binding energies in iodine and europium compounds and indicate that these shifts may be explained in terms of two approximate theoretical models. Finally, we discuss briefly a few of the potential applications of this spectroscopic method to problems in coordination chemistry, biochemistry, and solid state physics.

Because previous chemical shift measurements have been made on the relatively light elements, carbon, nitrogen, sulfur and chlorine (2), a study of the chemical shifts for heavier atoms is of interest. In addition, the transition elements and rare earths possess unfilled inner d and f shells respectively. These inner electrons can participate in chemical bonding, in contrast with other elements in which it is predominantly outer valence shell electrons that serve this role. The selection of iodine ( $Z = 53$ ) and europium ( $Z = 63$ )

for investigation permits a comparison of these two classes of elements, as the neutral atom valence electron configurations are  $5s^25p^5$  and  $4f^76s^2$ , respectively. Chemical shifts were studied in iodine for nine core levels (out of a possible 13). The four iodine compounds selected for study span a range of 8 in oxidation number. Three core levels were studied in europium in both divalent and trivalent compounds.

### Experimental Procedure

The experimental technique involves expelling an electron from some inner level,  $i$ , with x-radiation of energy well above the photoelectric threshold. Neglecting contact potential effects, the x-ray energy  $h\nu$  is divided according to

$$h\nu = E_b(i, \underline{X}) + E_{kin} \quad (1)$$

where  $E_b(i, \underline{X})$  is the binding energy of the  $i$ -th level of an atom in compound  $\underline{X}$  and  $E_{kin}$  is the photoelectron kinetic energy. Since x-ray energies are known to high accuracy, only the kinetic energy need be measured to obtain a binding energy. For this purpose a double-focusing magnetic spectrometer was used (3). The energy resolution of this spectrometer was adjusted to be 0.06% full width at half maximum, thereby yielding instrumental line widths of 0.6 eV to 4.8 eV over the kinetic energy range of interest (1 to 8 keV). As the natural line widths are also a few eV, it is easily possible to detect shifts in binding energy of the order of one eV with such a spectrometer.

The apparatus used in this investigation is shown schematically in Figure 1. Radiation from the x-ray tube is filtered slightly with aluminum foil and then impinges upon a thin rectangular (10 mm x 13 mm) powdered sample of the compound under study. Photoelectrons emitted from the sample pass through a narrow slit (0.5 mm x 10 mm) into the spectrometer. For a given current in the spectrometer coils, electrons of a narrow energy range are brought to a focus at the entrance to the Geiger counter. The current is scanned in a stepwise fashion over the region of interest and the resulting pulses from the Geiger counter stored in a multiscaler (multichannel analyzer). Multiple scans were made in order to average out variations in x-ray flux. Although the radiation from an x-ray tube is not monochromatic, the characteristic x-ray lines interact with the core electron levels to give photoelectron peaks that are easily distinguishable above the background.

### Results

Typical photoelectron peaks are shown in Figure 2. The notation  $I2p_{3/2} (CuK\alpha_1)KI$  indicates a peak due to photoelectrons expelled from the  $2p_{3/2}$  level of iodine in KI by the  $K\alpha_1$  x-ray line of Cu. A chemical shift of about 6 eV is apparent between the peaks from KI and  $KIO_4$ . In iodine such shifts were measured for 9 levels from  $2S_{1/2}$  ( $E_b \approx 5191$  eV) to  $4d_{5/2}$  ( $E_b \approx 54$  eV). The compounds studied were KI (-1 oxidation number),  $KIO_3$  (+5),  $KIO_4$  (+7) and the potassium salt of p-iodobenzoic acid--[KIBA] (?). The shifts are essentially the same for all measured

levels in spite of the hundred-fold change in binding energy. This observation agrees well with theory, as we discuss below. It is thus possible to speak of an average core shift between compounds. These shifts, relative to KI, are: KIBA - 0.0 eV,  $\text{KIO}_3$  - 5.3 eV, and  $\text{KIO}_4$  - 6.3 eV. The shifts are all in the direction predicted by a simple shielding model--that is, electrons are bound more tightly in compounds of higher oxidation number. Thus the shift is approximately 0.8 eV per unit change in oxidation number.

Similar shifts were measured for the  $3d_{3/2}$  ( $E_b \approx 1158$  eV),  $3d_{5/2}$  ( $E_b \approx 1128$  eV), and  $4p_{3/2}$  ( $E_b \approx 258$  eV) levels in europium. The compounds studied were  $\text{EuAl}_2$  (+2),  $\text{EuO}$  (+2) and  $\text{Eu}_2\text{O}_3$  (+3). The shifts in this case were again very nearly the same for the three levels, and the binding energies for the two +2 compounds agreed to within experimental error ( $\pm 0.5$  eV). The average shift in Eu for this unit change in oxidation number is 9.6 eV, and it is again in the direction predicted by the simple shielding model. Note that this is 12 times larger than the corresponding figure for iodine. Figure 3 gives an illustration of the rather striking chemical shift which results from the oxidation of europium metal. Spectrum 3a was obtained from  $\text{EuAl}_2$ , which apparently had oxidized slightly to the +3 state on the surface. The peak arising from electrons in +2 ions is still clearly visible, however. Spectra 3b and 3c were obtained from a piece of europium metal which was initially polished in air to give a shiny surface. This surface oxidized immediately to a mixture of the +2 state ( $\text{EuO}$ ) and the +3 state ( $\text{Eu}_2\text{O}_3$ ), as can be seen by comparing the Spectra 3a and 3b. Upon prolonged

exposure to air, the same sample oxidized completely to the +3 state ( $\text{Eu}_2\text{O}_3$ ) as can be seen by comparing Spectra 3c and 3d. The spectral intensity does not decrease to background level on the left side of the peaks, principally because of the close proximity of the peak arising from the  $K\alpha_2$  x-ray line, which is 20 eV lower in energy than  $K\alpha_1$  for copper. The interpretation in terms of chemical reaction is nevertheless straightforward.

### Theory and Interpretation

In order to extract useful information about chemical bonding from chemical shift data, some theoretical model must be considered. We present here two such models. Both are partly classical (and therefore approximate), but the first gives some essential insights into the nature of core electron chemical shifts as well as semi-quantitative estimates of their magnitude, and the second should be able to predict such shifts with reasonably good accuracy for solids with long range order. A detailed description of these models will soon be published elsewhere (4), so we indicate here only their salient features and the results of their application to our iodine and europium data.

The first model is constructed by assuming that all electronic charge participating in chemical bonding is removed from the valence shell (a quantum state) and subsequently becomes a spherical shell of charge of some radius  $r$  centered on the atom of interest (a classical state). The radius  $r$  will be larger than the average radius of the valence shell, as the sphere must somehow approximate the molecular electron orbitals that exist between the central atom and its nearest

neighbors. The net energy shift of a core level upon forming a chemical bond can thus be calculated in two steps, the first representing the decrease in shielding when valence electrons are removed to infinity, the second representing the repulsive potential of the spherical shell of charge outside the core electrons. The first quantity can be calculated with existing free-ion (atom) computer programs, and for this calculation we have used such a program written by Roothaan and Bagus (5). The second quantity is obtained from elementary electrostatics. This model was applied to our europium data as a qualitative check of its validity. We assume to a first approximation that only the 4f subshell of europium is altered in going from  $\text{EuAl}_2$  to  $\text{Eu}_2\text{O}_3$ . It is known that the 4f configurations in these compounds are  $4f^7$  and  $4f^6$ , respectively (6)(7). From our calculations, the free-ion shift between  $\text{Eu}^{+2}(4f^7)$  and  $\text{Eu}^{+3}(4f^6)$  is approximately 20 eV. Thus a 10 eV repulsive correction is required to give the experimental value we have observed. This corresponds to a spherical shell radius of approximately 1.3 Å, which is approximately half the Eu-O interatomic distance in  $\text{Eu}_2\text{O}_3$ . The model thus correctly predicts that the bonding charge is located at a position intermediate between the Eu and O atoms.

The second model is a generalized and slightly modified version of one used previously to predict valence electron binding energies in the alkali halides (8). Suppose we are interested in the binding energy of the  $i^{\text{th}}$  core level of atom A in the solid compound  $\underline{X}$  ( $E_b(i, \underline{X})$ ). Atom A is assumed to possess some net charge  $Z_x$ , and all other atoms in the compound are given net charges also, the only restriction being overall electroneutrality. For strictly ionic solids all charges are assumed to be integral numbers, but for solids with some covalent character the charges can be used as variable parameters. The binding energy can

now be calculated by means of the following energy cycle: The first step is to remove A from the lattice to form the free ion  $A^{Z_X}$ . The energy required is denoted by  $E_1$ . Next an electron is removed from the  $i^{\text{th}}$  level of this ion. The energy required is the binding energy of an  $i^{\text{th}}$  level electron in a free ion of charge  $Z_X$  ( $E_b(i, Z_X)$ ). Then the ion  $A^{Z_X+1}$  is inserted back into the lattice. The energy is denoted  $E_2$ . Since the net result of this cycle is the same as that of a photoelectric process (subtracting any kinetic energy), the experimental binding energy in the solid should be given by  $E_1 + E_b(i, Z_X) + E_2$ . To obtain the chemical shift in binding energy between two compounds  $X$  and  $Y$ , we simply take a difference and find

$$\begin{aligned} \Delta E_b(i, X-Y) &= E_b(i, X) - E_b(i, Y) \\ &= E_b(i, Z_X) - E_b(i, Z_Y) \\ &+ (E_1 + E_2)_X - (E_1 + E_2)_Y \end{aligned} \quad (2)$$

The necessary free-ion binding energies can be calculated with the aforementioned computer program. The sums,  $E_1 + E_2$ , represent the classical Coulomb interaction energy of an electron in the ion of interest with all the other ions in the lattice, which are treated as point charges. This is true provided we neglect lattice distortion and electron-cloud polarization during the photoelectric process. This classical Coulomb energy is related to the Madelung constant of the solid and for certain simple lattice structures can be derived from this constant. For solids of more complex structure this "Madelung energy" is more complicated to evaluate, although by no means impossible.

As a rough estimate of its magnitude the Madelung energy for alkali halides ranges from 5 - 10 eV. This is to be compared with free-ion core shifts upon removing a valence electron, which are roughly 10 eV for iodine and 20 eV for europium. We also note that because the photoelectrons of interest are expelled from a shallow region near the surface, the full Madelung energy may not be required in equation 2. Further experimental investigation is needed to evaluate this surface correction accurately, however.

A consideration of equation 2 explains why all the core levels in iodine and those measured in europium are shifted by very nearly the same amount. Note that the Madelung energies do not vary with  $i$ , so that any differences in the shifts of various core levels must be due solely to the free-ion terms in equation 2. Table 1 gives the results of our free-ion calculations on iodine, and it is apparent that over a broad charge range all core levels shift by the same amount to within  $\pm 2\%$ . Similar calculations indicate the same pattern for europium, but to a lesser degree, as the 4f shell penetrates much more deeply into the atom than the 5p shell. In fact, free-ion calculations on europium indicate up to a 50% variation in shifts between inner and outer core levels. This points out a potentiality of the photoelectron spectroscopic method, in that it may be possible to determine which electrons enter into chemical bonding by means of the relative shifts of various core electron binding energies.

Calculations of the Madelung energy were made for the three inorganic iodine compounds in such a way that the chemical shifts relative to KI were obtained as a function of the charge on the iodine

atom in  $\text{KIO}_3$  and  $\text{KIO}_4$ . By simply matching the observed shifts to the appropriate charge values, it is thus possible to estimate, for both compounds, the iodine charge and a corresponding fractional ionic character of the I-O bond. These are shown in Table 2, along with analogous results obtained from Mössbauer measurements (9). The use of 75% of the full Madelung values represents a surface correction corresponding to a photoelectron-producing layer approximately as thick as the length required for convergence of a Madelung sum over lattice sites.

The agreement between the two sets of values is satisfactory in the sense that Madelung corrections in the allowable range can bring our derived values into agreement with the Mössbauer results. With more accurate calculations of the Madelung energy and more sophisticated data treatment involving all the atoms in the compounds under consideration, it should be possible to obtain values of charge and ionic character with much better accuracy. We also note that our results have been obtained without any detailed assumptions as to the bonding orbitals involved in each compound, whereas the Mössbauer results rely heavily on such assumptions. There is thus a possibility in the photoelectron spectroscopic technique of inferring the orbital makeup directly, instead of assuming it in order to calculate some other property.

The fact that the shift per unit change in oxidation number is 12 times larger in europium than in iodine can be qualitatively understood. As has been stated, the free-ion shift for a given change in charge is about twice as large for europium. Also, the actual charge that is being moved into bonding orbitals is much greater between  $\text{Eu}^{+2}$  and  $\text{Eu}^{+3}$  than it is between, e.g.,  $\text{I}^{-1}$  and  $\text{I}^0$ . As we have mentioned, one 4f electron is transferred between  $\text{EuAl}_2$  and  $\text{Eu}_2\text{O}_3$

( $4f^7$  to  $4f^6$ ). However, the results of Table 2 indicate that for a similar unit change in the oxidation number of iodine less than 0.5 electrons are transferred.

Our experimental results for the potassium salt of p-iodobenzoic acid are presented largely to indicate the feasibility of making measurements on heavy atoms as constituents in organic compounds. Since iodine is bonded only to carbon in this molecule and the two atoms have equal electronegativities, it is not surprising that the binding energies are close to those of KI rather than to those of  $KIO_3$  or  $KIO_4$ .

#### Further Applications of the Technique

The theoretical interpretation of the chemical shifts reported here and the observations of the chemical shifts in carbon, nitrogen, sulfur, and chlorine reported by the Uppsala group provide a firm basis for anticipating a wide range of applications of this spectroscopic method. We illustrate this potential by describing three problems of current interest in this laboratory.

A number of investigators are focusing attention on a class of non-heme iron proteins, called Ferredoxins (10), which act as electron transport proteins in both photosynthesis and bacterial metabolism. The common characteristic of these proteins is their content of from two to seven iron atoms together with four sulfur atoms per iron. The photoelectron spectra will be examined in order to measure the nature and diversity of the iron and sulfur atoms contained in these proteins both before and after reduction.

It is also planned to study the coordination chemistry of metal porphyrins by examining the photoelectron spectra of the central metal ion and the nitrogen ligands. Comparison and interpretation of the spectra in the presence of and absence of the metal ion should permit a determination of the fractional contribution to the bonds of each of the constituents of the complex. In fact, the valence electronic levels have already been examined by low energy photoelectron spectroscopy in a closely related compound, copper phthalocyanine (11).

The fractional charge or degree of ionization of impurity atoms in elemental semiconductors, as well as the relative charges on the atoms in compound semiconductors of the III-V and II-VI types, could also be investigated.

#### Summary

The technique of photoelectron spectroscopy has already been shown to be sensitive to changes in the chemical environment of a given atom. We have used this technique to measure shifts in the core electron binding energies of iodine and europium. We have found shifts of 0.8 eV and 9.6 eV respectively for a unit change in oxidation number.

Two theoretical models are proposed for the interpretation of these shifts and are applied to the analysis of our experimental results. The first consists of a charged shell approximation for the molecular orbitals. The second uses an energy cycle to divide the binding energy into a free-ion term and a lattice interaction (Madelung) term. All our observations can be understood in terms of one or the other of these models, and in particular, we can estimate the iodine charge in the

Table 1. Calculated binding energy shifts arising from removal of a 5p electron from various free-ion configurations of iodine. Since the calculations were non-relativistic, levels are not distinguished by the quantum number  $j$ , and the notation 2p, for example, represents both  $2p_{1/2}$  and  $2p_{3/2}$ .

	I-1 $5s^2 5p^6$	I <sup>0</sup> $5s^2 5p^5$	I+1 $5s^2 5p^4$	I+2 $5s^2 5p^3$	I+3 $5s^2 5p^2$	I+4 $5s^2 5p^1$
Level i	$\Delta E_b(i, 0-[-1])$ (eV)	$\Delta E_b(i, 1-0)$ (eV)	$\Delta E_b(i, 2-1)$ (eV)	$\Delta E_b(i, 3-2)$ (eV)	$\Delta E_b(i, 4-3)$ (eV)	
2s	8.80	9.90	10.93	12.23	13.14	
2p	8.79	9.87	10.93	12.19	13.16	
3s	8.83	9.89	10.91	12.15	13.04	
3p	8.79	9.87	10.89	12.12	13.01	
3d	8.78	9.87	10.89	12.15	13.06	
4s	8.85	9.87	10.82	11.97	12.78	
4p	8.84	9.86	10.79	11.92	12.73	
4d	8.84	9.85	10.78	11.92	12.72	
5s	8.10	8.65	9.22	9.77	10.21	
5p	8.39	9.37	10.73	9.44	9.90	

Table 2. Comparison of our results for iodine charge and fractional ionic character in  $\text{KIO}_3$  and  $\text{KIO}_4$ , with those obtained from Mössbauer measurements (reference 7). Those denoted "3/4 Madelung" represent a possible surface correction to our results.

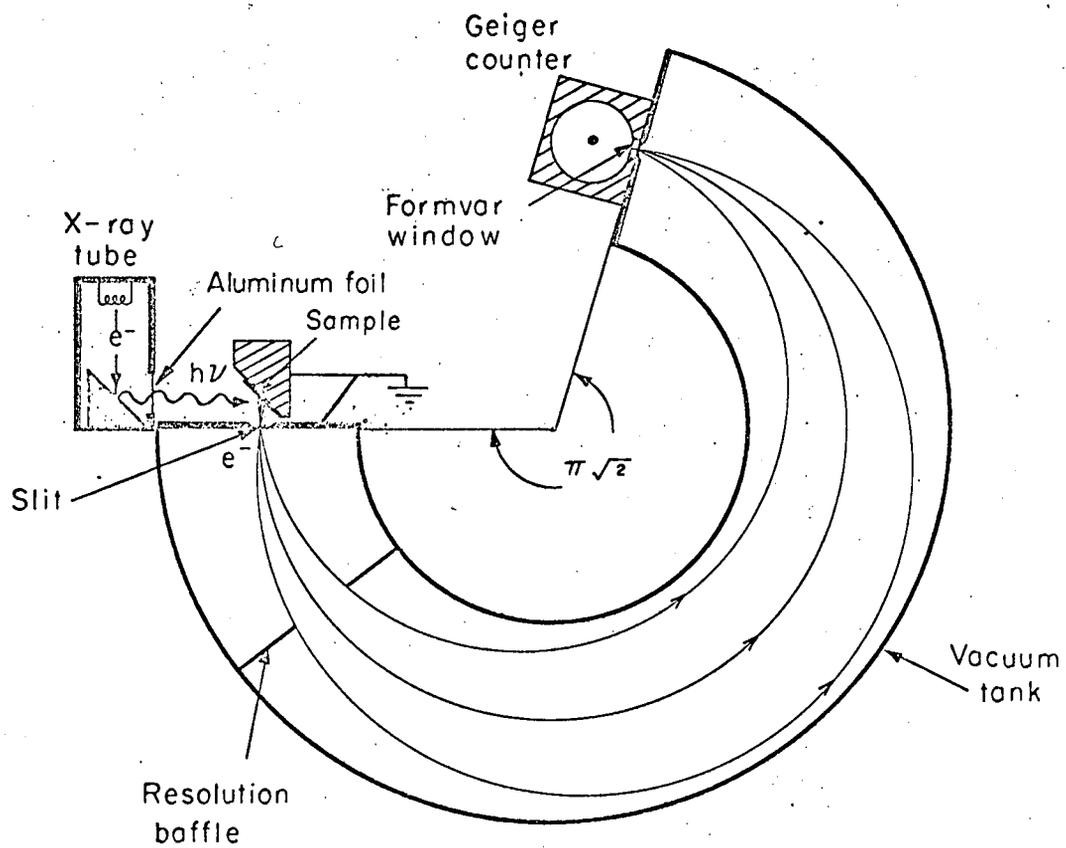
Compound	I-O bond fractional ionic character	Charge on iodine
<u>Photoelectron spectroscopy:</u>		
Full Madelung-		
$\text{KIO}_3$	0.67	2.99
$\text{KIO}_4$	0.48	2.86
3/4 Madelung-		
$\text{KIO}_3$	0.35	1.10
$\text{KIO}_4$	0.46	2.71
<u>Mössbauer:</u>		
$\text{KIO}_3$	0.31	0.83
$\text{KIO}_4$	0.31	1.44

Figure Legends

Fig. 1. Schematic illustration of the experimental apparatus.

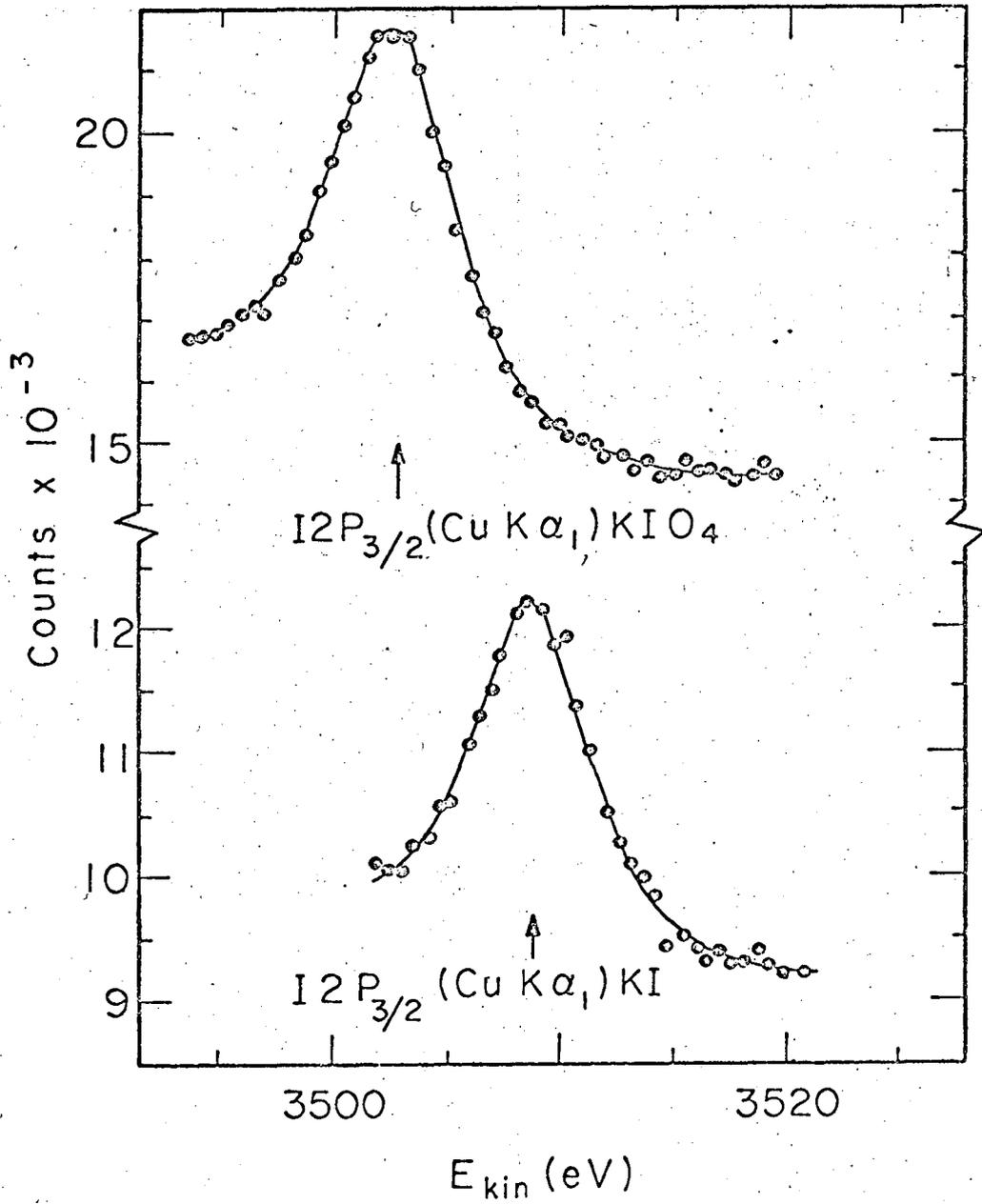
Fig. 2. Photoelectron peaks from KI and  $\text{KIO}_4$ .

Fig. 3. Photoelectron peaks from various europium compounds.



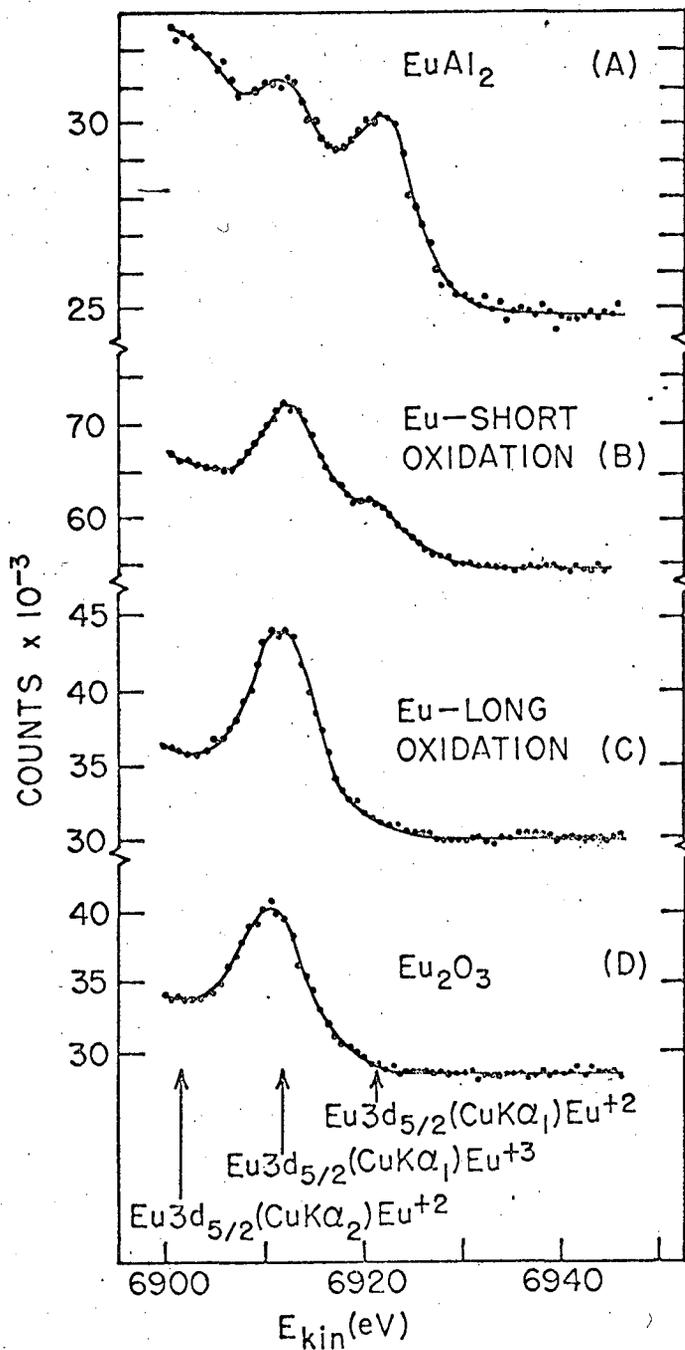
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Fig. 1.



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Fig. 2.



XBL 672-632

Fig. 3.

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