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X-RAY PHOTOELECTRON SPECTROSCOPY

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X-ray Photoelectron Spectroscopy

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Introduction

As far as most chemists are concerned, atomic core electrons are as inaccessible and inert as the nucleus, neither contributing to nor being affected by chemical bonding. However the recent development of X-ray photoelectron spectroscopy is rapidly changing this view, and these "forgotten electrons" are playing an important and growing role in chemistry.

X-ray photoelectron spectroscopy (also called "ESCA" and "XPS") is the study of the energy distribution of the electrons emitted from X-ray irradiated compounds. In principle all electrons, from the core to the valence levels, can be studied. In this respect the technique differs from ultraviolet photoelectron spectroscopy, in which only the valence electrons can be studied.[1] In this account we describe this new technique and discuss some of its chemical applications.

Although the principles of X-ray photoelectron spectroscopy have long been known and although some early attempts were made to apply the technique in chemistry, it remained for nuclear spectroscopists to provide devices of sufficient resolving power for the successful chemical application of the technique. By employing a high-resolution iron-free magnetic beta spectrometer in which an X-ray tube had been installed, K. Siegbahn and his associates in Uppsala produced in 1957 the first high-quality X-ray-induced photoelectron spectra.[2]

The relevance of photoelectron spectroscopy to chemical structure became evident with the discovery by the Uppsala group of shifts in the K-shell photolines of different compounds of the same element.[3] As the result of extensive studies of these binding energy shifts and related

phenomena by a number of workers, photoelectron spectroscopy has developed into a research tool of wide application in chemistry and solid-state physics. A detailed description of the method is given in a book by Siegbahn et al.[4]

Experimental Technique

The photoelectric interaction between monoenergetic X-rays and a solid or gaseous sample causes electrons to be ejected with discrete kinetic energies. The observable quantities in photoelectron spectroscopy are thus the kinetic energies corresponding to discrete electron "lines". Electrons that suffer energy losses in traversing the sample are seen in the spectral background.

Energy conservation for the photoemission process can be expressed by the equation

$$E_{h\nu} = E_k + E_\phi + E_B(i)$$

where $E_{h\nu}$ is the X-ray energy, E_k is the photoelectron kinetic energy, E_ϕ is a small correction for solid effects (work function, etc.), and $E_B(i)$ is the electron binding energy of the ith level. An electron energy analyzer is used to scan the kinetic energy spectrum and to record the E_k values of the discrete photolines. The value of E_ϕ is either known or is assumed to be constant for a given system. Thus binding energies $E_B(i)$ can be determined by use of the energy conservation equation.

An X-ray photoelectron spectrometer is shown, in plan view, in Figure 1. Its essential components are: (1) a specially constructed X-ray tube with a magnesium anode that produces a beam of the Mg K_α X-rays (1253.6 eV). (2) an apparatus for exposing solid or gaseous samples to the X-ray beam under a variety of conditions (cooled, heated, etc.) (3) a double-focusing magnetic spectrometer constructed from two precision-wound iron-free solenoids. Its energy resolution can be as good as 0.06%. (4) an open-window electron multiplier detector (such as the Bendix "Channeltron") for counting the focused electrons. (5) a flexibly programmable current-control and data-recording system consisting of a small computer and associated electronics with which the spectrum can be scanned automatically.

With this equipment, photoelectron line-widths of about 1.5 eV are obtained for solid sources, and 1.0 eV for gas sources, in the kinetic energy

region of interest. With magnesium radiation, it is convenient to study K levels of elements up to about Z = 10, L levels to about Z = 27, M levels to about Z = 57, and N levels through the transuranium elements.

Electron energy analyzers based on electrostatic focusing may also be used in photoelectron spectroscopy, and several spectrometers of this type have been constructed.[3,5] A new magnetic spectrometer design that allows the possibility of ultra-high vacuum operation has also been proposed.[6]

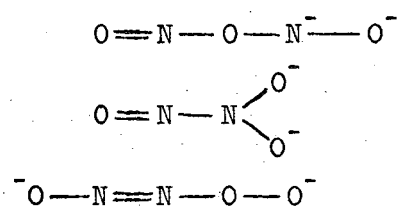
Chemical Shift

The power of the X-ray photoelectron method lies in the fact that the measured quantity, the electron binding energy of an atom, is a function of the chemical environment of the atom. A good illustration of the chemical-structure dependence of binding energy in an organic compound is seen in the spectrum of the carbon 1s levels in ethyl trifluoroacetate, Figure 2, recorded by Siegbahn and coworkers.[4] In this molecule there are four structurally-distinguishable carbon atoms, corresponding to the four resolved lines that appear in the spectrum. These large shifts in the carbon 1s level, due to different environments, indicate that many interesting studies of carbon-containing molecules should be possible. An example of chemical shifts in an inorganic compound is seen in the nitrogen 1s spectrum of trans-dinitrobis(ethylenediamine)cobalt(III) nitrate, $[Co(NH_2CH_2CH_2NH_2)_2(NO_2)_2]NO_3$, shown in Figure 3.[7] This substance contains three types of nitrogen atoms, in an abundance ratio of 4:2:1, and three peaks with approximately this intensity ratio are seen in the spectrum.

It was early realized that the core electron binding energy of an atom should be related to the oxidation state or effective charge of the atom.[3,4] One would expect that the energy for removing an electron from an atom would increase with increasing positive charge or decreasing negative charge. Indeed, when binding energies for a given element are plotted against estimated atomic charge, this type of correlation is observed. In making plots of this type, several methods have been used to estimate atomic charges: (1) the Pauling method, based on the fractional ionic character of bonds,[4,8] (2) the extended Hückel molecular orbital method,[7] and (3) the CNDO molecular orbital method.[7,9] A plot of nitrogen 1s binding energies for a wide variety

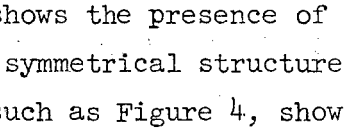
of nitrogen compounds against atomic charges estimated by the extended Hückel method is given in Figure 4.

The use of X-ray photoelectron spectroscopy in structure determination is illustrated by the nitrogen 1s spectrum of Angeli's salt ($Na_2N_2O_3$), shown in Figure 5. Three plausible structures previously proposed for the anion of this salt are shown below.



I

II



III

The spectrum, which shows the presence of structurally different nitrogen atoms, rules out the symmetrical structure I. Molecular orbital calculations,[7] combined with plots such as Figure 4, show that the observed binding energies are consistent only with structure II.

The application of X-ray photoelectron spectroscopy to the study of chemical binding is illustrated by the study of the nitrogen 1s spectra of some transition metal nitrosyl complexes.[7] The binding energies for the compound $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, which is believed to be an Fe(II) complex of NO^+, are 398.2 eV (for CN^-) and 403.3 eV (for the NO group). The corresponding binding energies for $K_3[Cr(CN)_5NO]\cdot H_2O$ (which has been interpreted as a Cr(I) complex of NO^+) are 398.4 and 400.7 eV, respectively. It is clear that the charge on the CN^- ions is about the same in the two compounds, but that the charge on the NO group is much lower in the chromium complex (lower binding energy). A possible explanation of this result is that the chromium complex is actually a Cr(III) complex of NO^-. Support for this interpretation is found in the fact that the chromium 3p binding energies of $K_3[Cr(CN)_5NO]\cdot H_2O$ and $K_3[Cr(CN)_6]$ are identical.[10]

Although correlations of binding energy with atomic charge, as discussed above, can be useful in structure determinations and in studies of chemical bonding, it is important to realize that such correlations are only approximate. There is no obvious reason for expecting a close one-to-one correspondence between binding energy and atomic charge, no matter how accurately the latter quantity is estimated. Three directions are being followed to improve the situation. The first is the study of simple gaseous molecules that are

susceptible to rigorous theoretical calculations of binding energy. The second is the use of only thermodynamic data to establish correlations. The third is the completely empirical correlation of binding energies with structural features of molecules. The latter two approaches are especially justified in the case of complicated molecules and solids.

In connection with the question of correlating binding energies with theory, it is useful to consider the dynamics of the photoemission process. The first step in the process is the creation of a hole, say in the K-shell, by the interaction of the X-ray with the atomic electrons. The filling of the K-hole by electronic transitions from outer orbitals takes a long time compared with the time required for the photoelectron to leave the atom. Therefore it is valid to consider the final state as containing a K-hole. (Were this not so, a single discrete line corresponding to the K level would not in fact be observed in the photoelectron spectrum.) The electrons in other shells can respond quickly to the positive K-hole by shrinking their orbits adiabatically, a process that is fast because no change in quantum state is involved. The additional Coulomb repulsion of the shrunken orbitals causes the kinetic energy of the outgoing electron to be greater than if the orbitals were "frozen " (i.e., E_B is lower). That the contribution of electron reorganization to the binding energy is significant has been demonstrated by the theoretical free-atom calculations of Bagus[11], which are in much better agreement with experiment when an adiabatic ("relaxed orbitals") approximation is used as compared with a "frozen orbitals" approximation.

A natural question is whether electronic reorganization effects in entire molecules are important when chemical shifts for compounds of a single element are considered. Such effects would manifest themselves as structure-dependent deviations of experimental binding energy shifts from the corresponding "frozen orbital" theoretical values. Basch and Snyder[12] have made SCF-MO calculations of binding energies for a number of small molecules with use of the "frozen orbital" approximation. Their results are given as shifts, so that there is cancellation of purely atomic relaxation effects; that is, the carbon 1s binding energy in various compounds is compared with that in CH_4, etc. Davis et al[13] have reported experimental binding energies for some of these molecules, and Figure 6 shows their data (also as shifts) plotted against the theoretical values of Basch and Snyder. Although a small, almost constant, deviation is

noted, the agreement is remarkably good and indicates that structure-dependent reorganization effects in the molecules represented here are small or of the same magnitude in the various molecules.

Inasmuch as the present state of calculational work on binding energies in molecules is rudimentary, it is desirable to develop semi-empirical methods for predicting binding energy shifts. One such method, utilizing thermodynamic data, is based on the approximation that, when a core electron is removed from an atom in a molecule or ion, the valence electrons relax as if the nuclear charge of the atom had increased by one unit.[14] Thus, atomic cores that have the same charge may be considered to be chemically equivalent. The significance of this approximation can be seen by considering the binding energies of some gaseous nitrogen compounds. The 1s binding energy of molecular nitrogen is the energy of the following process:

$$N_2 \rightarrow NN^{*+} + e^- \qquad (1)$$

(The asterisk indicates a 1s electron vacancy in one of the nitrogen atoms.) Now consider reaction (2), in which the electron-deficient core of the N^* atom is replaced by the normal core of an oxygen atom, and for which, according to the above approximation, ΔE is zero.[15]

$$NN^{*+} + O^{6+} \rightarrow NO^+ + N^{*6+} \qquad (2)$$

By adding reactions (1) and (2), we obtain reaction (3), for which ΔE should be approximately the same as that for reaction (1), i.e., equal to the binding energy.[16]

$$N_2 + O^{6+} \rightarrow NO^+ + N^{*6+} + e^- \qquad (3)$$

We can write similar reactions for the binding energies of other nitrogen compounds; thus for ammonia we write

$$NH_3 + O^{6+} \rightarrow OH_3^+ + N^{*6+} + e^- \qquad (4)$$

The difference in the energies of reactions (3) and (4) is the energy of reaction (5) and should equal the shift in binding energies for N_2 and NH_3.[16]

$$N_2 + OH_3^+ \rightarrow NO^+ + NH_3 \qquad (5)$$

By similar arguments it can be shown that the nitrogen 1s binding energy shifts (relative to NH_3) for CH_3NH_2 and HCN should be equal to the energies of the following reactions.

$$CH_3NH_2 + OH_3^+ \rightarrow CH_3OH_2^+ + NH_3 \qquad (6)$$

$$HCN + OH_3^+ \rightarrow HCO^+ + NH_3 \qquad (7)$$

Indeed similar chemical reactions can be written for many other nitrogen compounds. In Table I we have listed the experimental relative binding energies and the energies of the corresponding chemical reactions for all the gaseous nitrogen compounds for which data are available. Similar data are tabulated for carbon 1s binding energies (relative to CH_4) and xenon 3d binding energies (relative to Xe). Reactions (8) and (9) are examples of the chemical reactions for two of these compounds (i.e., CO and XeF_2).

$$CO + NH_4^+ \rightarrow NO^+ + CH_4 \qquad (8)$$

$$XeF_2 + Cs^+ \rightarrow CsF_2^+ + Xe \qquad (9)$$

The data of Table I indicate that by use of the above "principle of equivalent cores" it is possible to predict relative core electron binding energies to ± 1 eV or better.

Table I.

Relative Core Electron Binding Energies:
Experimental Values and Values Predicted from
the "Principle of Equivalent Cores"

Atomic Level	Compound	Relative Binding Energy, eV	Ref.	Chemical Rxn. Energy, eV	Ref.
N 1s	$(CH_3)_2NH$	-0.7	17	-0.7	19,20
N 1s	CH_3NH_2	-0.3	17	-0.4	19,21
N 1s	NH_3	0		0	
N 1s	HCN	1.2	17	0.95	19,22
N 1s	NNO	3.2	17,13	2.6	19,23
N 1s	N_2	4.35	13	3.5	19,23
N 1s	NO	5.5	17	4.4	19,23
N 1s	N_2F_4	6.8	17	6.3	19,23,24
N 1s	NO_2	7.3	17	6.8	19,23
C 1s	CH_4	0		0	
C 1s	CO	5.4	13	4.1	23,25
C 1s	CO_2	6.8	13	6.9	23,25
C 1s	CF_4	11.0	13	12.3	25,26
Xe $3d_{5/2}$	Xe	0		0	
Xe $3d_{5/2}$	XeF_2	2.95	18	2.7	27,28
Xe $3d_{5/2}$	XeF_4	5.5	18	5.4	27,28
Xe $3d_{5/2}$	$XeOF_4$	7.0	18	6.3	27,28
Xe $3d_{5/2}$	XeF_6	7.9	18	7.85	27,28

In the case of solid compounds, it is more difficult to write a chemical reaction having an energy equal to a given difference in binding energy, and more approximations must be made. However the method has been successfully applied to the correlation of binding energies for solid compounds of nitrogen, boron, carbon, and iodine.[14]

The principal difficulty with the application of the "principle of equivalent cores" is that the necessary thermodynamic data are often lacking. Therefore there is a need for a good general method for estimating differences in the heats of formation for pairs of isoelectronic species. A very crude method of this type, based on Pauling's concept of electronegativities, has been devised and successfully applied to the calculation of relative carbon 1s binding energies for a wide variety of organic compounds.[29]

It has also been shown that the core electron binding energy for an atom in a molecule is calculable as the sum of parameters, p_i, characteristic of the atoms or groups directly bonded to the atom from which the electron is ejected.

$$E_B = \sum p_i$$

These parameters can be evaluated empirically from experimental binding energies and used to predict unknown binding energies.[29]

Level Splittings

An interesting application of photoelectron spectroscopy is the study of splittings of atomic levels that are normally degenerate. The novel feature of these splittings is that they occur in inner core atomic levels that are not accessible to study by classical techniques. The ejection of a photoelectron from a filled shell creates a hole in that shell, and the splittings can be thought of as arising from the interaction of the final-state electron hole with the electronic environment of the atom.

Two types of splitting have been observed, which may be characterized as (1) electrostatic splitting, and (2) magnetic, or exchange splitting.

Electrostatic Splitting

A study of heavy-element photoemission spectra has revealed a complex structure of photolines from $5p_{3/2}$ core levels.[30] Figure 7 shows some of the results for uranium and thorium, where structure of the $5p_{3/2}$ lines is evident, in contrast to the situation in d and f levels. The splitting energy ranged from 3 to 10 eV in various compounds. These splittings were interpreted as arising from the differential interaction of the internal electrostatic field with the $M = \pm 1/2$ and $\pm 3/2$ substates of the $5p_{3/2}$ electron.

Splittings of the $5p_{3/2}$ level have also been found in linear gold(I) compounds. The splitting is about 1.8 eV for $KAu(CN)_2$, and about half that amount for AuCN. The Au-C bond in these molecules has been characterized in terms of s-p hybridization involving the 6s,6p and 2s,2p orbitals of the Au and C atoms, respectively.

Theoretical calculations of the splitting made by Apai et al[31] for the case of $Au(CN)_2^-$ indicate that the splittings cannot be fully explained by the Coulomb interaction of the 5p electron only with the 6p electrons of the gold atom, but that the electrons of the ligand must be considered as well.

Exchange Splitting

A splitting in core levels of transition-element compounds studied by photoelectron spectroscopy has been predicted by Watson and Freeman.[32] The splitting comes about because of the fact that, in a system with unpaired valence electrons, the exchange interaction affects core electrons with spin-up (α) and spin-down (β) differently. Unrestricted Hartee-Fock calculations on free atoms[33] indicate that splittings of up to 12 eV can be expected. The free-atom model predicts also that the relative intensities of the two lines are simply the statistical weights of the two final states. Taking the example of the emission of a core s electron from the Mn^{2+} ion, which has five unpaired d electrons, the final-state spin (J) can be $5/2 \pm 1/2$, and the intensities of the two lines would be expected to be in the ratio $2J + 1$, or 7:5.

Recently Fadley et al[34] have reported an experimental confirmation of the predicted exchange splitting in the 3s levels of the transition group compounds MnF_2, MnO, and FeF_3. A portion of one of their spectra is shown

in Figure 8. The observed splitting (~ 6 eV) is about one-half that predicted on the free-atom model. In the case of MnF_2 good agreement is obtained if the model is extended to take into account the fluorine coordination in the MnF_6^{4-} cluster. The observed relative intensities also differ somewhat from the free-atom predictions.

Exchange splittings have also been seen in gaseous molecules, by Hedman et al[35] in Uppsala. The 1s level of the O_2 molecule, which has two unpaired electrons, is split, and a similar result is obtained for the N 1s level in NO, with one unpaired electron. The N_2 molecule, which has no unpaired electrons, shows no splitting. The observed relative intensities are in agreement with simple statistical weight predictions.

Electronic Structure of Metals

Studies of the low binding energy region of the X-ray photoelectron spectrum of metals can in principle provide a direct means of determining N(E), the density of states near the Fermi level. This subject has also been investigated extensively with UV-photoelectron spectroscopy.

Fadley and Shirley[36] have studied the spectra of metallic iron, cobalt, nickel, copper, and platinum, and Figure 9 shows some of their results. It can be seen from the figure that discrepancies exist between the X-ray and UV-photoelectron results, and that the X-ray results correspond more closely to the theoretically calculated electron distributions. A problem with UV-photoelectron spectroscopy may be that the 21 eV radiation which has been used is not of sufficient energy to eject the photoelectrons far enough into the continuum so that the final states are free from the effects of discrete levels lying just above the Fermi level and/or from plasmon oscillations.

In order to produce clean metallic surfaces for the study of N(E), Fadley and Shirley[36] have used a technique of heating the sample in the presence of a low pressure of hydrogen. The surface cleanliness was monitored by following the oxygen 1s line as well as a core-level line of the metal. At higher temperatures the intensity of the oxygen line decreases and the iron 3p line narrows to a width characteristic of the metal.

Catalysis

Because of the sensitivity of the photoelectron method to surface conditions in solids, it is likely that useful applications will be found in the study of catalysis. Identification of oxidation states present in an activated catalyst may allow correlations with catalytic activity and possibly optimization of catalyst performance.

The thickness of surface layer that is accessible to study depends on variable factors such as photoelectron kinetic energy and atomic number of the material. In one case involving a photoelectron kinetic energy of ~ 670 eV and a carbon-containing material (iodostearic acid) it was found[4] that the average depth of electron emission is less than 100Å. For lower kinetic energies or high atomic number materials, the depth will be much less. The sensitivity of photoemission to depth may make possible studies of particle size because particles whose sizes are equal to or smaller than the penetration depth will be heavily weighted, giving an enhancement of lines from the small particles.

Figure 10 shows some portions of the photoelectron spectrum taken of a catalytic material, FeV_2O_4, which was used for the dehydrogenation of cyclohexane[37]. It is seen that following the chemical reaction the oxygen lines of the catalyst shifted toward lower binding energy (more negative), the vanadium lines shifted toward higher binding energy (more positive), and the Fe 3p line showed no shift. While these results are not yet well understood, it appears that there has been some electron transfer from vanadium to oxygen in the reaction.

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(16) As indicated in footnote 15, the energies of reactions 3 and 4 may differ from the binding energies of N_2 and NH_3, respectively, by a constant which cancels out when the difference in these energies is calculated.

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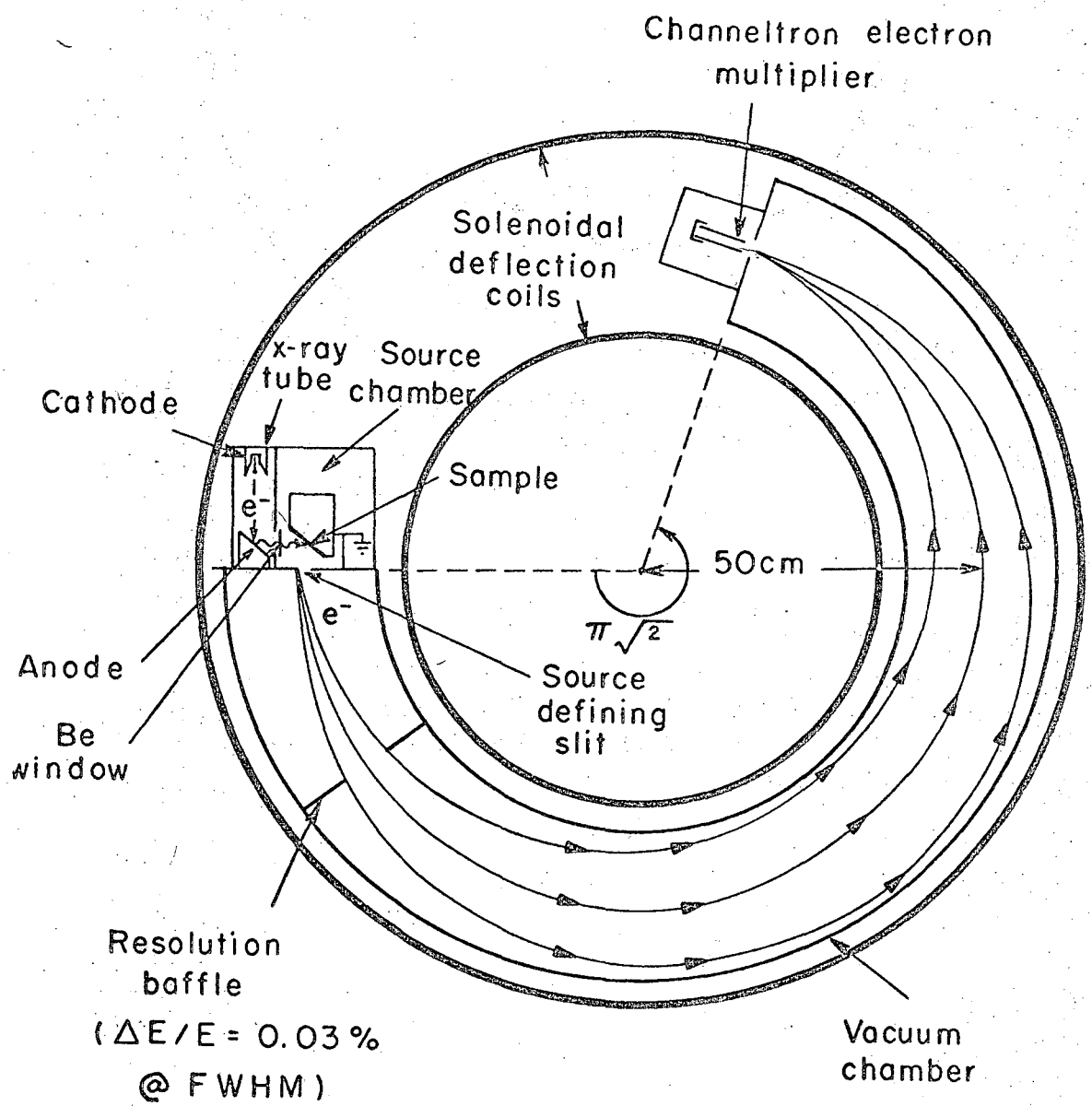

Fig. 1. Plan view of Berkeley iron-free spectrometer as adapted for X-ray photoelectron spectroscopy.

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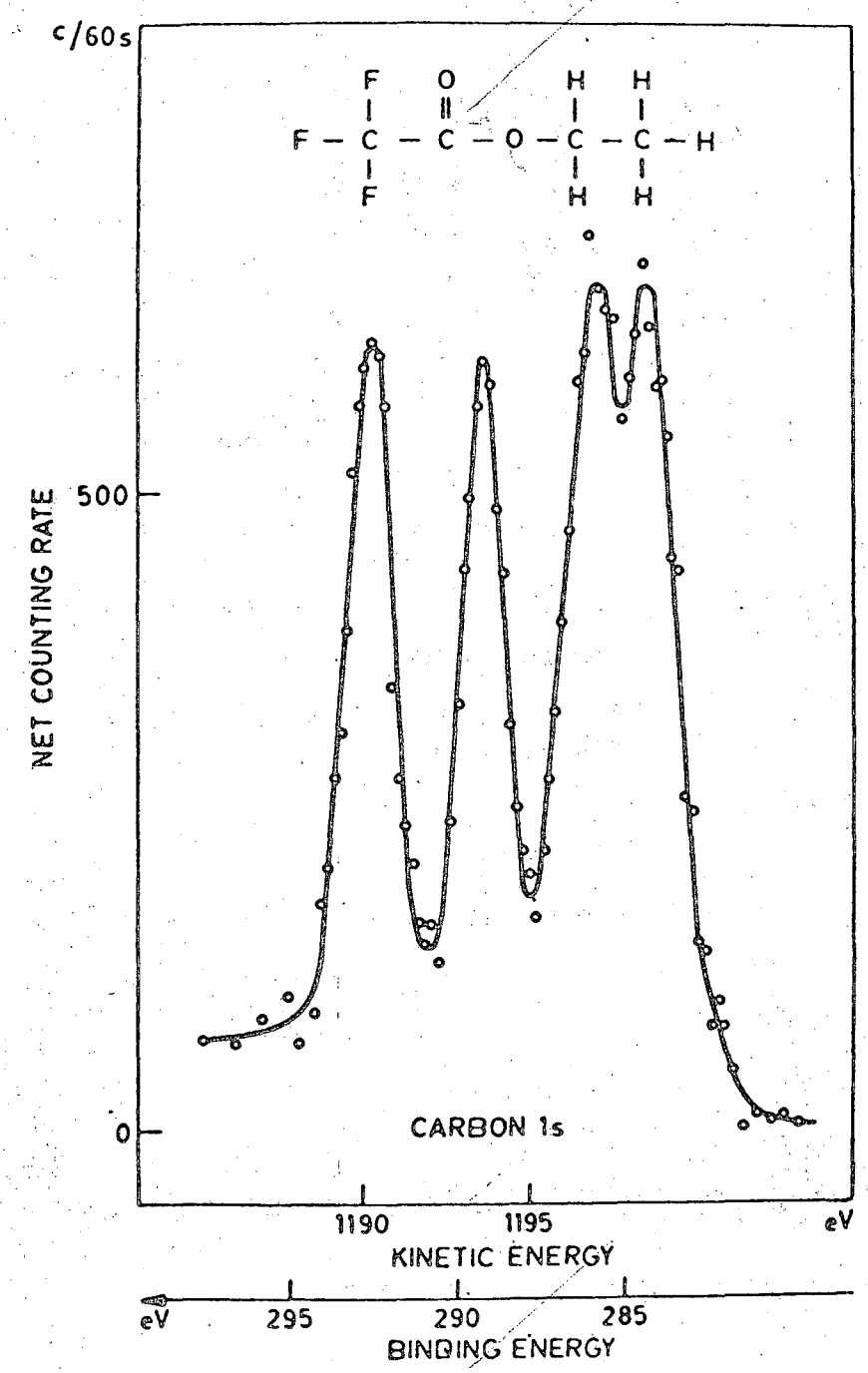
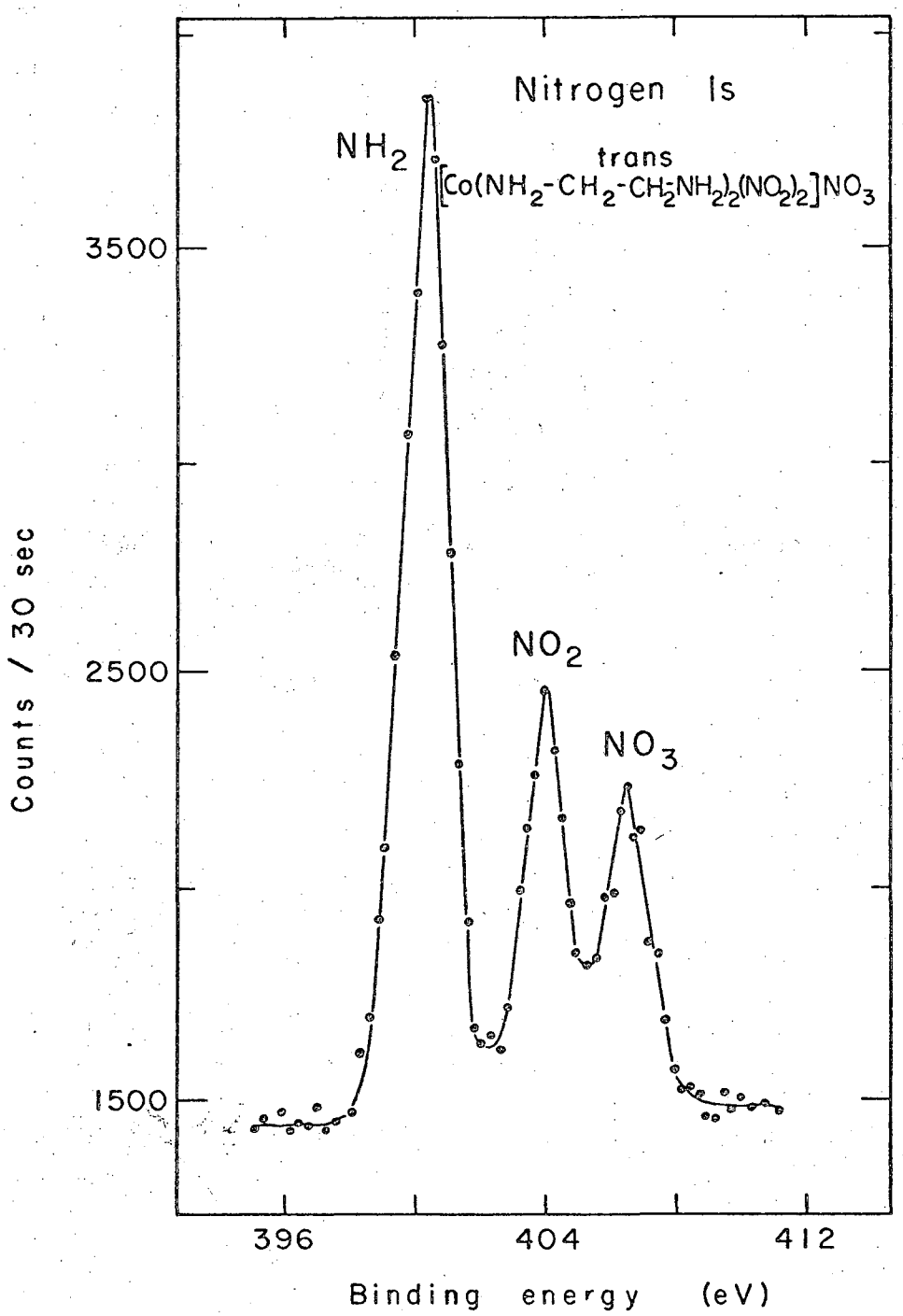


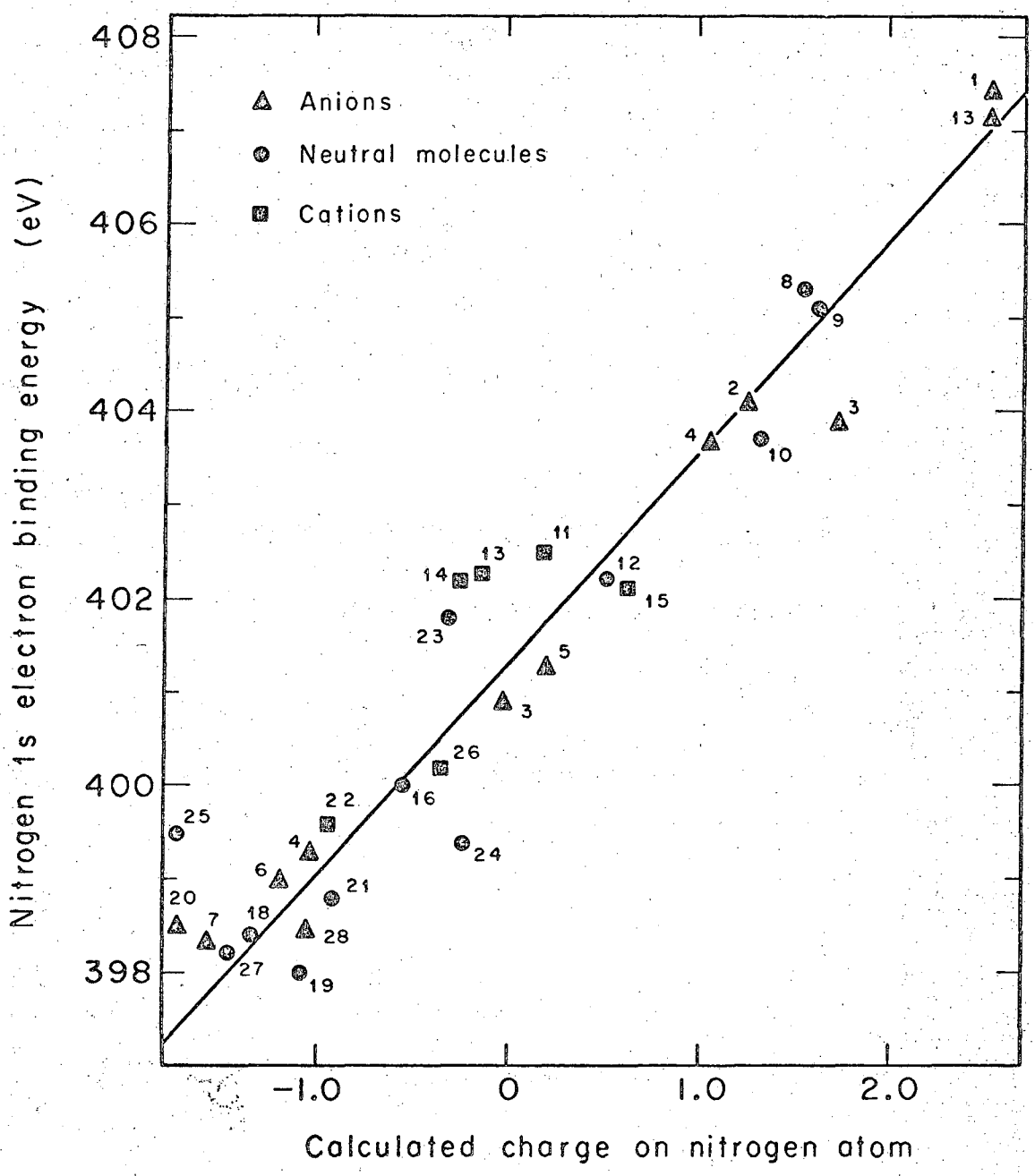
XBL 698-1340

Fig. 2. Carbon 1s photoelectron spectrum of ethyl trifluoroacetate. From reference 4.



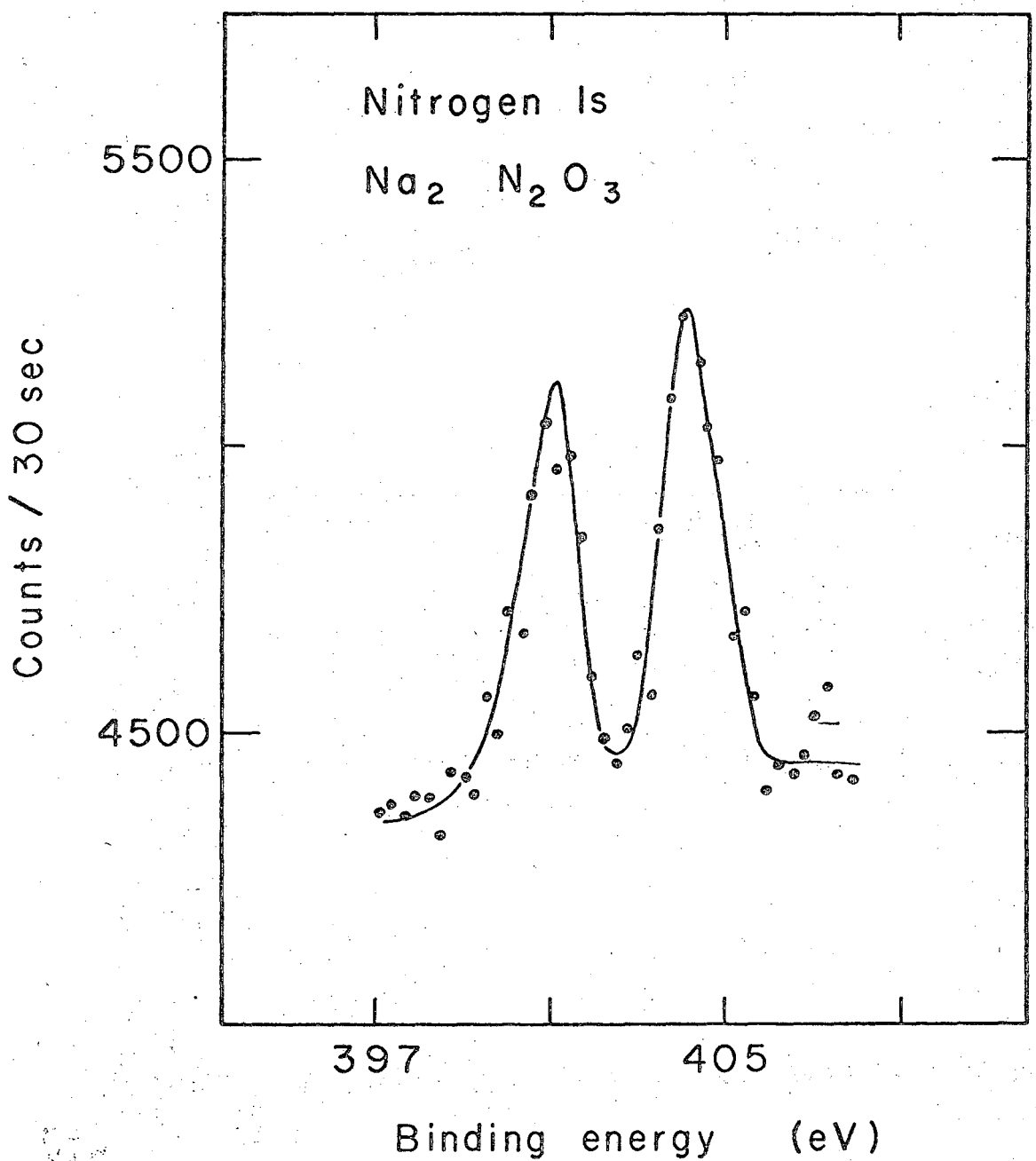
XBL 696-2975

Fig. 3. Nitrogen 1s photoelectron spectrum of trnas-dinitrobis(ethylenediamine)cobalt(III) nitrate.



XBL695-2645

Fig. 4. Plot of nitrogen 1s binding energies versus nitrogen atomic charges calculated by the extended Hückel method.



XBL 696-2976

Fig. 5. Nitrogen 1s spectrum of Angeli's salt, $Na_2N_2O_3$.

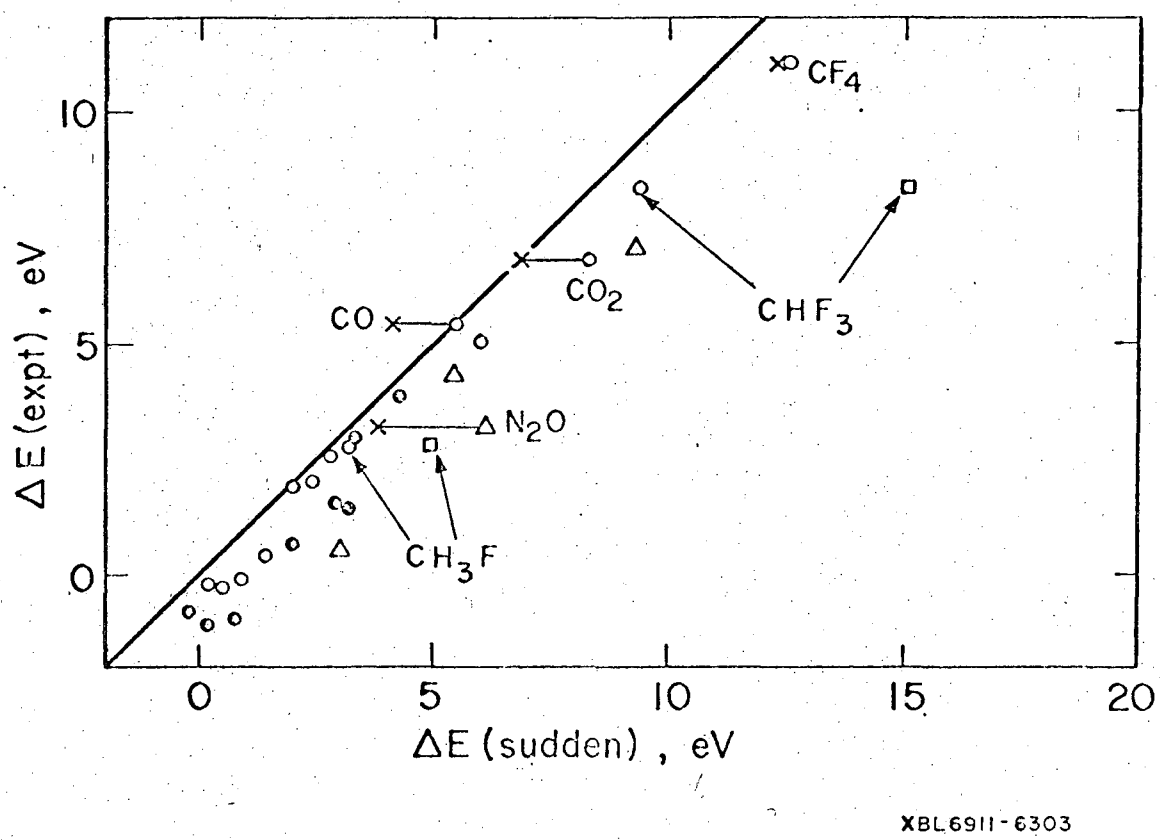


Fig. 6. Experimental Chemical shifts of carbon, nitrogen, and oxygen 1s levels plotted against theoretical values (ΔE_{sudden}) from reference 12.

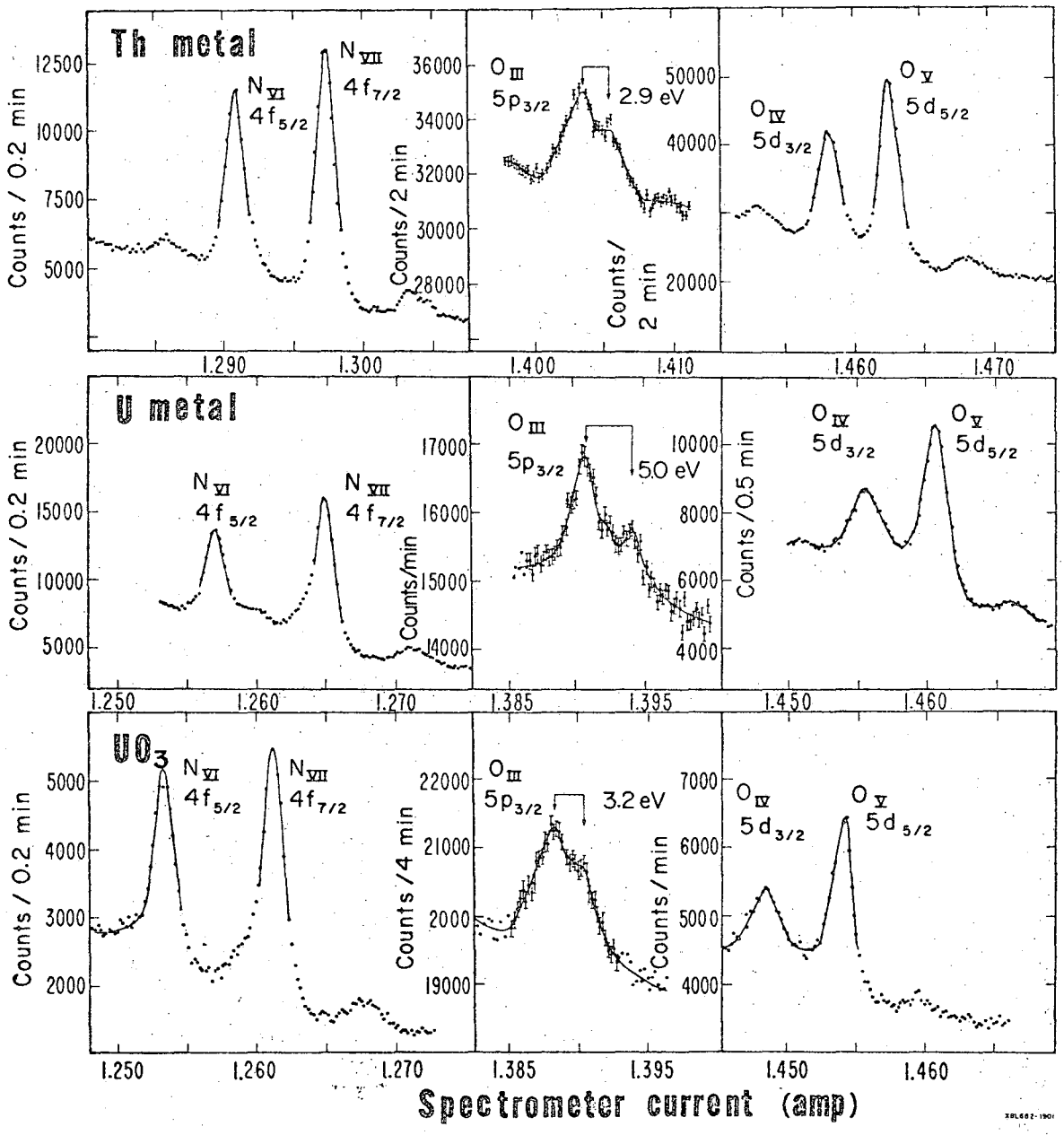


Fig. 7. Photoelectron spectra of 4f, 5p, levels in Th, U, and UO_3, showing splitting in $5p_{3/2}$ level.

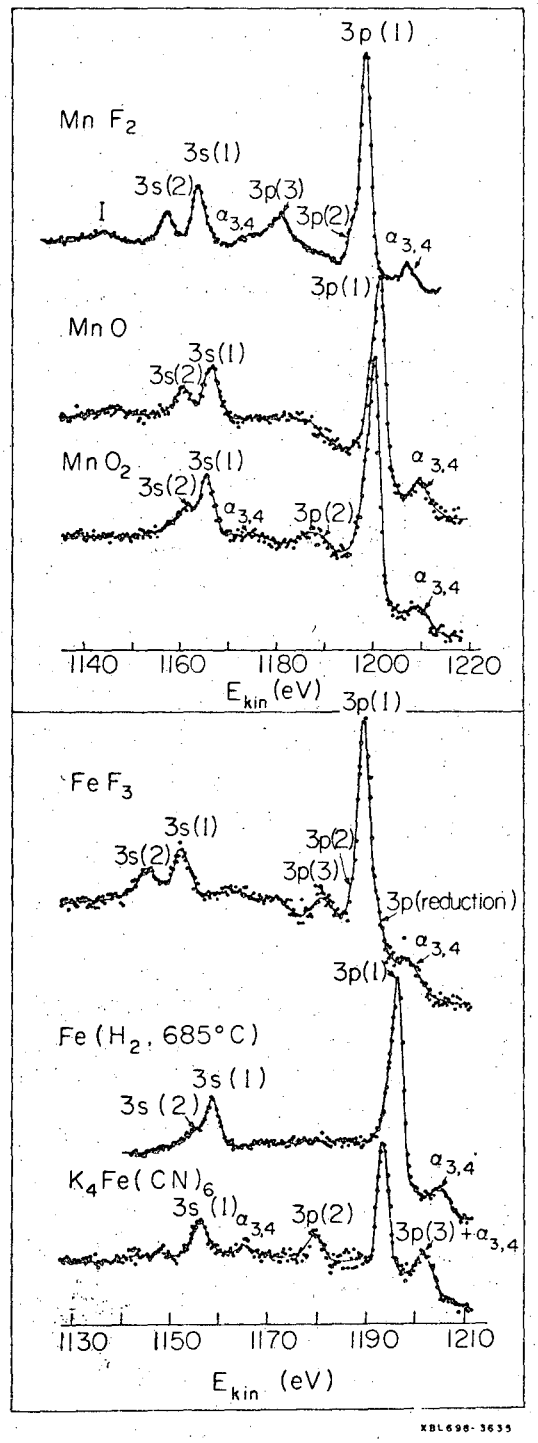
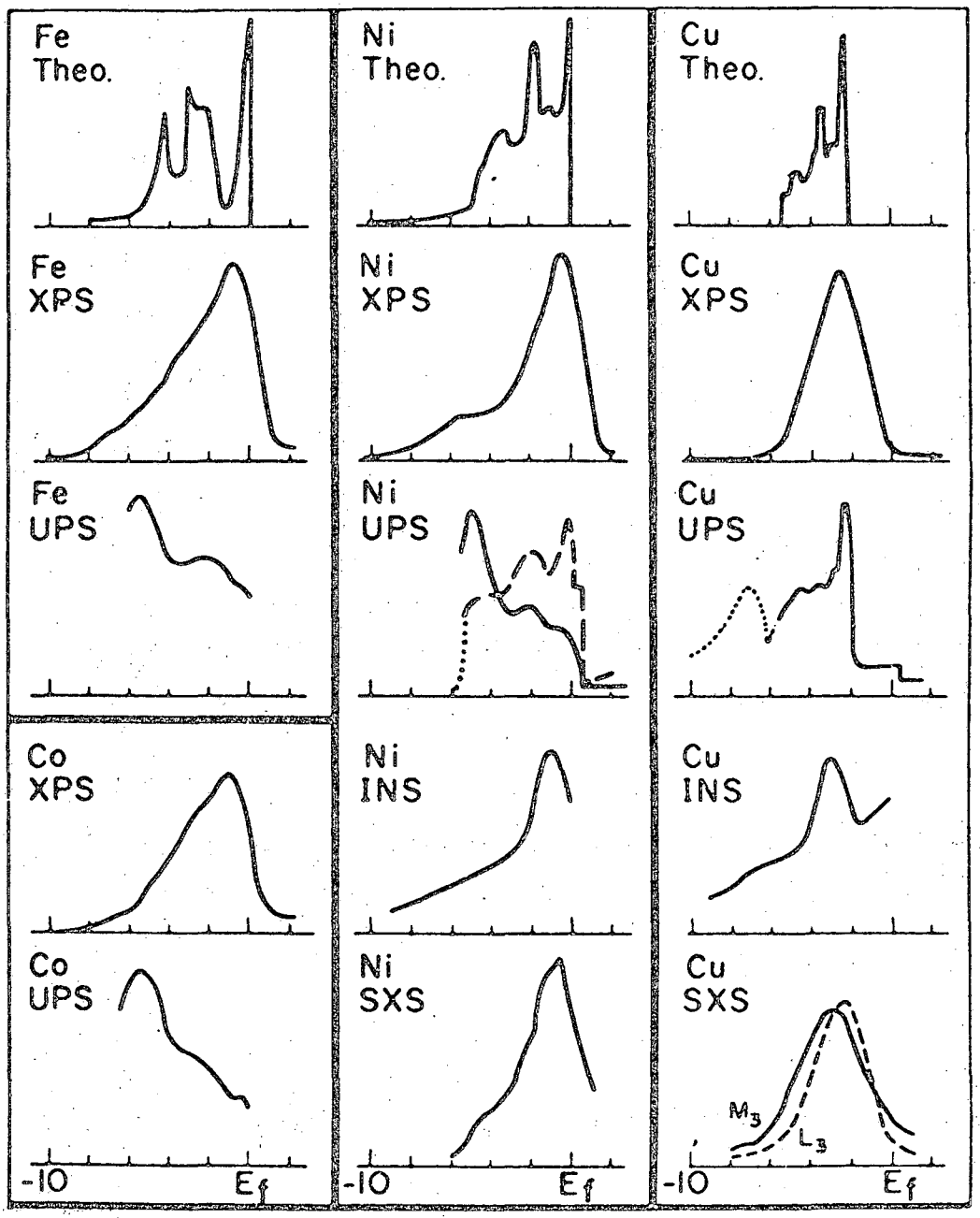


Fig. 8. Portion of photoelectron spectrum of Mn and Fe compounds, showing exchange splitting in 3s level. From reference 34.



XBL 698-1345

Fig. 9. Spectra showing densities of states near the Fermi level in several metals, from X-ray (XPS) and UV (UPS) photoelectron spectroscopy. From reference 36.

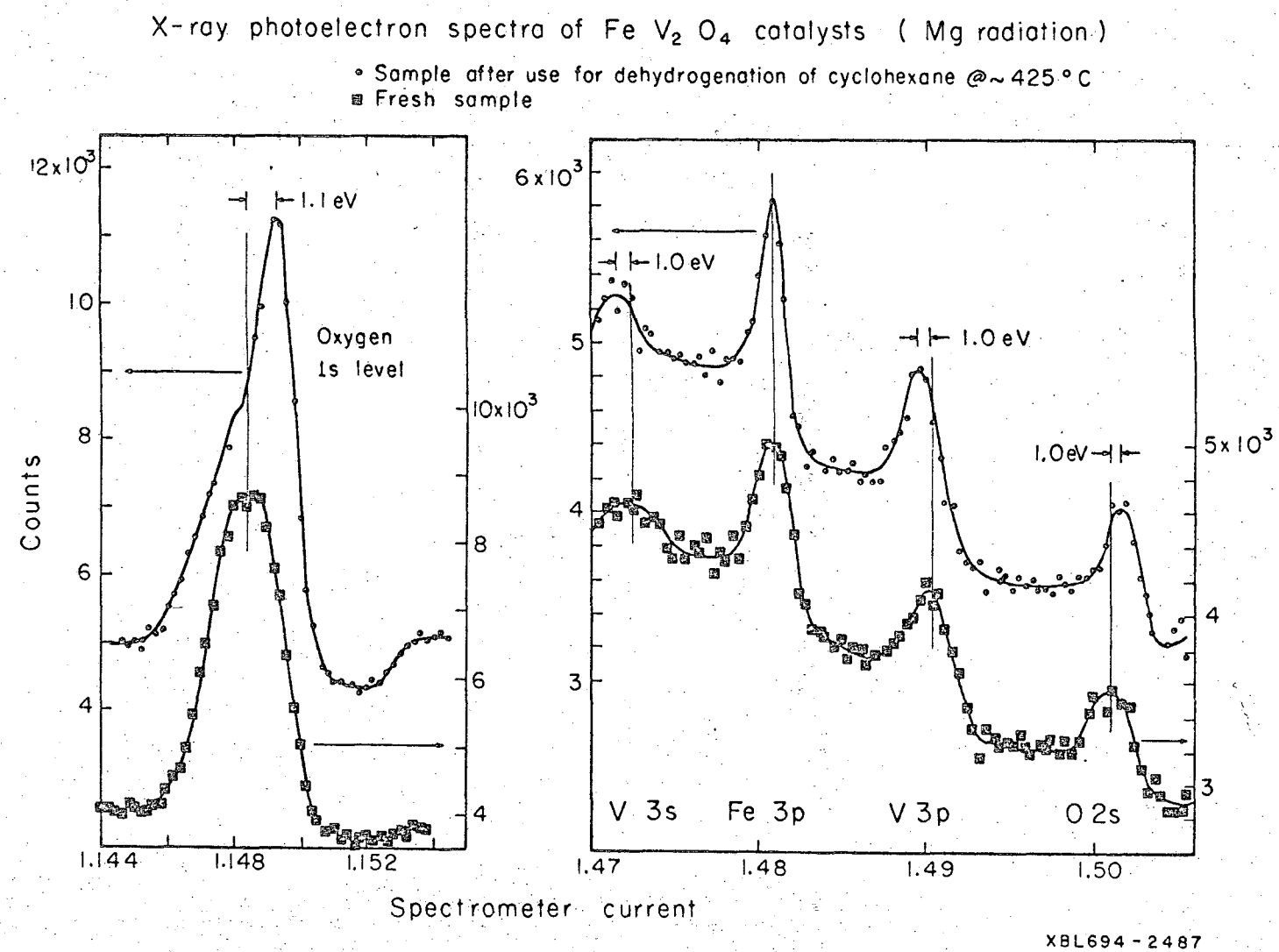


Fig. 10. X-ray photoelectron spectrum of FeV_2O_4 catalyst. From reference 37.

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