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Authors

Hollander, J.M.
Shirley, D.A.

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J. M. Hollander and D. A. Shirley

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CHEMICAL INFORMATION FROM PHOTOELECTRON AND CONVERSION ELECTRON SPECTROSCOPY[1]

J. M. Hollander and D. A. Shirley

Department of Chemistry and
Lawrence Radiation Laboratory
University of California
Berkeley, California 94720

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I. INTRODUCTION

The traditional view of nuclear properties holds that these properties

are not appreciably affected by chemical change, which involves electrons in

the outermost shells of the atom. This view was supported by an abundance of

experience, largely related to the insensitivity of nuclear decay rates to

changes in chemical state, temperature, and pressure. It has, however, been

modified as a result of the development of techniques such as the Mössbauer

effect that can detect exceedingly small changes in nuclear properties.

The chemist has regarded the atom core, like the nucleus, as being

essentially indifferent to chemistry. The tightly-bound atomic core electrons,

occupying filled shells, exhibit little influence on chemical properties and

are themselves hardly affected by changes that occur in the valence shells of

---

the atom.   Thus, these "inner" electrons have traditionally been excluded from

chemical thought, to the extent that in chemistry textbooks reference to the

core levels is usually confined to their inclusion in the "aufbau" table of

atomic structure, to be seen once and then ignored.

The inner electrons do of course feel some, albeit small, influence from

the valence electrons.   The long absence of chemical interest in the inner shells

was primarily due to the lack of an inner-shell spectroscopic method of suf-

ficient sensitivity to produce useful chemical information.   This situation has

been changed by recent developments in photoelectron spectroscopy, so that it

is presently possible to detect changes in binding energies of the core elec-

trons resulting from ordinary chemical processes.   As a result, the atomic core

electrons are taking on a new and growing relevance to chemistry.

Photoelectron spectroscopy is the study of the kinetic energy distribu-

tions of electrons ejected from atomic, molecular, or solid systems by photon

irradiation.   The physical quantity measured is the electron "binding energy",

E_B.   Chemical information is obtained via observation of chemistry-induced

changes in the binding energies.   In principle all electrons from the K shell

out to the valence levels can be studied.

In contrast to their meager historical influence in chemistry, the

atomic core electrons have always played an important role in nuclear physics.

Several modes of nuclear de-excitation involve atomic transitions in the inner

atomic levels. Among these decay modes are electron capture, a beta decay

process competing with positron emission by which the nucleus decreases its

charge by one unit, leaving a hole in the K, L, ... shell as the final state,

and internal conversion, a decay mode competitive with photon emission in which

nuclear excitation results in the ejection of a K, L, ... electron. Internal

conversion electron spectroscopy has been one of the principal methods for

determining nuclear level energies accurately, and measurement of the internal

conversion coefficient (ratio of conversion electron intensity to photon inten-

sity) is a valuable tool for studying the multipole character of nuclear

transitions.

Because of the involvement of atomic electrons, these nuclear processes

in principle also exhibit a dependence on chemical state and should therefore

be capable of yielding chemical information. Although in certain special cir-

cumstances this has actually been the case and a few elegant experiments have

been performed, a general or systematic method for obtaining chemical informa-

tion from studies of nuclear decay processes involving the inner shells has

not yet evolved. Thus in this review our reference to internal conversion

spectroscopy as a means of obtaining chemical information will be brief. In

Section II the various "inner-shell" spectroscopies are compared. Section III

describes the measurement and interpretation of chemical shifts by x-ray photo-

electron spectroscopy, especially in atoms and molecules. Its application to

solids is covered in Section IV, and a special class of new effects--core level

splitting-- is described in Section V.

Because of the brevity of this review, we have chosen not to include a

discussion of experimental techniques used in the practice of photoelectron

spectroscopy. For this the reader is referred to references 1-5 and to the

journal references cited herein.

II. THE INNER-SHELL SPECTROSCOPIES COMPARED

There are four "inner-shell" spectroscopies than can yield chemical

information. We shall describe them briefly and specify the chemical param-

eters that can be derived from each. They are considered in the order:

1) Chemical effects on the nuclear decay rate, 2) Isomer shifts in Mössbauer

spectra, 3) Chemical effects on conversion-electron spectra, and 4) Chemical

shifts in the spectra of photoelectrons from inner shells. The four spectros-

copies are discussed in a way that allows comparison and assessment of the

chemical information which they provide.

A. Decay Rate Effects

Although in principle the rates of all nuclear decay processes can be

altered by the chemical environment, effects of observable magnitude are

expected only for the two types of decay that directly involve bound atomic

electrons, namely electron capture and internal conversion. For both cases the

initial and final states can be represented by product wave functions,

$$\psi^{(i)} = \psi_e^{(i)} \psi_n^{(i)} \qquad\qquad \text{1a.}$$

$$\psi^{(f)} = \psi_e^{(f)} \psi_n^{(f)} \psi_k^{(f)} \qquad\qquad \text{1b.}$$

where $\psi_k^{(f)}$ is the continuum wave function of the emitted particle (a neutrino

or electron, respectively, in capture or conversion). The transition Hamiltonian

for either process contains a factor $\delta(r_e - r_n)$ that selects only the electrons

with finite probability of being found "at" the nucleus, yielding a transition

probability W that is proportional to the electron density at the nucleus:

$$W \propto |\langle \Psi^{(f)} | \mathcal{H} | \Psi^{(i)} \rangle|^2 \propto |\psi_e^{(i)}(0)|^2 \quad . \qquad 2.$$

If the difference between the decay rates of a given transition in two chemical

environments is observed, then the ratio

$$\frac{\Delta W}{W} = \frac{\Delta |\psi_e^{(i)}(0)|^2}{|\psi_e^{(i)}(0)|^2} \qquad 3.$$

is obtained directly, and it is this ratio which must be maximized to yield a

large effect. For point nuclei in the nonrelativistic approximation $|\psi_e(0)|^2$

is nonzero only for s electrons. Relativistic $p_{1/2}$ electrons have s-like

small components in their wave functions; thus their $|\psi_e(0)|^2$ is also nonzero,

albeit much smaller than for s electrons. The finite volume of the nucleus

alters the effective value of $|\psi_e(0)|^2$ somewhat, but still only s and $p_{1/2}$

electrons are important. For brevity we shall refer only to the effect of s

electrons on $|\psi_e(0)|^2$ in the following discussion.

Only the outermost atomic s electrons are strongly involved in chemi-

cal structure, and their contributions to $|\psi_e(0)|^2$ are relatively small in

comparison to those of the inner s electrons. In a heavy atom the one-

electron contribution to $|\psi_e^{(0)}|^2$ decreases by about an order of magnitude for

each unit increase in the principal quantum number. Thus observation of chemical

effects on nuclear decay rates is clearly not a method of wide applicability in

chemistry. Detectable effects may be realized, however, under either of two

conditions: 1) A very light element may be used, as in the well-known studies

on the electron capture of [7]Be. With only the 1s and 2s shells occupied,

$|\psi_e(0)|^2$ can be observably affected by the chemical environment. Half-life

changes of 0.07% have been reported (6). To our knowledge [7]Be is the only low-Z

isotope to which this approach has been successfully applied. 2) One may study

a transition having an energy so low that only loosely-bound electrons can be

captured or converted. This approach has proved successful for studies of

chemical effects on internal conversion in several isotopes with low energy

isomeric transitions. In [99]Tc a 0.3% change in half-life was detected (6,7).

In [90]Mo and [235]U much larger half-life changes have been found, 3.4% in the

former (6,8) and 5.7% in the latter (9-12). Recent results on the ^{235}U isomer

are of particular interest: Nève de Mevergnies has found a correlation between

$T_{1/2}$ and the electronegativity of the host lattice into which the ^{235}U recoils

were implanted (11), with the correlation being reversed for the more electro-

positive metals Hf and Zr (12). These results are illustrated in Figure 1.

These effects have been reviewed recently (6), and we shall not go into

further detail here except to make two observations: First we note that, by

Equation 3, an experimental value of $\Delta W/W$, together with a reliable theoretical

estimate of $|\psi_e(0)|^2$, will yield $\Delta|\psi_e(0)|^2$. (In "approach 2" above $|\psi_e(0)|^2$

must be understood as only that portion of the total electron density at the

nucleus that contributes to the transition under study.) Secondly, even if a

reliable value of $\Delta|\psi_e(0)|^2$ is obtained its interpretation in terms of chemi-

cal structure may be quite subtle or even ambiguous. This complexity arises

because $|\psi_e(0)|^2$ can increase, for example, in two ways: either directly,

by loss of outer s electrons, or indirectly, through loss of p or d electrons

and consequent reduction in screening of the s electrons.

B. Isomer Shifts

The Mössbauer isomer shift has been reviewed extensively (13), so we

mention it here only for purposes of comparison. A formal analogy may be made with

the above case, but equation 1 must be modified to indicate that the electronic

state is not directly involved in the transition (i.e., $\psi_e^{(i)} = \psi_e^{(f)}$), and that

the emitted particle is a gamma quantum. Thus

$$\psi^{(i)} = \psi_e \, \psi_n^{(i)} \qquad\qquad 4a.$$

$$\psi^{(f)} = \psi_e \, \psi_n^{(f)} \, \psi_r \qquad\qquad 4b.$$

The "effect" in this case appears as a shift in the transition energy, which is

brought about in first order by the Coulombic interaction of the nuclear and

electronic charge distributions. For a single level this interaction has the

form

$$\Delta E = \langle\, \psi \,|\, \Sigma \frac{e^2}{r} \,|\, \psi \,\rangle \propto N |\psi_e(0)|^2 \quad,$$

where N is a nuclear factor. An observed isomer shift involves two nuclear

factors, one each for the ground and excited states, and two electron densities,

for source and absorber,

$$\text{I.S.} \propto (\Delta N)(\Delta |\psi_e(0)|^2) \quad.$$

Although shifts can be measured with great accuracy, ΔN is rarely known very

well, and the quantity $\Delta|\psi_e(0)|^2$ can therefore be determined only to within a

rather uncertain scale factor even if a good estimate of $|\psi_e(0)|^2$ is avail-

able. This is in contrast to the situation for decay-rate measurements, dis-

cussed above. Isomer-shift studies have abundant sensitivity: in favorable

cases the range of isomer shifts is 10-100 times the natural line width.

C. Conversion Electron Spectra

If conversion-electron spectra are studied by energy-analyzing the

emitted electrons, then a more detailed chemical interpretation can be made.

A spectral peak appears for each possible electronic final state, corresponding

usually to a hole in each atomic subshell. Thus the different decay "channels"

may be studied separately and equations analogous to Equations 1 to 3 apply to

each channel. This specificity has particularly valuable implications for

structural chemistry. It permits rather subtle comparisons, among different

compounds, of the atomic-orbital populations of molecular orbitals. Such

populations are of more direct chemical interest than is $|\psi_e(0)|^2$.

Bocquet et al. (14) reported the first experiment of this kind, on the

23.8-keV state of ^{119}Sn in SnO_2 and white tin. Their experiment not only

established the effect: at the same time it yielded the definitive inequality

$$\psi_e(0)^2_{5s,Sn} > \psi_e(0)^2_{5s,SnO_2} \quad ,$$

which resolved a long-standing controversy in Mössbauer spectroscopy over the

sign of the nuclear factor ΔN in ^{119}Sn. It was no accident that conversion-

electron spectroscopy could solve this problem, while extensive Mössbauer

isomer-shift studies had been unable to do so: the former established unam-

biguously from peak intensity ratios that $|\psi_e(0)|^2$ is larger in white tin

than in SnO_2, while the interpretation of even the sign of the isomer shifts

was model-dependent and therefore uncertain. The effects observed in conver-

sion-electron spectra can be large: Bocquet et al. concluded that the 5s (O_I)

peak from the 23.8-keV transition of ^{119}Sn in SnO_2 is 30% less intense than in

white tin.

The value of the conversion-electron spectroscopy method is clear;

unfortunately its range of application appears to be quite small. This is also

true, to different extents, of the other two methods discussed above. Only

Mössbauer spectroscopy enjoys a wide enough range of applicability to be of

much consequence in structural chemistry, and it is severely limited both by

the absence of any suitable transitions in isotopes of the chemically most

important light elements (C, N, O, etc.) and by the difficulty of making quanti-

tative interpretations of isomer shifts.

D.   Photoelectron Spectroscopy

The last inner shell method--photoelectron spectroscopy--differs from

the above three in several important respects. It does not involve the nucleus

directly and therefore does not require any special nuclear properties. Conse-

quently it can be applied to all elements with inner shells (all except H and

He). In photoelectron spectroscopy a photon--usually in the x-ray region--

ejects an electron from an inner level. The initial and final states may be

written

$$\psi^{(i)} = \psi_\phi \, \psi_e$$

$$\psi^{(f)} = \psi_e^* \, \psi_k$$

where ϕ and k represent the incoming photon and outgoing photoelectron ψ_e

the electronic ground state, and ψ_e^* an excited "hole" state. The electron

kinetic-energy spectrum is observed, as in conversion-electron spectroscopy,

but here (as in isomer-shift studies) chemical information is extracted from

peak energies, shifted through Coulombic shielding by valence electrons, rather

than from peak intensities. This shielding is proportional to, and therefore

yields, the total electron populations of the valence shell, rather than the

less useful parameter $|\psi_e(0)|^2$.

High-resolution x-ray photoelectron spectroscopy was introduced by

K. Siegbahn and colleagues (1) of Uppsala University. Its potential was

quickly recognized, and it is currently being developed and applied in several

laboratories. The bulk of this review is devoted to a discussion of this

method.

The essential features of the four inner-shell spectroscopies are sum-

marized in Table I.

Table I. Comparison of Inner-Shell Spectroscopies

Method	Process	Outgoing quantum	Measured property	Derived quantity	Magnitude or quality factor [a]	Range of application [b]
Shifts in total decay rate	Electron capture or conversion	ν or e^-	decay-rate change	$\Delta\psi_e^2(0)$	~0.1%	A few isotopes (^{7}Be)
Decay rate shifts in low-energy transitions	Electron capture or conversion	ν or e^-	decay-rate change	$\Delta\psi_e^2(0)$ [c]	a few percent or less	Several isotopes ^{90}Nb, ^{99}Tc, ^{235}U
Isomer shifts	γ emission	γ	shifts in peak energies	$(\Delta N)\ \Delta\psi_e^2(0)$ [d]	$Q \sim 10\text{--}100$	~20 heavy elements
Conversion electron spectroscopy	Electron conversion	e^-	peak intensity changes	valence s electron population	tens of percent	A few isotopes (^{119}Sn)
Photoelectron spectroscopy	Photoelectric effect	e^-	shifts in peak energies	total atomic charges	$Q \sim 10$	All elements with $Z \geq 3$

[a] Q = range of shifts $\div$ peak width.

[b] These estimates are subjective: they represent the level at which we would seriously consider using each method to obtain chemical information.

[c] Assuming that the appropriate $\psi_e^2(0)$ is known.

[d] Here ΔN is the nuclear factor.

III.   CORE-ELECTRON BINDING ENERGY SHIFTS FROM PHOTOELECTRON SPECTROSCOPY:
The data and their interpretation

The first clear demonstration of chemical shifts in a photoelectron

spectrum came in 1964 with the observation by Hagström, Nordling, & Siegbahn (15)

of two lines in the sulfur 1s spectrum of sodium thiosulfate, $Na_2S_2O_3$. At the

time of this experiment, the instrumental line-widths were typically around

6.5 eV, but the separation between the two lines in this case was also 6.5 eV,

so that the doublet structure was easily visible. Because of the known chemical

structure of the sodium thiosulfate molecule, the origin of the two lines was

quickly understood: in this molecule the two sulfur atoms are non-equivalent,

one being in the -2 formal oxidation state and the other in the +6 state. This

observation gave rise to the idea of correlating the electron binding energy

with chemical oxidation state, and this procedure in turn provided the basis

and incentive for the development of a large number of increasingly realistic

correlations and theoretical interpretations from which chemical information

can be obtained.

As the experimental technique of photoelectron spectroscopy became

refined and the instrumental line widths were reduced, it became possible to

detect much smaller chemical effects on the binding energy than occur in the

case of sodium thiosulfate. Photoelectrons ejected from inner shells by x-rays

have kinetic energies in the 10^3 eV range; presently, line widths of about 1 eV

are obtained. In a typical element shifts of up to 10 eV may be observed, and

these shifts can be measured to about 0.1 eV accuracy.

As an illustration of the range of chemical shifts that has been observed

in core-level binding energies we show in Figures 2 and 3 two extreme cases; the

first, where the shift is less than one line-width, and the second, where a near-

maximum shift is observed. Figure 2 shows the photoelectron spectrum from the

carbon ls levels in ethylene, acetylene, and benzene, relative to CHF_3; the

shifts here are ≈0.3 eV. Figure 3 shows the carbon ls spectrum obtained from

ethyl trifluoroacetate, by Siegbahn et al. (1) in which shifts of up to 9 eV

are seen. In this molecule there are four structurally different carbon atoms,

corresponding to the four lines appearing in the spectrum. The chemical en-

vironments of the two terminal carbon atoms can be considered as opposite

extremes, the one carbon atom being attached to three fluorine atoms, which are

the most electronegative of all atoms, and the other being attached to three

hydrogen atoms, which are highly electropositive. The latter spectrum gives a

good idea of the range of shifts that can be expected in practice (at least

for organic compounds).

An example of chemical shifts, in an inorganic compound, that are inter-

mediate in magnitude between those of the examples just given is seen in the

nitrogen 1s spectrum of trans-dinitro-bis(ethylenediamine) cobalt(III) nitrate,

$[Co(NH_2CH_2CH_2NH_2)_2(NO_2)_2]NO_3$, shown in Figure 4. This substance contains three

structural types of nitrogen atom, in an abundance ratio of 4:2:1, and three

peaks with approximately this intensity ratio are seen in the spectrum (17).

For historical reasons, as cited above, the first chemical property

to be correlated with inner-shell electron binding energy was the classical

property, oxidation state. This is intuitively sound: one would expect that

the energy necessary to remove an electron from an atom would increase with

increasing positive charge or decreasing negative charge on the atom. In

Figure 5 we show a plot of binding energy versus oxidation number for a series

of halogen compounds, combined from the data of references 1 and 3. Since

oxidation number is only a formal concept, however, it should not be expected

that a correlation with binding energy would be more than qualitatively useful.

Such correlations do nonetheless demonstrate the direction and approximate

magnitude of typical chemical shifts in ionic compounds. From the data of

Figure 5 we see that the binding energy increases on the average by about 0.8 eV

and 1.2 eV per unit increase in oxidation number for iodine and chlorine,

respectively.

A. Free-Atom Descriptions

As the basis for discussion of the chemical interpretation of binding

energy shifts, let us consider the origin of these shifts: When a chemical

reaction takes place, electron movements occur within the molecules involved.

These redistributions of charge affect the potential of the inner electrons and

thereby bring about the observed changes in their binding energies.

Perhaps the simplest quantitative theoretical description of shifts in

core-level binding energy can be given in terms of a classical charged-shell

atomic model, in which the valence electrons are represented by a spherical

shell of negative charge. The potential exerted by this shell on the core

electrons inside the shell, is $V = \gamma e/r$, where γ is the number of electrons in

the valence shell, and r is its radius. If a chemical reaction causes one

electron to be removed from the valence shell (to infinity) the potential of

the core electrons is reduced by the amount $\Delta E = e/r$ and thus their binding

energy is increased by this amount. If $r = 1\text{Å}$, $\Delta E = 14$ eV.

In spite of the crudeness of this model, the magnitude of the predicted

shifts is in the range of the observed shifts. For example, the reaction

$Eu^{+2} \rightarrow Eu^{+3}$ results in a shift in the binding energy of the $3d_{5/2}$ level of

9.6 eV (3,18). This is a case where the simple model should be most nearly

valid because the europium compounds are highly ionic: one $4f$ electron is in

fact removed in the oxidation of Eu^{+2} to Eu^{+3}.

In most cases the actual chemical shifts are considerably smaller than

those predicted by this simple charged-shell model. In terms of the model this

can be justified on the basis that 1) electrons do not typically move to

infinity but rather only to a nearby atom as the result of a chemical reaction,

and 2) less than one unit of charge is usually transferred. For example, the

oxidation of KIO_3 to KIO_4 (oxidation number change from +5 to +7), results in a

core-level shift of only 1.0 eV (3,18). These iodine compounds are not strongly

ionic, and the oxidation does not involve the absolute loss of two electrons

but rather only the sharing of the iodine electrons among one additional oxygen

atom, which corresponds to a transfer of much less than one unit of charge.

An interesting result obtained from the charged-shell model is that

the chemical shifts of all core levels are predicted to be the same because

they are in a region of constant potential. In fact this result has been con-

firmed experimentally: in an investigation of iodine compounds, Fadley et al. (3)

found that the shifts in the $2s_{1/2}$, $2p_{1/2}$, $2p_{3/2}$, $3d_{3/2}$, $3d_{5/2}$, $4s_{1/2}$, and

$4p_{3/2}$ levels of iodine were equal within experimental error for KIO_3 and KIO_4

(5.3 ± 0.6 eV for KIO_3 and 6.3 ± 0.6 eV for KIO_4, relative to KI).

More accurate calculations of chemical shifts in free atoms can be made

by using Hartree-Fock methods. The results of such calculations in general

verify the qualitative conclusions given by the simple charged-shell model.

As an example of the results from Hartree-Fock free-ion calculations, we show

Figure 6 the binding-energy shifts due to removing a 5p electron from various

free-ion configurations of iodine, calculated by Fadley et al. (3). Several

observations can be made from this figure. The shift in binding energy increases

with the degree of ionization. And as in the classical theory, all core levels

are shifted by approximately the same amount. In fact, for iodine the cal-

culated shift of all core levels is the same to within 1.5%. Therefore, as

long as only these levels are of interest, the shifts need not be calculated

for each level, but an average value over the core can be taken.

B. Rigorous Calculations for Free Molecules

Although calculations of binding energy shifts from free-atom models

have provided useful insights into the origin and magnitude of chemical

effects, the chemist is primarily interested in more realistic systems, i.e.,

molecules and solids. Let us consider first the case of molecules. It is

desirable to compare rigorously calculated binding energy shifts with experi-

mental values in simple molecules with known structure in order to build up a

systematic collection of shifts (or binding energies), which could be useful in

several ways: 1) to search for binding energy anomalies in molecules whose

structures are presumably known, 2) to obtain structural information for mole-

cules that are measurable but too complicated to calculate, and 3) as a check

on the assumptions of the calculations.

The degree of difficulty in making calculations of binding energy in
molecules depends on how the dynamics of the photoelectric process is treated,
and an important question in this regard is the assumed behavior of the remaining
"passive" electrons of the molecule upon emission of a photoelectron. If the
photoelectric event is described as a "sudden" process, that is, with no
readjustment of the other electrons accompanying the emission of a 1s electron,
then by "Koopmans' theorem" the 1s binding energy is simply the one-electron
orbital energy, which can be evaluated from a Hartree-Fock calculation. A more
realistic description is an "adiabatic" process, which can be approximated by
two (fictitious) steps: 1) the photoelectron is ejected suddenly, leaving a
hole in the K shell and leaving the other (passive) electrons "frozen" in their
initial ground-state orbitals, and 2) the passive orbitals quickly relax toward
the positive hole, accelerating the outgoing electron. Adiabatic binding
energies are naturally more difficult to calculate, because for these the
energies of both the initial state and the (unstable) final "hole-state" must be
evaluated. It is of interest to know how the "sudden" and "adiabatic" binding
energy values compare with experiment.

Bagus (19) clarified this question by making Hartree-Fock quality cal-

culations of binding energy for the isoelectronic free-atom sets F^-, Ne, Na^+,

and Cl^-, Ar, and K^+. Bagus found that K-shell binding energies calculated from

the "sudden" approximation were about 23 eV greater than experiment for the

first set (with absolute value $\approx$870 eV) and about 36 eV greater for the

second set (with   absolute value $\approx$3200 eV). On the other hand, when the

values were computed as the difference between the two Hartree-Fock energies

corresponding to the initial state (atom) and the final state (ion with a 1s

hole) the agreement with experiment was much improved (less than 1 eV deviation

for the first set and 3-4 eV for the second set). Clearly, the "adiabatic"

approximation is more realistic than the "sudden" approximation, for describing

the absolute values of electron binding energies. Nonetheless, the use of the

"sudden" (Koopmans' theorem) approximation would still be adequate for pre-

dicting chemical shifts in molecules, provided that the energy of electronic

relaxation in the molecular environment remains constant for the particular

set of molecules under consideration. If on the other hand relaxation effects

in the molecule are significant, experiment should reveal differential,

structure-dependent, violations of the Koopmans' theorem values.

In order to test this question it is necessary to have accurate theo-

retical values for a number of molecules. Basch & Snyder (20) have carried out

"ab initio" SCF-molecular orbital calculations of 1s binding energies for mole-

cules containing first row atoms, in the Koopmans'-theorem approximation.

Experimental shifts of some of these molecules in the gaseous state have been

measured by Davis et al. (21) and by Siegbahn et al. (2) by photoelectron spec-

troscopy. Figure 7 shows the data of Davis et al. plotted against Basch &

Snyder's theoretical shifts, for C, N, and O. From this comparison it is evident

that the SCF calculations give quite good predictions of the shifts; no dif-

ferential violation of Koopmans' theorem is noted.

Another series of ab initio orbital energy calculations using the

"sudden" approximation has been made by Gelius et al. (22) for the 2p orbital

in some sulfur-containing molecules. The correlation of the shifts with

experiment is shown in Figure 8; again no structure-dependent violation of

Koopmans' theorem is evident, when 3d orbitals were taken into account.

The fact that one can use Koopmans'-theorem-calculated values in

correlating binding energy shift data is significant for the application of

photoelectron spectroscopy in chemistry. The problem of making theoretical

calculations is of course thereby greatly simplified; more important for the

chemist is the fact that the shifts can be understood in terms of ground-state

molecular properties.

C. The Equivalent-Cores Approach

Although the agreement between the calculations described above and

experiment is gratifying, such calculations are presently feasible only for

relatively simple molecules having few orbitals. In order to obtain chemical

information more generally from binding energy shift data, it is necessary to

devise more accessible parameters with which to correlate the experimental data.

A powerful semi-empirical method that has had good success in correlating

core-level binding energies has been developed by Jolly & Hendrickson (23).

This method makes use of ground-state thermochemical data. Its basis was given

in terms of a principle of equivalent cores: "When a core electron is removed

from an atom in a molecule or ion, the valence electrons adjust as if the

nuclear charge of the atom had increased by one unit" (23).

This statement is analogous to the adiabatic description of photo-emission, with only the added assumption that atomic cores having the same charge are chemically equivalent.

Consider as an example the nitrogen 1s binding energy in N_2, which is the energy of the following reaction:

1. $\qquad N_2 \longrightarrow NN^{*+} + e^- \qquad\qquad \Delta E = E_{B_{N_2}}$
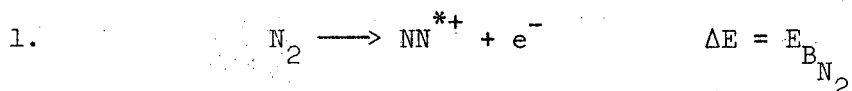
where the asterisk indicates a 1s electron vacancy in one of the nitrogen atoms.

Now consider Reaction 2, in which the electron deficient core of the N^* atom is replaced by the normal core of an oxygen atom.

2. $\qquad NN^{*+} + O^{6+} \longrightarrow NO^+ + N^{*6+} \qquad\qquad \Delta E = \delta_1 .$
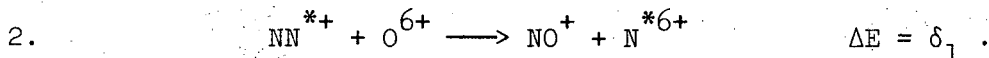
In this Reaction NN^{*+} and NO^+ are approximately equivalent chemically, as are O^{6+} and N^{*6+}. Thus the energy of Reaction 2 is small. By adding Reactions 1 and 2 we get

3. $\qquad N_2 + O^{6+} \longrightarrow NO^+ + N^{*6+} + e^- \qquad\qquad \Delta E = E_{B_{N_2}} + \delta_1 .$
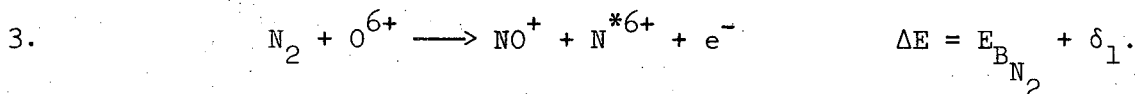
Writing a similar pair of reactions for the nitrogen binding energy in another compound, NH_3, we get

4. $\qquad NH_3 + O^{6+} \longrightarrow OH_3^+ + N^{*6+} + e^- \qquad\qquad \Delta E = E_{B_{NH_3}} + \delta_2$
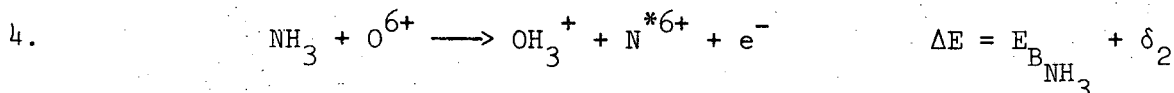
The difference in the energies of Reactions 3 and 4 is the energy of Reaction 5:

5.$$N_2 + OH_3^+ \longrightarrow NO^+ + NH_3 \qquad \Delta E = E_{B_{N_2}} - E_{B_{NH_3}} + (\delta_1 - \delta_2)$$
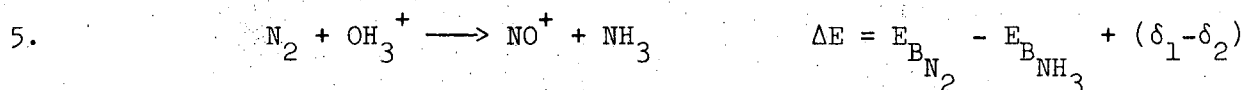
Chemical reactions similar to 5 can be written for many other nitrogen

compounds, as in Reaction 6:

6.$$NO + OH_3^+ \longrightarrow O_2^+ + NH_3 \qquad \Delta E = E_{B_{NO}} - E_{B_{NH_3}} + (\delta_2 - \delta_3)$$
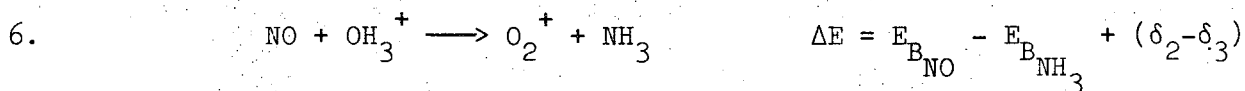
and the energies (ΔE) of these reactions can be evaluated from available thermo-

chemical data. A correlation diagram is obtained by plotting the thermochemical

energies ΔE against the experimentally determined binding energy shifts

($E_B - E_{B_{ref}}$). Figure 9 is such a plot, for a series of nitrogen compounds. It

is evident that where the thermochemical data are available, this method is

capable of correlating core-electron binding energies to ± 1 eV or better, and

it also establishes the essential validity of the equivalent core approximation.

The success of this model is a result of its close relationship to experimentally-

derived thermochemical data and to the validity of the basic assumption. In

fact the method can be extended in two ways. The energies of reactions such as

5 and 6 could also be obtained from SCF calculations on the individual molecules

in their ground states. Also the statement of the principle of equivalent cores

need not be so strong.   All that is really required is that the core-exchange

Reaction 2 above should be essentially independent of the chemical environment

of N.   Thus only $\delta_1 - \delta_2$, not δ_1 itself, must be small.   A weaker form of the

principle that satisfies this requirement is "The energy of exchange of a bare

nucleus Z^{+Z} for the core $(Z+1)^{+Z}$ is independent of the molecular environment".

D.   Approximate Molecular Models

As stated earlier, the first correlations of binding energy with a

theoretical quantity were made with oxidation number.   This parameter is of

course not related in a realistic way to the actual charge distribution within

the molecule, because of the arbitrary way in which electrons are assigned

completely to one atom or another in the molecule.   The molecular charge dis-

tribution is in fact a parameter that is pertinent to the orbital binding

energy, because the binding energy is determined by the electrostatic potential

at the atom created by that distribution (plus the nuclear charge).   Thus it

is natural to seek relationships between the observed binding energies and

quantities related to the atom charge which can be calculated by empirical

or semi-empirical molecular models.

Many authors have discussed the relationship between orbital binding

energy and atomic charge. Recently, for example, Gelius et al. (22) have

described the inner-shell chemical shift ΔE_i for atom i in a molecule as

$$\Delta E_i = kq_i + V_i + \ell$$

where

$$V_i = \sum_{j \neq i} \frac{q_i}{R_{ij}} \qquad\qquad 5.$$

and q_i is the charge on the ith atom,

   k is the proportionality constant for the inner shell studied,

   V_i is the potential from the charge distribution in the rest of the

      molecule at the considered atom,

  R_{ij} is the distance between nuclei i and j,

   ℓ is a constant determined by the choice of reference level.

From Equation 5 one sees that if the atom charge and the molecular potential

are linearly related, so also will be the chemical shift and the atom charge.

This need not always be the case, but one might expect in general an approxi-

mately linear relationship between atom charge and the molecular potential if

the bond distances from atom i to the other atoms are not very different in

the set of molecules. Gelius et al. show this to be the case for the series of

sulfur compounds they investigated.

A problem in relating experimental binding energies with simple molecular

parameters has also been caused by the fact that a large number of experiments

have been done with solid samples, whereas free-molecule models are strictly

valid only for gaseous molecules. For want of something better, however,

chemists have made wide use of various free-molecule models for the purpose of

correlating their data and obtaining chemical information. The approximate

models now to be described have been so used, and the correlation plots shown

below have all been made with use of solid-sample data. We defer our discus-

sion of the specific problem of solids to Section IV.

To obtain theoretical estimates of atom charge in molecules for the

purposes of correlating binding energy data, several approximate free-molecule

models have been employed, of which three are: 1) the Pauling Valence-Bond

(PVB) model, 2) the extended Hückel molecular orbital model, and 3) the CNDO

molecular orbital method.

The PVB approach, which has the great virtue of simplicity, makes use

of bond-length and electronegativity information to estimate the charge dis-

tribution among the bonds formed by the atom of interest. This method has

been employed extensively in a modified form by Siegbahn et al. (1).

According to this model (25), the atom charge, q_A, is given by the

algebraic sum of the charge on atom A formally calculated on the basis of equal

sharing of electrons (covalent bond) plus the charge transferred if the bonded

atoms are of unequal electronegativities (partial ionic character). That is,

$$q_A = Q_A + \sum_{B \neq A} nI .$$

where Q_A = formal charge on covalently bonded atom A.

$\sum$ = summation over all bonds to atom A.

n = average bond number. n = 1 for a single bond, n = 2 for a double

bond, etc.

I = partial ionic character of bond

$= 1 - e^{-0.25 (X_A - X_B)^2}$

where $X_A - X_B$ = electronegativity difference between A and B.

The following is an example of a valence-bond calculation for the

sulfur atom in sulfate ion, SO_4^{--}. The sulfate ion can be represented by the

formal covalent structure

$$\left[\begin{array}{c} \overset{..}{:}\overset{..}{O}: \\ :O:S:O: \\ :\overset{..}{O}: \end{array}\right]^{--}$$
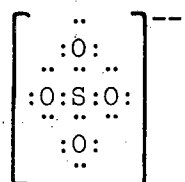
The bond number of the S - O bonds in this structure is estimated to be 1.83

(from bond length data), which means that in each S - O bond, 0.83 extra elec-

trons are associated with the sulfur atom. Thus the formal charge on the sulfur

atom (assuming covalent bonds) is

$$Q_A = + 6 - 4 - 4 \times 0.83$$

$$= -1.32$$

The S - O bond is not fully covalent because of the electronegativity

difference between S and O. This "partial ionic character" causes a certain

fraction of the charge in the bond to be transferred from the sulfur to the

oxygen atom. In this case, $X_A - X_B = 1.0$; thus the partial ionic character of

the S - O bond is 0.22. The amount of charge loss to O by the S atoms is

$4 \times 1.83 \times 0.22 = 1.61$. The overall charge q_A, on the S atom in the SO_4^{--} ion

is thus $1.61 - 1.32 = +0.29$.

Extended Hückel molecular orbital (EHMO) theory is the second method

commonly used to estimate atomic charges. In 1931 Hückel (26) introduced the

Hückel molecular orbital (HMO) theory, in which the atomic cores and "σ skeleton"

are held fixed while molecular orbitals in the "π system" are written as linear

combinations of atomic orbitals. The Roothaan self-consistent field equations (27)

$$ F \, c = \Lambda \, c \, \epsilon $$

are   solved after a number of drastic approximations have been made. The

F matrix, which actually contains one- and two-electron integrals, is reduced

to a set of Coulomb integrals, α, and resonance integrals, β, which are treated

as empirical parameters. They are estimated by one of several semiempirical

schemes. The determinant $[F - \epsilon\Delta]$ is then set equal to zero, and eigenenergies

are thus determined. The overlap integrals are often approximated as δ_{ij}.

The Hückel theory was extended by Hoffman (28), who partitioned the

atomic orbitals into (valence orbitals) and (core orbitals), then used the

entire former group as a basis set for molecular orbitals. A minimum basis set

of Slater-type orbitals is used, and the diagonal elements of the F matrix are

approximated as valence-state ionization potentials. For the off-diagonal

elements an arithemetic or geometric mean is used (often $F_{ij} \cong \frac{7}{8} \Delta_{ij} (F_{ii} + F_{jj})$).

Finally atomic charges are assigned by a Mulliken population analysis (29). In

this scheme a molecular orbital may be written as a linear combination of nor-

malized atomic orbitals ϕ_A and ϕ_B on atoms A and B:

$$\psi = C_A \phi_A + C_B \phi_B .$$

The net atomic populations of C_A^2 and C_B^2 are assigned to atoms A and B,

respectively, while the <u>overlap population</u>, $2C_A C_B \Delta_{AB}$, is divided equally

between the two. The EHMO calculation, like the PVB approach, can be carried

out iteratively, with F_{ii} and the Slater exponents both being charge-dependent (30).

The CNDO approach (30) is an "intermediate" theory between the rela-

tively crude EHMO model and an ab initio LCAOSCF calculation. It also starts

from Roothaan's equations, but it treats electron-electron repulsion specifically.

As the name implies, differential overlap between atomic orbitals is neglected,

both in the overlap integrals, and two-electron integrals. If this alone were

done, the theory would not be invariant to transformation of the basis set.

Invariance is assured by three additional approximations, all of which require

certain matrix elements to depend only on the set of atoms involved in the

molecular orbitals and not on the symmetry of the orbitals on each atom. (In

the EHMO theory the resonance integral β_{ij} is not invariant). Population

analysis in CNDO theory is trivial: there is no overlap population, so atomic

charges are obtained from diagonal elements of the charge density matrix.

One expects a narrower range of atomic charges from CNDO than from EHMO because

electron repulsion is operative, and this expectation is borne out.

E. Comparison of PVB, EHMO, and CNDO Predictions

Chemical shifts in the nitrogen 1s binding energy provide a good context

within which to compare atomic charges calculated on the three models described

above. Nordberg et al. (32) studied a series of solid nitrogen compounds and

plotted the resulting values of E_B against atomic charge on the nitrogen, q_N,

calculated for single molecules or complexes with the PVB model. The correla-

tion plot showed curvature (it need not necessarily be linear), and some of

the points were as much as 4 eV off the curve. Another study of nitrogen com-

pounds was carried out by Hollander, Hendrickson, & Jolly (17), who calculated

q_N by both the EHMO and the CNDO models. They found a linear correlation of

E_B with the EHMO charges. $\underline{Two}$ E_B-q_N correlations were found with the CNDO

charges, one for anions and another for cations and neutral molecules. Cor-

relations for all three models are shown in Figure 10. In the interpretation

of the correlations two interesting points arise:

1) A good, but not excellent, overall correlation is found with atomic

charge for each model. This is in accord with the characteristics of non-

metallic solids discussed in Section IV. These would give a 1 eV "random"

scatter in correlation plots, rather than spoiling the overall correlation.

2) While the qualities of the correlations are not strikingly different,

the total range of the calculated q_N varies from 1.0 for the CNDO method

through 1.7 for the PVB method to 4.3 from the EHMO estimates. Clearly at

least two of these are incorrect. Thus even when a good correlation is observed

one cannot necessarily take the magnitudes of the q_N seriously.

By interpreting the $\underline{slopes}$ of the E_B-q_N curves it is possible to make

some judgment among the different schemes for calculating q_N. If electronic

charge δq is removed from the valence shell of an atom to a neighboring atom

at distance r, the binding energy of inner electrons increases by

$$\delta E = \delta q \left[\left(\frac{\delta E}{\delta q} \right)_{atomic} - \frac{1}{r} \right] \quad .$$

Free atom calculations have given

$$\left(\frac{\delta E}{\delta q} \right)_{atomic} = 17 \text{ eV/electronic charge}$$

for atomic nitrogen (5). The $1/r$ term can diminish this shift, usually by

not quite a factor of two. Thus on the average a slope of

$$\frac{dE}{dq} \cong 10 \text{ eV/electron}$$

is expected for the nitrogen 1s electron binding energy in a series of compounds.

For the three ways of extracting q_N, the resulting slopes are 2.2 (EHMO),

∿6.5 (PVB), and 8.4-10.8 (CNDO). The first is far too small, and the experi-

mental value of dE/dq favors the CNDO charges over the PVB charges. We con-

clude that the range of CNDO charges can perhaps be accepted as plausible while

the charges estimated by the other two methods should be regarded as empirical

parameters.

IV. SOLIDS

The majority of x-ray photoemission studies to date have utilized solid

samples, and the intrinsic interest in compounds that are solids at convenient

temperatures as well as in solid-state problems per se implies that this will

continue to be the case.   The study of solids presents some special problems,

however, which are outlined below.

A.   The Reference Level

First there is the reference-level question (1,3). If a sample is a

good electrical conductor and is grounded to the spectrometer, the two will have

a common Fermi energy, E_F (Figure 11), but the "vacuum level", or energy which

an electron must have to be separated completely from the solid, will differ

from sample to spectrometer by the difference between the work functions of the

two, $\Delta\phi = \phi - \phi_s$ (here s denotes spectrometer). Thus an electron ejected by

a photon of energy $h\nu$ from a state with binding energy E_B relative to the vacuum

level leaves the sample with kinetic energy $K = h\nu - E_B$. It is accelerated by

$\Delta\phi$ on entering the spectrometer, and is focused by a field corresponding to

kinetic energy

$$K' = h\nu - E_B + \Delta\phi \quad .$$

With $h\nu$ and ϕ_s known and K' measured, E_B can be obtained only if ϕ is known,

and binding energy shifts among different solids can therefore be determined

exactly only after correction for the work function difference. Even for metals

it is difficult to determine ϕ accurately, and for non-metals the problem is

usually ambiguous because the position of the Fermi level is unknown. In

spite of these limitations a number of investigations have been made on insula-

tors. For these studies the work-function problem has been neglected, and the

"effective" binding energies referred to the Fermi energy, $E_B^{eff} \equiv E_B - \phi$, or to

the spectrometer vacuum level, $E_B^{eff'} = E_B - \Delta\phi$, were found to correlate rather

well with chemical expectation. For a given compound E_B tends to be a few eV

smaller in the solid state than in free molecules. The gas-solid shift is not

constant: for example the Uppsala group found a larger shift for aminobenzene

than for nitrobenzene, 3.1 eV vs 2.4 eV (2). This effect introduces an uncer-

tainty of ≈ 1 eV in E_B, which is about the shift accompanying a change of one

unit in oxidation state. For this reason alone <u>the oxidation state cannot be</u>

<u>determined by simply measuring E_B^{eff} in a solid</u> (33).

In two circumstances the reference level problem does not arise. First,

for metals E_B^{eff} may be of direct interest because it is the binding energy

relative to the Fermi level. Second, within a given solid the work-function

correction will cancel out in comparing binding energies from different sites.

Thus, in their study of the carbon 1s lines from nucleic-acid bases, Barber &

Clark were able to intercompare the lines from each solid sample (34).

B. Sample Condition

The second major problem that arises in the studies of solid samples

is that of surface condition and stability. The x-ray photoelectron method

samples only a small active region, of 10^2-10^3 Å depth, near the surface of a

solid sample. Electrons ejected from greater depths may enter the spectrometer,

but the probability is very low that they will appear in the full-energy peaks.

Thus the chemical integrity of the first 10^2-10^3 Å layer is crucial.

Many compounds are simply not stable under the vacuum conditions of

the spectrometers. Hydrates lose water very rapidly from the 100 Å "surface"

layer. Other compounds can lose oxygen or other volatile products. Alter-

natively impurities may be deposited, either reactively or by physical adsorp-

tion. Nearly all metals will form oxide layers. For gold this problem is

negligible, but in iron at room temperature, for example, the iron oxide M_{II},

M_{III} peak is as large as that of the metal (35) and for aluminum the L_{II}, L_{III}

peak can be almost completely attributed to oxide (36). If only an ordinary

"high" vacuum is maintained (10^{-5} - 10^{-6} torr), prominent peaks appear from

absorbed O_2 and N_2, as well as C and/or Si peaks from pump oil and vacuum

gaskets. This is expected from kinetic-theory arguments: it takes only a few

seconds for a monolayer to form at 10^{-6} torr. Thus it is incumbent upon the

spectroscopist to demonstrate the chemical purity of the surfaces of his

samples. The analytical application (37) of photoelectron spectroscopy,

"electron spectroscopy for chemical analysis" or "ESCA", can be of great value

here. The surface impurity peaks can be monitored, as can those corresponding

to different oxidation states of the element under study, and the quality of the

sample is thus tested during each experiment. This method was employed, for

example, in the first studies of iron metal (35).

C.   Additional Peaks

Spectral features other than the main photopeak can complicate interpretation, although they also may yield useful information. There are minor peaks in the incident radiation. With a magnesium anode these appear as the $K_{\alpha_{3,4}}$, etc., peaks, and they extend up to about 50 eV above the main $K_{\alpha_{1,2}}$ peaks, though in much lower intensity (38). Two-electron and Auger processes create additional peaks (39-42), as do characteristic energy losses (phonon formation). Other inelastic processes produce "tails" on the photoelectron peaks. Finally the bremsstrahlung component in the incident x-ray beam ejects electrons from deeper within the sample. These electrons initially possess kinetic energies up to several times that of the characteristic x-rays. After energy loss in the sample they contribute to a rather high continuous background under the photoelectron peaks. This background obviates the use of ESCA as a method for studying trace impurities unless the incident radiation is monochromatized to eliminate bremsstrahlung. Several monochromatization schemes are presently under study (43).

The above comments apply to all solids. We turn to now to metals,

after which we shall treat nonmetallic solids.

D.   Metals

The first high-resolution spectra of metals were reported by Siegbahn,

et al., who studied Cu, Ag, Au, and AgAu alloys (44). As these samples were

apparently run at room temperature, it is probable that the Cu and Ag spectra

are characteristic of oxidized surfaces. Fadley and Shirley studied the 3d

metals Fe, Co, Ni, and Cu, using a procedure to reduce the surfaces by in situ

high-temperature reduction with H_2 gas (35). They have applied this technique

also to the 4d and 5d series analogues of these metals (45), obtaining the

density-of-states functions shown in Figure 12. These functions were derived

from the raw data by operating on the spectra with an inverse response function

R^{-1}. For each sample a response function R was constructed by comparing an

observed core-level spectrum X'(E)' to the known energy level spectrum of the

core, X(E):

$$\vec{X}(E') = R(E',E) \ \vec{X}(E) \quad .$$

The $R(E',E)$ matrix, which describes inelastic processes, was then inverted and

applied to the valence-band spectrum. The Uppsala group has used the technique

of in situ high-temperature H_2 reduction in studies of Ni, Cu, Pd, Ag, Pt, and

Au (46). Their untreated spectra agree well with those of Fadley and Shirley (45).

Fadley et al. studied the intermetallic compound $EuAl_2$, finding that the

Eu peaks appeared in positions consistent with the Eu^{2+} configuration (3).

Nilsson et al. (47) studied metal samples, but surface oxidation occurred so

rapidly that their Eu^{2+} peak probably arose from EuO, while the Eu^{3+} peak was

more intense. Broden et al. (48) have studied Eu and Ba as metals under con-

trolled high-vacuum conditions, finding a prominent 4f peak in Eu. With con-

trolled oxidation the Eu spectrum changed to resemble those reported by Nilsson

et al. Recently Chan and Shirley (49) studied the intermetallic compounds $AuAl_2$

and $AuGa_2$, finding prominent 5d peaks about 6 eV below the Fermi energy and

establishing thereby that the 5d bands cannot account completely for the

interesting optical properties of these compounds.

E. Nonmetals

In nonmetallic solids correlations have been established for several

elements between binding energy and chemical parameters such as oxidation state

or calculated atomic charge. Such correlations have been found for sulfur and

chlorine compounds (1) and for nitrogen compounds (1,17); in iodine compounds

the shifts were correlated (3,18) with oxidation state (Figure 5). The correla-

tion is striking for these cases. It is also probably somewhat fortuitous, for

in addition to the usual problems of solids these ionic salts have the additional

difficulty that the binding energy is strongly affected by electrostatic lattice

energies (Madelung-type sums). That a good correlation exists in these and

other cases, however, provides empirical evidence that the chemical oxidation

state influences E_B strongly enough to overcome the differences in work function,

lattice energy, etc., among the different compounds. Thus in the correlations of

E_B with calculated charge on N atoms discussed in Section III the scatter in the

points probably arises from, and gives a good measure of, solid effects.

Correlations have also been made with data from solid samples for the

elements carbon (50,51), boron (51), chromium (51), phosphorus (52), iron (53),

and xenon (54). The results tend generally to support the above conclusion.

In phosphorus, for example, the rather unimpressive E_B-charge correlation is

probably a result of the small range of the shifts in comparison with the

scatter in energy caused by solid effects.

Space restrictions and the newness of the field preclude further

detailed review. We note, however, that applications of the photoelectron

spectroscopy of solids already extend from semiconductors (1,55) to molecular

biology (1,53).

V. SPLITTING OF ORBITAL PEAKS

Most of the full-energy peaks in x-ray photoemission spectra stand in

a one-to-one relation to atomic core levels or molecular orbitals in the initial

state.   There are, however, two exceptions. If the initial state has non-zero

angular momentum J, then the hole created by ejection of a core electron can

couple to J in more than one way to form two or more final states, each of

which will appear as a peak. This effect may be termed <u>multiplet</u> splitting.

For a case with an initial state of spin zero but with a non-spherically sym-

metric electrostatic environment, Coulombic and exchange effects can lead to

<u>electrostatic</u> splitting. The two are discussed separately below.

A. Multiplet Splitting

The simplest example that could exhibit multiplet splitting would be

atomic lithium, $Li^+(1s2s; {}^3S)$ or $Li^+(1s2s; {}^1S)$. The energies of these two final

states may be calculated in two steps: 1) calculate the one-electron energies

ignoring the electron-electron interactions, and 2) introduce these interac-

tions as an e^2/r_{12} correction term. After 1) the two states will be degenerate

in energy, lying at E_0, but 2) adds $(H_c + H_x)$ to $E_0(^1S)$ and $(H_c - H_x)$ to

$E_0(^3S)$, yielding a splitting $E(^1S) - E(^3S) = 2H_x$. Here H_c and H_x are the (1s2s)

Coulomb and exchange integrals. Two peaks would be observed in the photoelec-

tron spectrum, spaced by $2H_x$. The relative intensities would be given by the

multiplicity ratio 1:3, with the ^3S peak falling at the higher kinetic energy.

This result can be generalized. For an atomic initial state with an outer

electronic configuration of spin S and total angular momentum J, ejection of

an inner s electron leads to two final states, of spins $J' = J \pm 1/2$, and

relative intensities $(S + 1)/S$. The spins J' are given by angular-momentum

conservation and the intensities by the fact that (spin) exchange leads to a

new total spin $S' = S \pm 1/2$ which must then be recoupled with L.

Splittings of this type were observed in molecular O_2 and NO by

Hedman et al. (56). In O_2 the coupling is especially simple: the $^3\Sigma_g^-$ ground

state of the neutral molecule is coupled to an O(1s) electron to form the

states $^2\Sigma^-$ and $^4\Sigma^-$ in O_2^+, which appear as peaks with relative intensities

of approximately 2:4. Neutral NO has a $^2\pi_{1/2}$ ground state that couples with

a N(1s) electron to form the states $^1\pi$ and $^3\pi$, which appear as peaks of

relative intensities approximately 1:3. An interesting feature of this mole-

cule is that the same arguments can be applied to the $O(1s)$ electron, but much

less splitting is then expected because (smaller) two-center change integrals

are involved. The $O(1s)$ peak in fact appears only broadened, rather than split.

For both O_2 and NO preliminary calculations using neutral-molecule wave functions

give splittings in satisfactory agreement with experiment (57). The N_2, NO, and

O_2 spectra are shown in Figure 13.

Relatively few molecular species have unpaired spins in their ground

states. However, this effect may play a useful role in establishing the dis-

tribution of spin density in free radicals, especially if higher-resolution

studies are made.

Atoms are intrinsically simpler than molecules, and one might expect

especially clean-cut core-level splittings in atoms. Unfortunately suitable

paramagnetic free-atom sources can be prepared only at high temperatures, and

with some difficulty. Fadley and Shirley (58) studied atomic Eu at 600°C.

Intensity limitations restricted this study to the $4d_{3/2,5/2}$ peaks. The multi-

plet coupling problem of the $4d$ hole state to the valence-electron $^8S_{7/2}$ level

is rather complicated, and no detailed interpreation has yet been made. An

effect was clearly present, however. The two-component peak showed an intensity

ratio of well over 2:1, in marked contrast to the unperturbed ratio of 3:2 that

was found for the $4d_{3/2,5/2}$ peaks in atomic Xe and Yb.

Paramagnetic ions in solids appear to offer the widest scope for multi-

plet-splitting studies. For half-filled shells such as $(d^5; \, ^6S_{5/2})$ or $(f^7; \, ^8S_{7/2})$

especially, exchange effects are expected to be very large. Fadley et al. (59)

reported splitting up to 6 eV for the Mn(3s) and Fe(3s) peaks in MnF_2, FeF_3,

and other salts of Mn^{2+} and Fe^{3+} $(3d^5; \, ^6S_{5/2})$. The splitting in these cases

is not negligible compared to the binding energies of the 3s electrons ($\sim$90 eV),

and the 3s peak intensity ratios were quite different from the simple multiplet

ratios expected from perturbation theory. In MnO_2 the $Mn^{4+}(3d^3)$ configuration

gave a smaller splitting, as expected. In iron metal evidence was found for

splitting in the 3s line, which is consistent with the presence of localized

spin moments on the iron atoms. For all of these cases the 3p line showed com-

plex behavior, arising from admixtures of other configurations into the final

^5P and ^7P states. The Mn and Fe spectra are shown in Figure 14.

Internal-conversion studies on the $^{57}Co(EC)^{57}Fe$ decay have also shown

evidence for splitting in the Fe(2s) line (60).

B.   Electrostatic Splitting

In multiplet splitting, as discussed above, both Coulomb and exchange

integrals with outer electrons in principle affect the inner-electron binding

energies.   Because of the spherical symmetries of the one-electron states,

however, the effects of the Coulomb integrals on the energies are identical

for singlet and triplet coupling.   Thus H_c did not contribute to the multi-

plet splitting.   When both the valence configuration and the inner orbital have

lower symmetry, however, Coulomb integrals can differ for different substates

and splitting may be present even when the electron spins are all paired.   We

denote this splitting as electrostatic.   There is an analogy between this effect

and crystal-field splitting, but it is a limited analogy because "point-charge"

assumptions are especially inappropriate for this case.

Electrostatic splittings of atomic core levels were first observed by

Novakov & Hollander (61) in 1964 by high-resolution internal conversion

spectroscopy. By placing radioactive sources of ^{233}Pa in a high external elec-

tric field, noticeable structure was induced in the internal conversion lines

involving atomic core $p_{3/2}$ orbitals. Later, similar results were obtained by

Novakov and colleagues (62,63) without the use of an external field, by

studying the conversion lines of a low energy (7.9 keV) nuclear transition

from the decay of ^{239}Np.

Subsequently, by means of photoelectron spectroscopy, Novakov &

Hollander (64) reported the observation of splitting in the $p_{3/2}$ levels of

thorium and uranium in several compounds. The splitting energy varied from

3-10 eV. With plutonium metal (oxidized surface) a $p_{3/2}$ splitting of about

16 eV was found. Some of their data are shown in Figure 15. In order to study

this effect in compounds for which the chemical bonding had been characterized

by other methods, photoelectron studies on linear complexes of Au(I) were

undertaken. Partially resolved splitting was observed in several cases (65).

In an attempt to explain these results a simple bonding model was

devised (66): In linear aurous complexes 6s6p hybrid bonding electrons, plus

the ligand atoms, create a strongly anisotropic charge distribution. Coulombic

interactions with the $5p_{3/2}$ shell lifted its degeneracy, splitting it into a

doublet $|5p_{3/2}, j_z = \pm \frac{3}{2}\rangle$ and another doublet $|5p_{3/2}, j_z = \pm \frac{1}{2}\rangle$. However,

quantitative agreement has not been attained. The observed splitting in

$KAu(CN)_2$, for example, is 1.8 eV, while this model gives only 0.2-0.3 eV. Thus

the origin of the splitting is unexplained.

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FIGURE CAPTIONS

Fig. 1. Half-life of ^{235}U isomer as a function of the average electronegativity

of the metal into which the U atoms were implanted. From reference 12.

Fig. 2. Photoelectron spectra of carbon 1s electrons from acetylene, ethylene,

and ethane relative to fluoroform. Radiation was Mg K$_\alpha$ x-rays. From

reference 16.

Fig. 3. Photoelectron spectrum of carbon 1s electrons from ethyl trifluoro-

acetate. From reference 1.

Fig. 4. Photoelectron spectrum of nitrogen 1s electrons from trans-dinitro

bis(ethylenediamine) cobalt(III) nitrate. From reference 17.

Fig. 5. Binding energy shifts versus halogen oxidation state for potassium

salts of oxy-halogen acids. Chlorine data were taken from reference 1, and

iodine data from reference 3. Bromine data were kindly provided by T. Carlson.

Fig. 6. Calculated binding-energy shifts of core electrons due to removing a

5p electron from various free-ion configurations of iodine, plotted against

position of radial maximum of core electron. Filled circles represent

experimental shift from KI to KIO$_4$. From reference 3.

Fig. 7. Experimental binding energy shifts for 1s electrons in small molecules

containing carbon, nitrogen, and oxygen (reference 21), plotted against

theoretical values obtained by the use of Koopman's theorem (reference 20).

Shifts were taken relative to NH_3, H_2O, and CH_4. Lines through data have

slopes 0.80 (N), 1.00 (O), and 0.95 (C).

Fig. 8. Calculated shifts in sulfur 2p binding energy, with and without

inclusion of 3d orbitals, versus experimental shifts. The two lines have

slopes 1.29 and 1.09, respectively. From reference 22.

Fig. 9. Experimental nitrogen 1s binding energies plotted against thermo-

chemical reaction energies, relative to NH_3. From reference 24.

Fig. 10. Correlations of nitrogen 1s-electron binding energies with atomic

charges calculated by a) modified Pauling valence bond model (reference

1), b) extended Hückel model (reference 17), and c) CNDO model (reference

17).

Fig. 11. Energy-level diagram for photoelectron studies with solid samples.

Note common Fermi energy of sample and spectrometer.

Fig. 12.   Density of states functions for twelve metals.   From reference 45.

Fig. 13.   Photoelectron spectra of N_2, NO, and O_2 showing multiplet splitting

. of 1s levels.   See reference 57.

Fig. 14.   Photoelectron spectra of Mn and Fe compounds, showing multiplet

splittings.   From reference 59.

Fig. 15.   Photoelectron spectra from thorium metal, uranium metal, and UO_3,

showing electrostatic splittings in $p_{3/2}$ levels.   From reference 64.
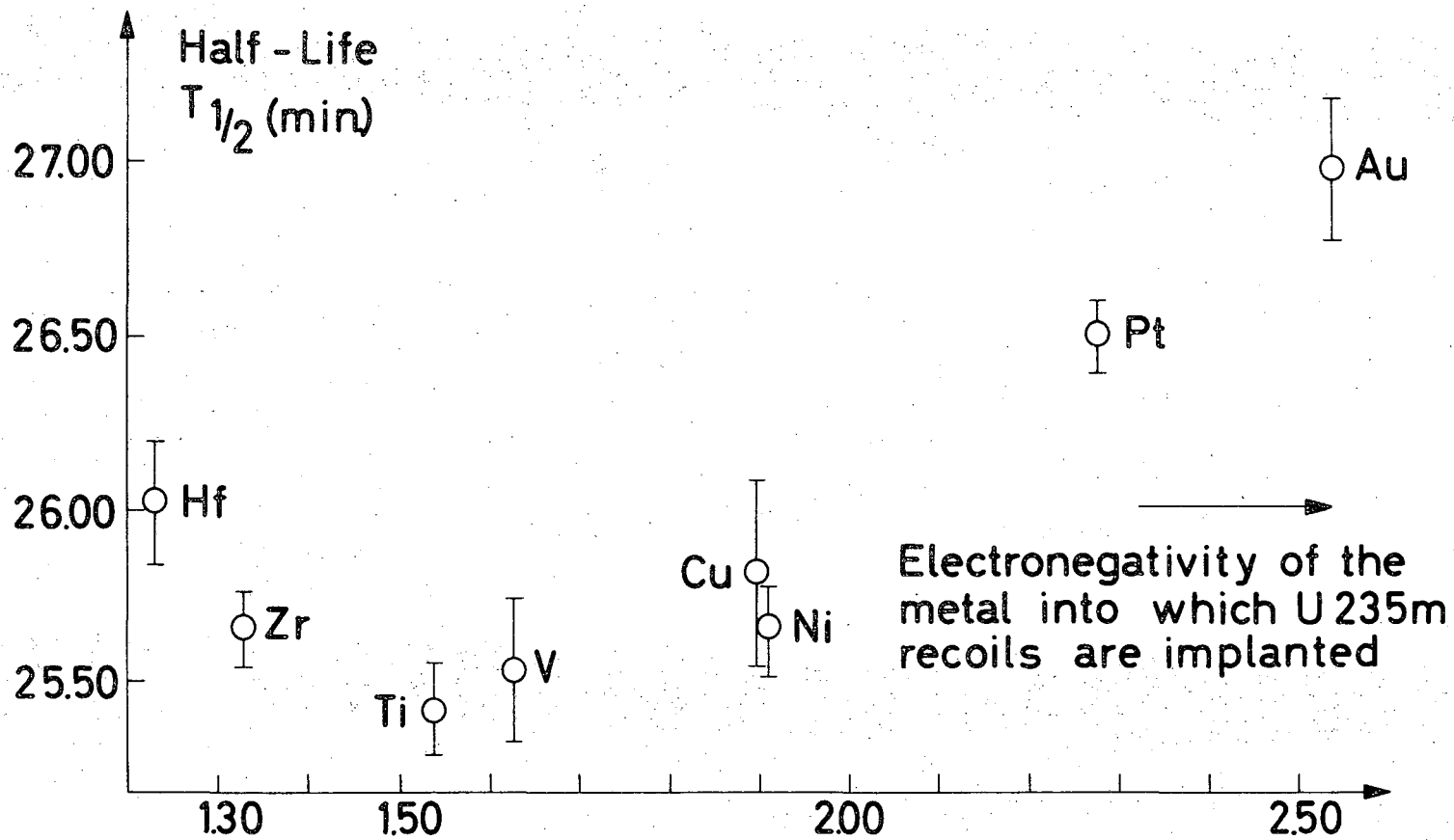
Half – Life
T 1/2 (min)

Electronegativity of the metal into which U 235m recoils are implanted

XBL 705-933

Fig. 1

Fig. 2

XBL697-3311

Fig. 3

XBL 698-1340

Fig. 4

XBL 696-2975

Fig. 5

i : 2s 3p 4p 5s 5p
2p 3d 3s 4s 4d

ΔE_b (eV)

— Classical
▲ ΔE_b^v (I, i, 4-3)
■ ΔE_b^v (I, i, 3-2)
△ ΔE_b^v (I, i, 2-1)
□ ΔE_b^v (I, i, 1-0)
○ ΔE_b^v (I, i, 0-[-1])
● ΔE_b^f (I, i, KIO_4-KI)

r_{max} (Bohr radii)
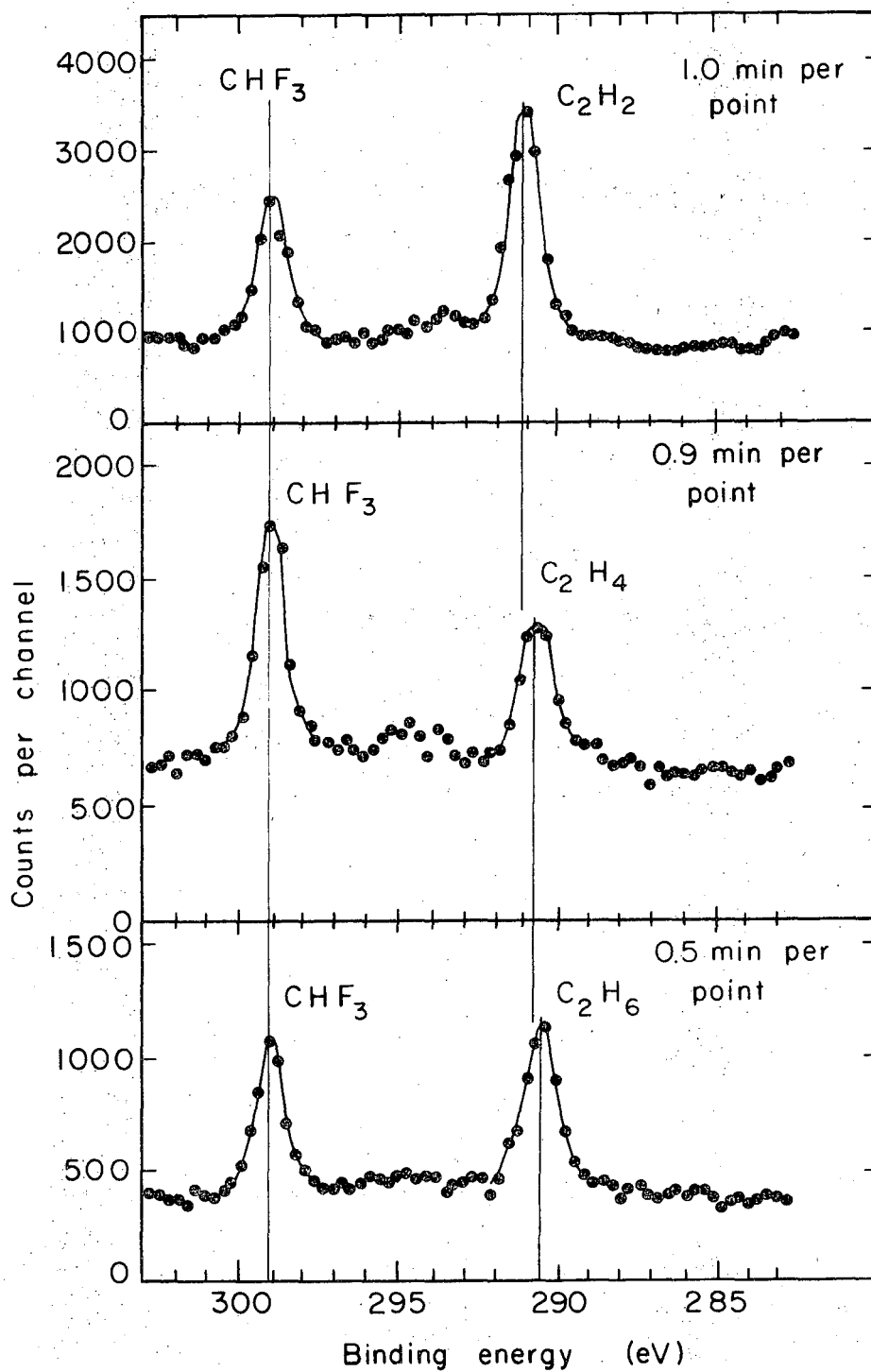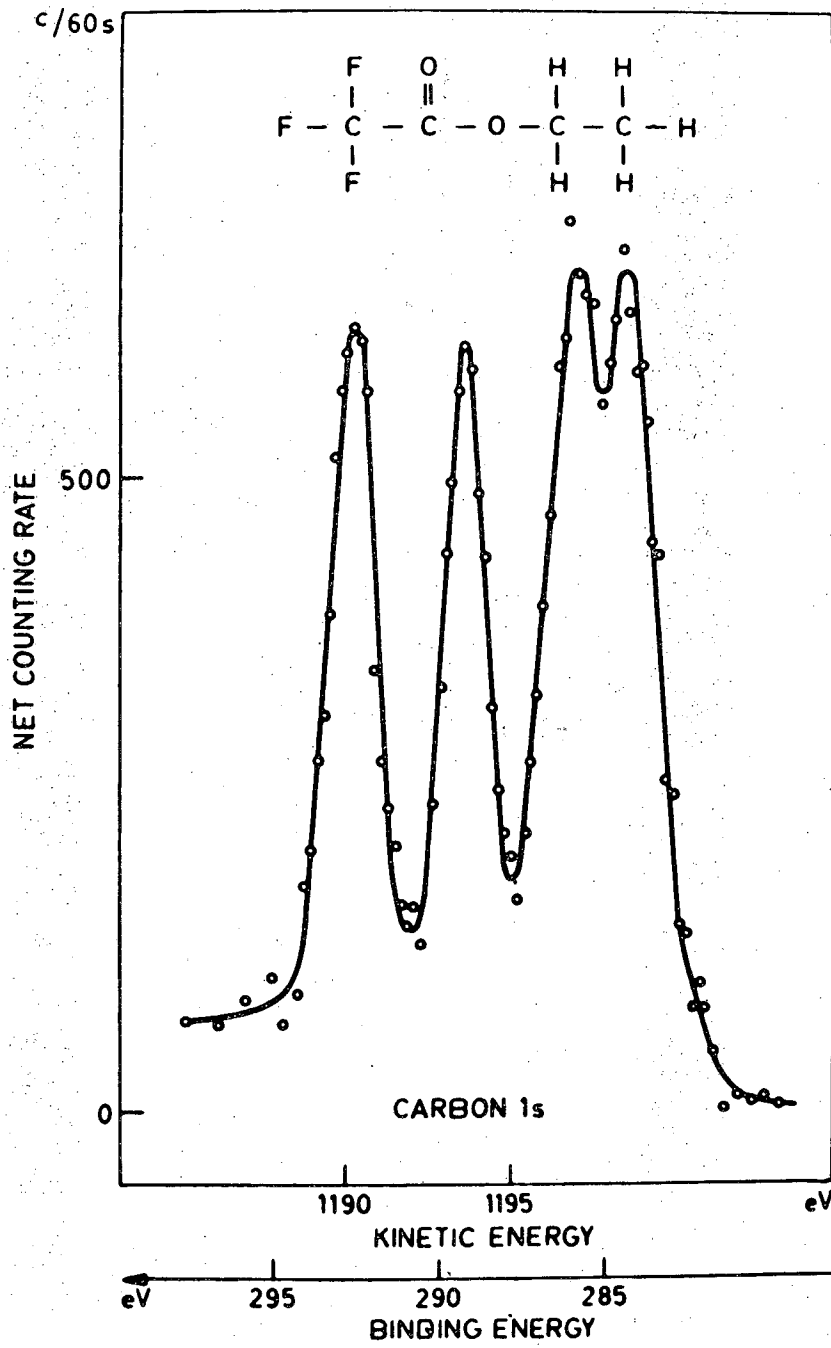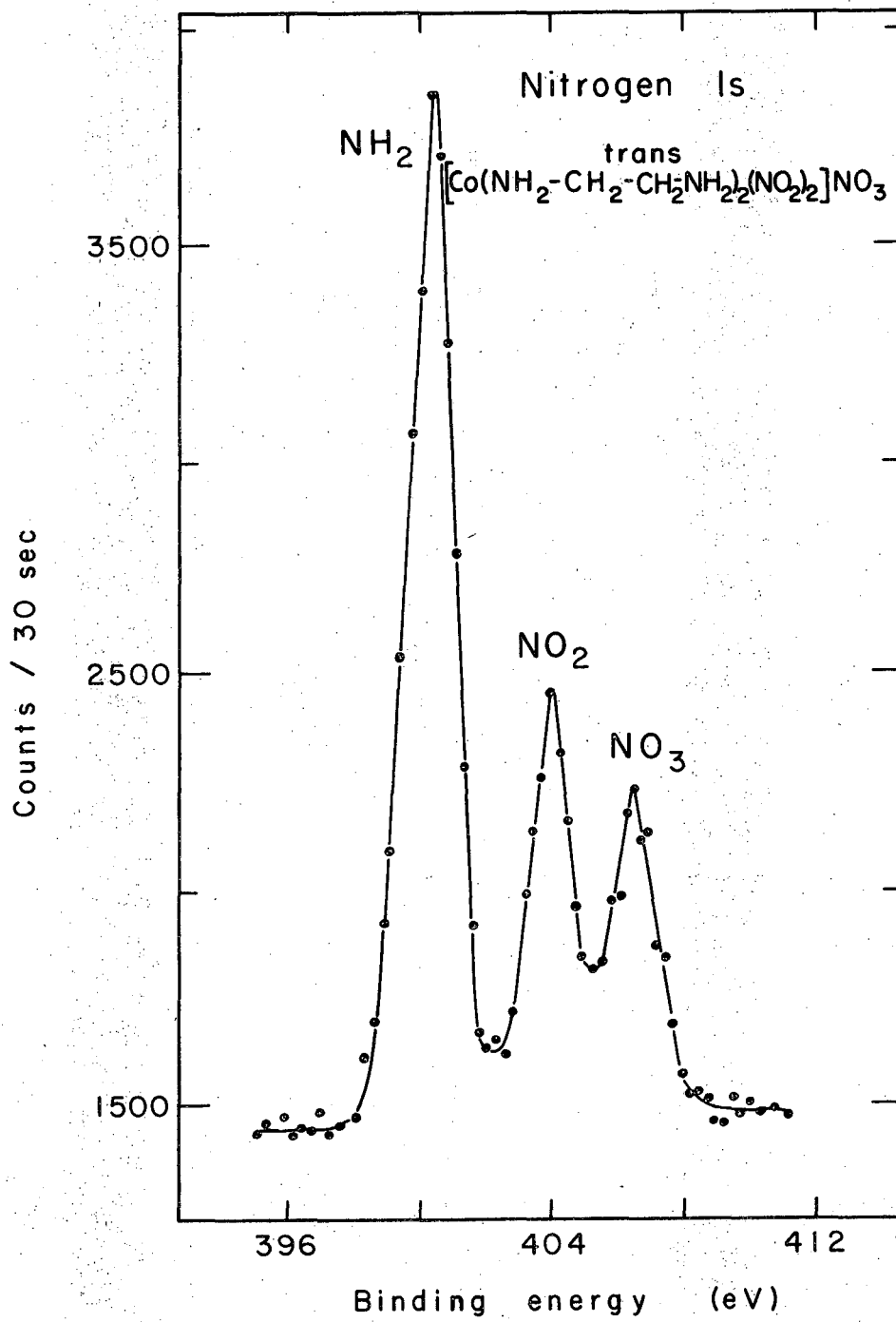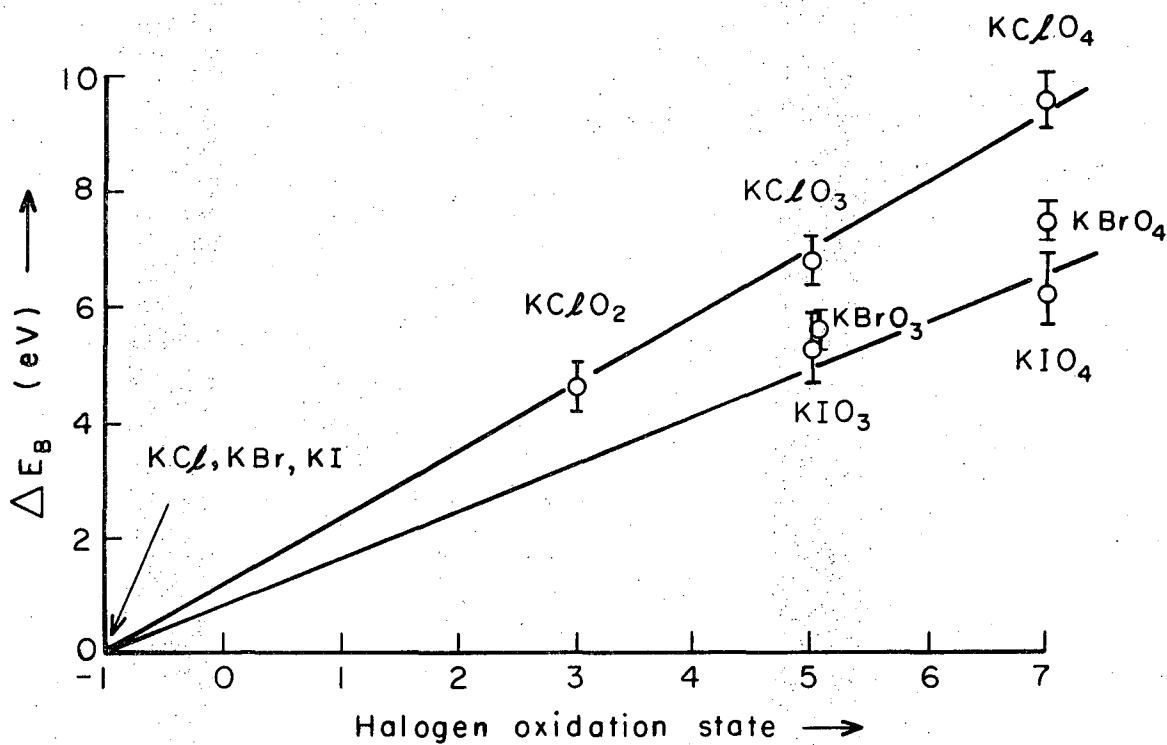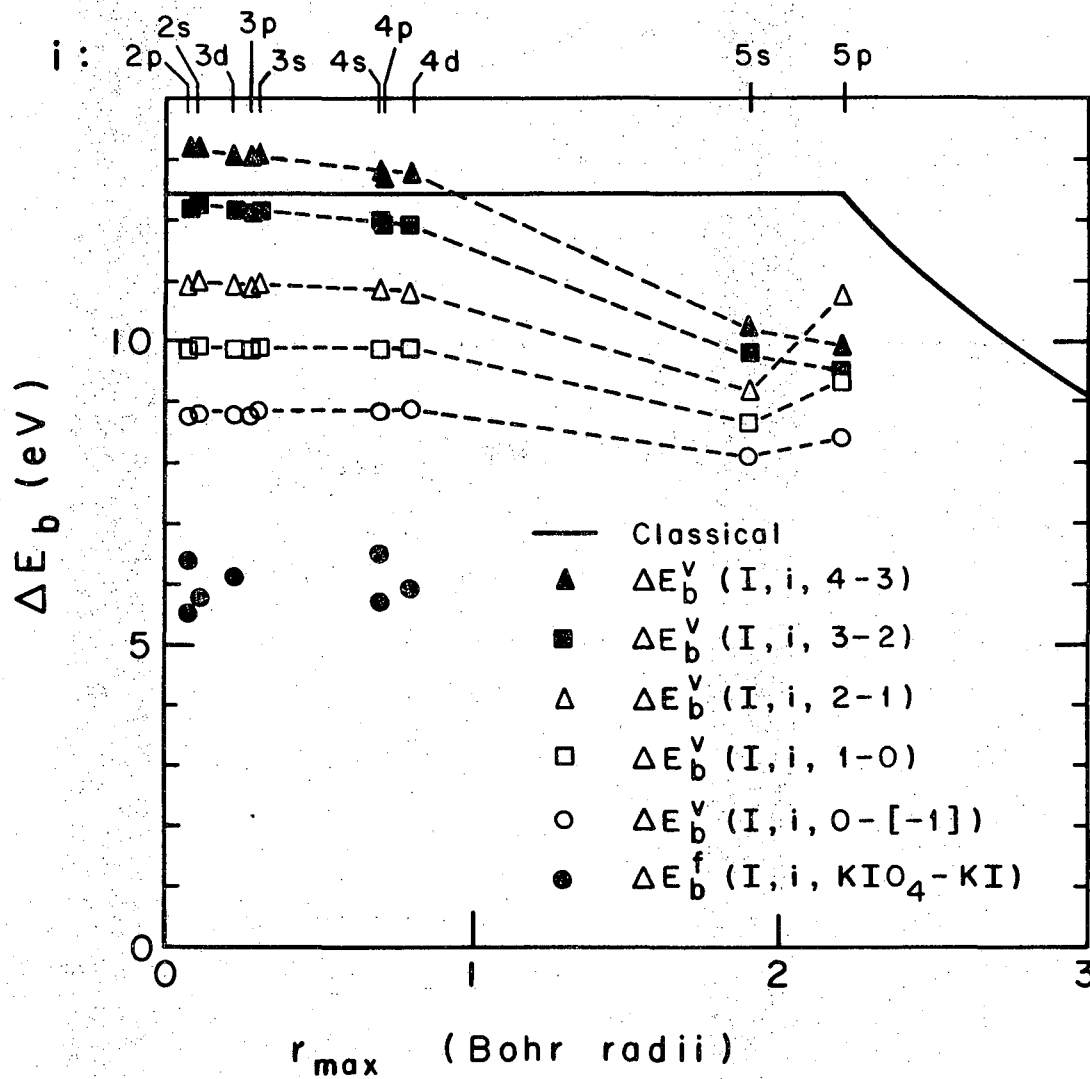
MUB-12292-A

Fig. 6
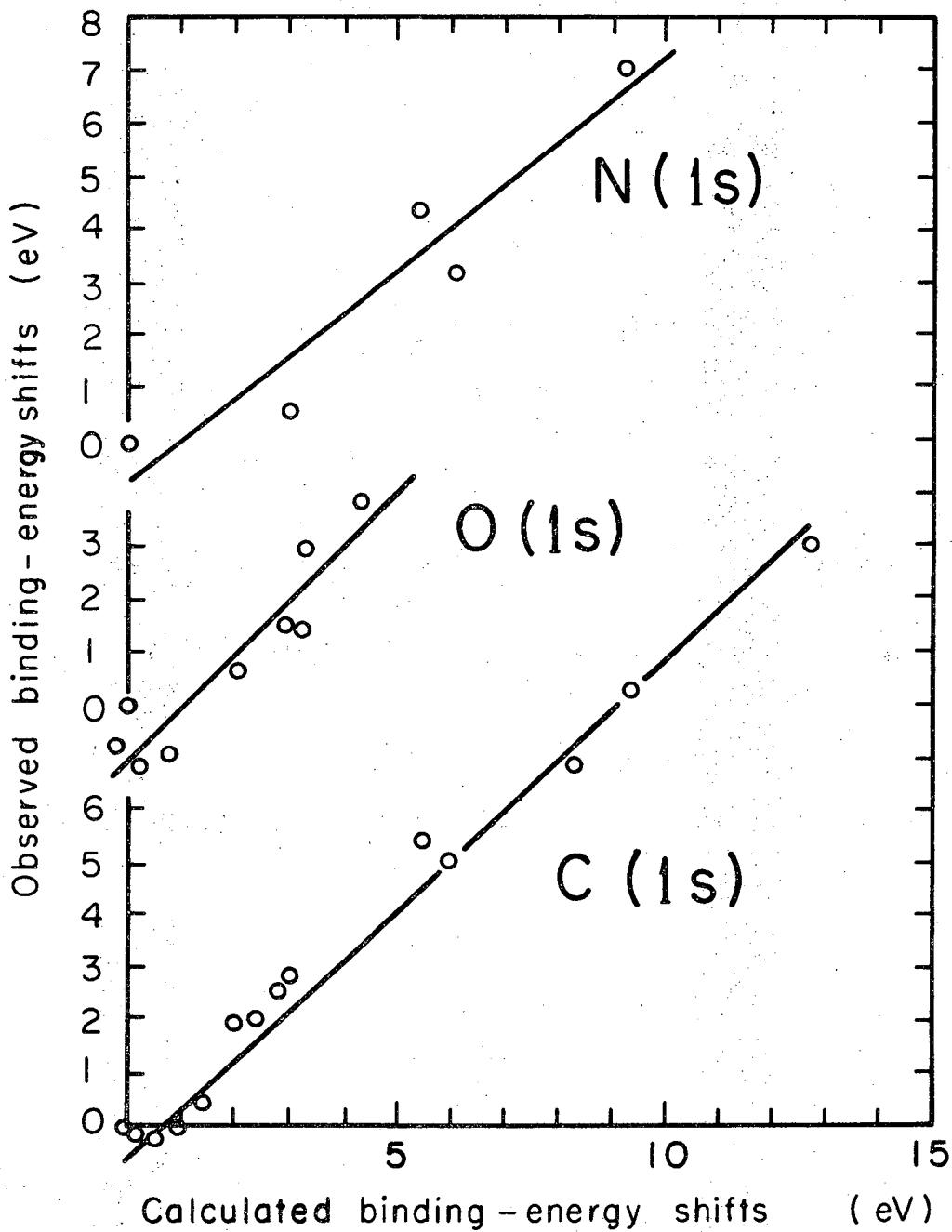
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Fig. 7
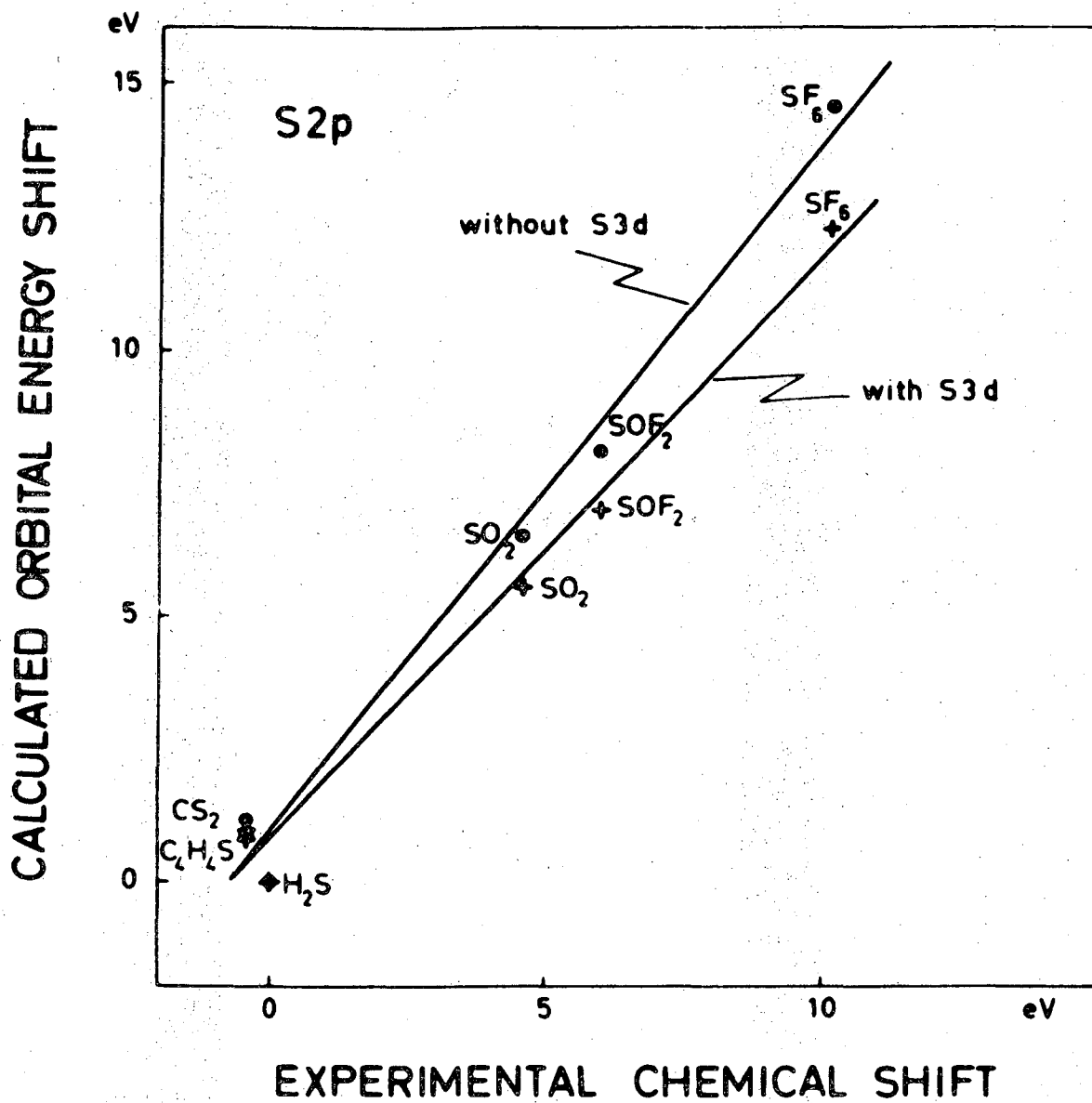
XBL 705-932

Fig. 8
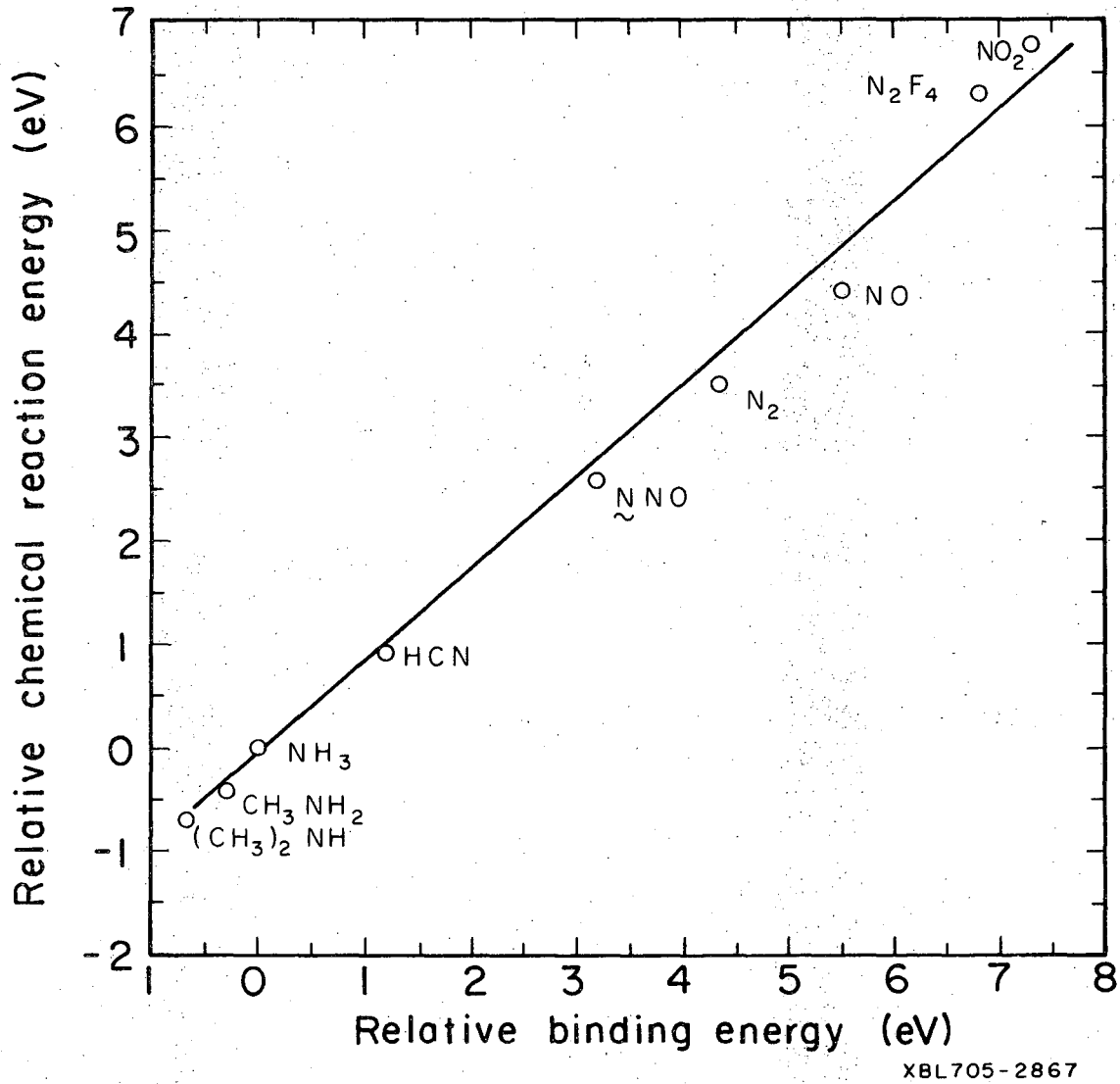
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Fig. 9
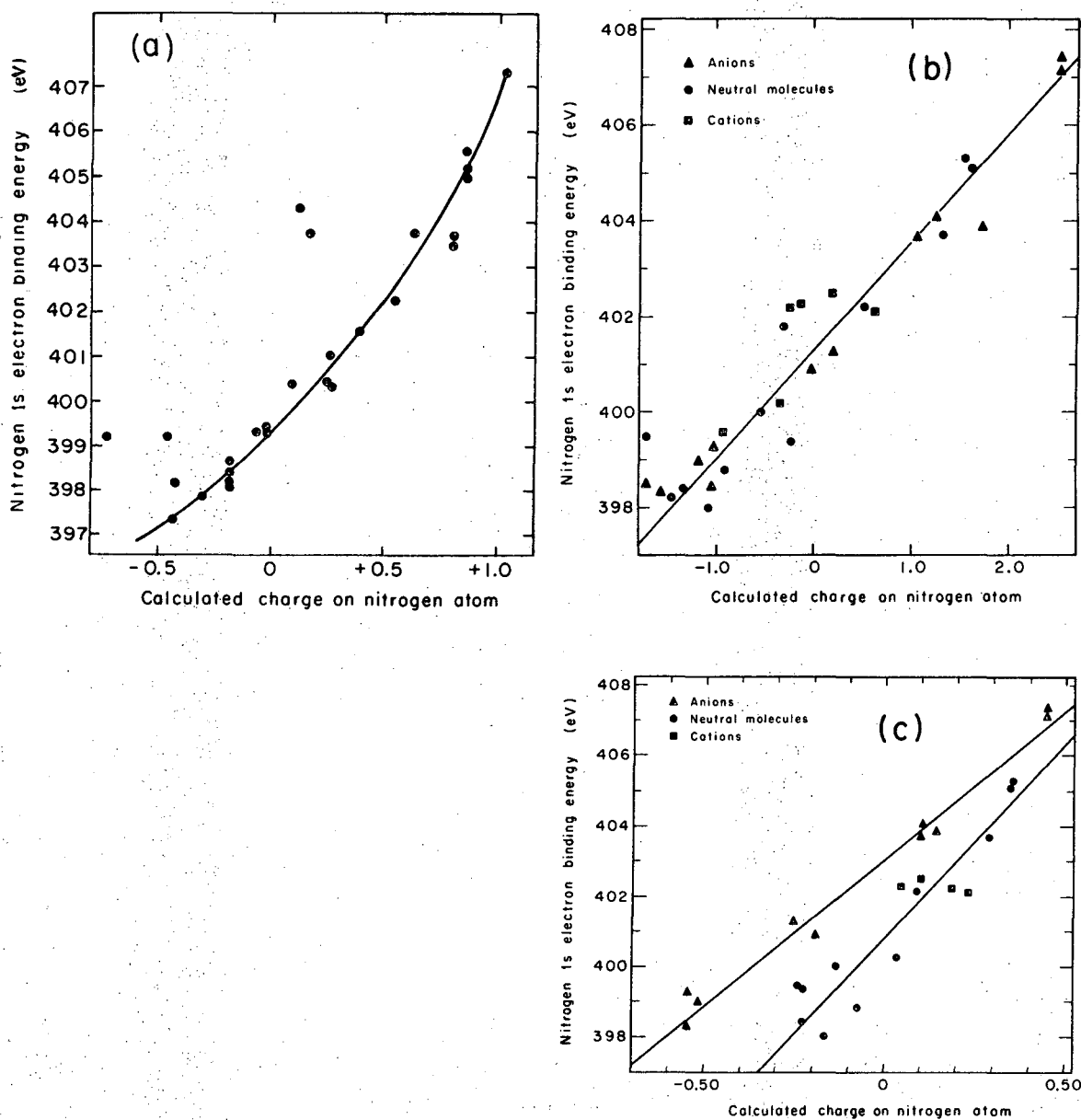
XBL 705-2865

Fig. 10
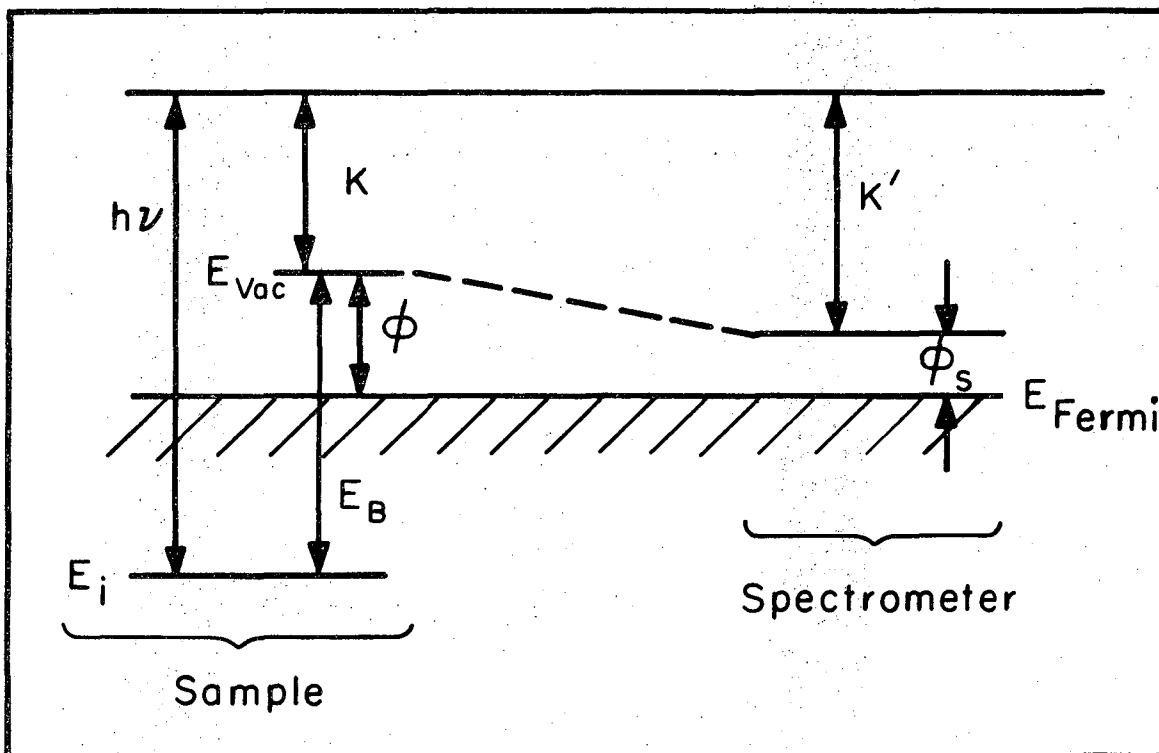
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Fig. 11
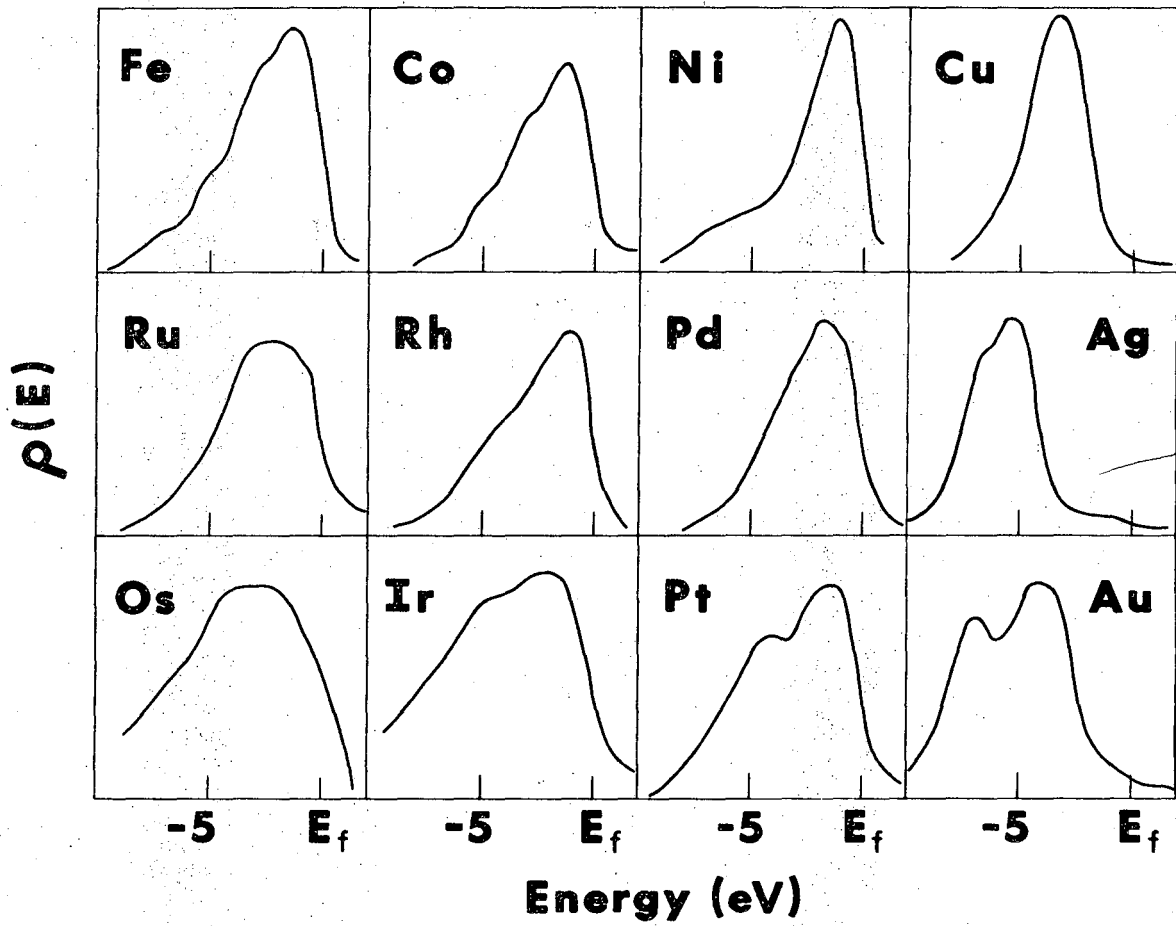
XBL 701-2059-A

Fig. 12

XBL 698-1342

Fig. 13

Fig. 14

Fig. 15