

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

THE APPLICATION OF X-RAY PHOTOELECTRON SPECTROSCOPY IN INORGANIC CHEMISTRY

### Permalink

<https://escholarship.org/uc/item/7kk6d7md>

### Author

Jolly, William L.

### Publication Date

1975-02-01

0 0 0 0 4 3 0 2 6 5 6  
Chapter in "Electron Spectroscopy,"  
Brundle and Baker, eds., Academic Press

LBL-3736

LAWRENCE  
RADIATION LABORATORY

c.1

MAR 31 1975

LIBRARY AND  
DOCUMENTS SECTION

THE APPLICATION OF X-RAY PHOTOELECTRON  
SPECTROSCOPY IN INORGANIC CHEMISTRY

William L. Jolly

February 1975

Prepared for the U. S. Atomic Energy Commission  
under Contract W-7405-ENG-48

**For Reference**

Not to be taken from this room



LBL-3736

c.1

## **DISCLAIMER**

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

The Application of X-Ray Photoelectron Spectroscopy  
in Inorganic Chemistry

by William L. Jolly

- I. Introduction
- II. The Equivalent Cores Approximation
  - A. Introduction and History
  - B. Prediction of Chemical Shifts
    1. Prediction from Chemical Reaction Energies
    2. Prediction from Estimated Chemical Reaction Energies
  - C. Other Aspects of the Method
    1. Relaxation Energy
    2. Comparison with the Potential Model
    3. Calculations for Monatomic Ions
    4. Vibrational Excitation of Molecules
      - (a) Effect on Binding Energy
      - (b) Effect on Line Width
    5. Estimation of Chemical Reaction Energies
- III. Correlation with Atomic Charge
  - A. Atomic Charge and the Potential Model
  - B. Solid Compounds
    1. Approximate Correlations
      - (a) Correlation with Q Alone
      - (b) Attempts to Include Potential Term
    2. Internal Referencing
      - (a) Mixed Valence Compounds
      - (b) Distinguishing Modes of Ligand Bonding
  - C. Gases
    1. Qualitative Interpretation of Chemical Shifts
      - (a)  $(\text{CO})_5\text{CrC}(\text{OCH}_3)\text{CH}_3$
      - (b) Hyperconjugation in Isoelectronic Compounds
    2. The "Transition State" Method
      - (a) Resonance in Core-Hole Ions
      - (b) Quantitative Treatment of Hyperconjugation

The Application of X-Ray Photoelectron Spectroscopy in Inorganic Chemistry

by William L. Jolly

Chemistry Department, University of California, and  
Inorganic Materials Research Division, Lawrence Berkeley Laboratory,  
Berkeley, California 94720

I. Introduction

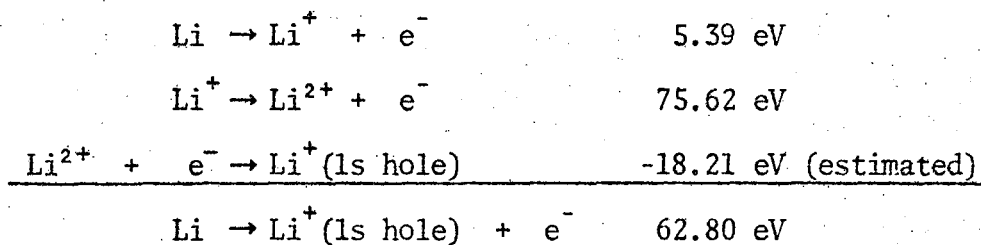
Excellent comprehensive reviews of the inorganic aspects of X-ray photoelectron spectroscopy have appeared in recent volumes of Electronic Structure and Magnetism of Inorganic Compounds<sup>1</sup> (from the Chemical Society series of Specialist Periodical Reports), and a review emphasizing applications of coordination chemistry was recently published.<sup>2</sup> Therefore in this chapter it was decided not to attempt a complete review of X-ray photoelectron spectroscopic studies of inorganic compounds, which would somewhat duplicate existing reviews, but rather to discuss certain important methods of systematization and to point out promising areas of research.

## II. The Equivalent Cores Approximation

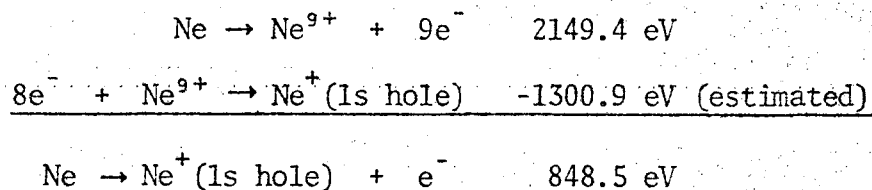
### A. Introduction and History

It is generally recognized that atomic core electrons are closely bound to the nucleus and that they are relatively inaccessible and inert compared to valence electrons. Therefore it is reasonable to assume that valence electrons are affected by the ionization of a core electron essentially the same as they would be by the addition of a proton to the nucleus. This approximation, in which an atomic core which lacks one electron is considered chemically equivalent to the complete core of the next element in the periodic table, is called the equivalent cores approximation.

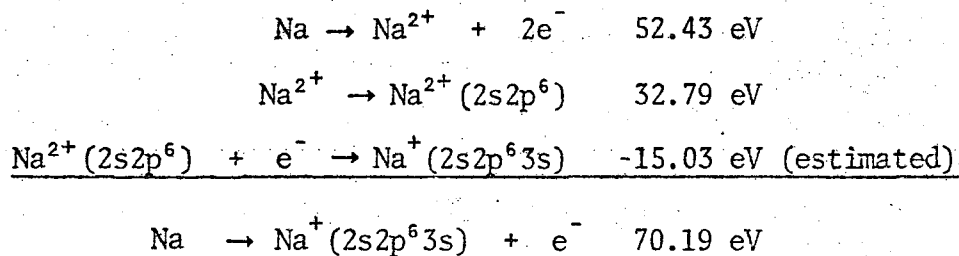
The approximation was used as long ago as 1932 by Skinner,<sup>3</sup> who calculated the 1s binding energy of lithium as the sum of three terms:<sup>4</sup>



The third term, the negative of the 2s binding energy of a lithium ion with the configuration (1s, 2s), was assumed to be equal to the negative of the ionization potential of  $\text{Be}^+$ . The experimental value<sup>5</sup> for the lithium 1s binding energy is 64.85 eV, in moderately good agreement with the estimated value, 62.8 eV. This type of calculation can give relatively poor estimates of 1s binding energies for atoms of higher atomic number.<sup>6</sup> Thus in the case of neon, we calculate



The energy of the second reaction is assumed to be the negative of the energy required to strip 8 electrons from  $\text{Na}^{+}$ . The estimated 1s binding energy is considerably lower than the experimental value, 870.2 eV.<sup>7</sup> Better results are obtained when calculations are made for a core which is well shielded by other electrons. For example, the 2s binding energy of sodium may be estimated as follows:<sup>8</sup>

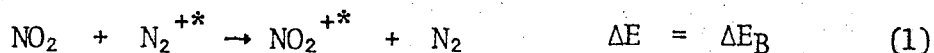


The energy of the third reaction is assumed to be the same as the negative of the ionization potential of  $\text{Mg}^{+}$ . In this case the estimated binding energy is within 1 eV of the experimental value,<sup>9</sup> 71.1 eV.

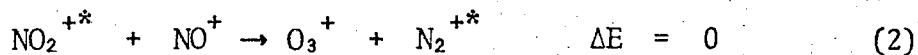
More recently, Best<sup>10</sup> has pointed out that it should be possible to correlate X-ray absorption edge data with thermodynamic data using the equivalent cores approximation. However a lack of the required thermodynamic data has prevented such correlations. Use of the equivalent cores approximation in the prediction of chemical shifts of core binding energies was first reported<sup>11-13</sup> in 1970, and since then the approximation has been widely applied in the systematization of core ionization data.

B. Prediction of Chemical Shifts

1. Prediction from Chemical Reaction Energies. - A chemical shift in core binding energy can be considered as the energy of a chemical reaction. For example, the difference between the nitrogen 1s energies of gaseous molecular nitrogen and nitrogen dioxide is the energy of the reaction



The asterisks indicate 1s holes. To transform this equation into one involving ground-state chemical species, we apply the equivalent cores approximation. We assume that the interchange of the +6 nitrogen core (with a 1s hole) in  $\text{NO}_2^{+*}$  and the +6 oxygen core in  $\text{NO}^+$  involves no energy.



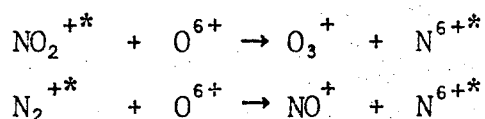
Addition of equations 1 and 2 yields equation 3.



Thus we find that the binding energy shift can be expressed as the energy (or heat) of an ordinary chemical reaction. The experimental binding energy shift,  $E_B(\text{NO}_2) - E_B(\text{N}_2)$ , is 3.0 eV;<sup>14</sup> this may be compared with the energy of reaction 3 as calculated from thermodynamic data, 3.3 eV. Similar comparisons for other nitrogen compounds are shown graphically in Fig. 1, where experimental shifts are plotted against the corresponding thermochemical energies. The straight line has unit slope; the average deviation of the points from the line is  $\pm 0.24$  eV.



It should be noted that the type of approximation made in equation 2, i.e. that the interchange of equally-charged cores involves no energy change, is not as severe an approximation as the assumption that the cores are chemically equivalent. Chemical equivalence corresponds to zero energy change for all substitution reactions of the following type.

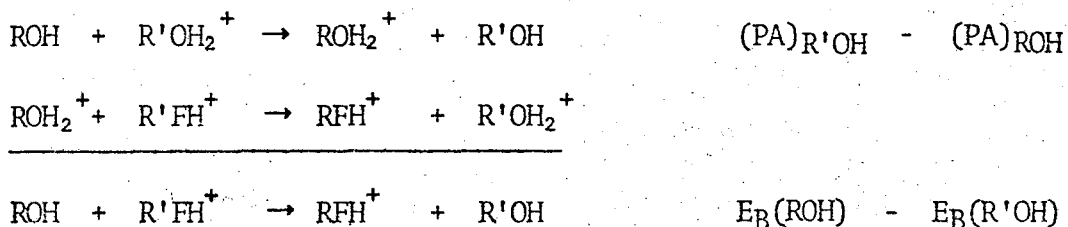


However when calculating chemical shifts, it is only necessary to assume that all such reactions involving the replacement of cores of a particular element have the same energy change, so that the difference in energy for any pair of reactions is zero.

The technique that we have just described - that is, the combination of the equivalent cores approximation with thermodynamic data to predict binding energy shifts - has also been successfully applied to gaseous compounds of boron,<sup>15</sup> carbon,<sup>16</sup> and xenon.<sup>13,16</sup> Relatively poor correlations were obtained for compounds of oxygen.<sup>16</sup> and fluorine,<sup>16</sup> principally because of the inaccuracy of the thermodynamic data employed. Application of the method to solid compounds is more complicated, requires assumptions, and is therefore less accurate than the application to gaseous compounds. However, fairly good correlations have been obtained for solid compounds of boron, carbon, nitrogen, and iodine.<sup>11,16</sup> In each case the correlation was restricted, because of the nature of the assumptions involved, to molecular compounds or to compounds in which the core-ionized atoms were in anions. It is hoped that further study will yield methods for treating all types of solids by this thermodynamic method.

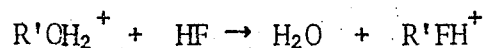
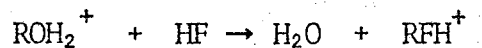
2. Prediction from Estimated Chemical Reaction Energies. -

When the experimental thermodynamic data required to calculate a binding energy shift by the equivalent cores method are unavailable, the data can sometimes be estimated or calculated with sufficient accuracy for use in the estimation of the binding energy shift. Various non-quantum mechanical methods for obtaining approximate thermochemical data have proved useful for estimating binding energy shifts for compounds of boron,<sup>15</sup> carbon,<sup>12</sup> fluorine,<sup>16</sup> and xenon.<sup>16</sup> It has recently been shown that, for a series of alcohols and a series of amines, the shifts in proton affinity are essentially equal to the corresponding negative shifts in the oxygen 1s and nitrogen 1s binding energies. (See Figures 2 and 3.) These results were taken as evidence that similar relaxation effects occur upon the attachment of a proton to an atom and upon the loss of a core electron from an atom. We shall now show that these results may also be rationalized by a simple extension of the equivalent cores method. We take as an example the oxygen 1s shift between two alcohols, ROH and R'OH. This binding energy shift may be taken as the energy of the sum of two reactions.



The energy of the first reaction is simply the proton affinity of R'OH less the proton affinity of ROH. The second reaction, for which we assume  $\Delta E = 0$ , corresponds to interchanging the isoelectronic groups

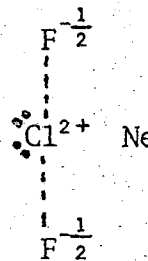
H<sub>2</sub>O and HF between the species ROH<sub>2</sub><sup>+</sup> and R'FH<sup>+</sup>. The assumption of ΔE = 0 does not require that ΔE = 0 for each of the following processes,



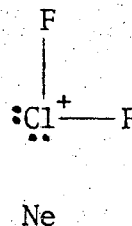
but rather that the energies of the two processes are equal. The assumption seems reasonable, particularly if the groups R and R' are similar. The fact that Figure shows Δ(PA) ≈ -ΔE<sub>B</sub> indicates that the assumption is justified.

It has been shown that even qualitative data can be useful for predicting which of two binding energies is the greater.<sup>19</sup> For example, in the case of chlorine trifluoride, core ionization of the two different types of fluorine atoms corresponds to the formation of two different neon-containing cations, as shown below.

Equivalent-cores representation of ClF<sub>3</sub> in which the equatorial fluorine has lost a 1s electron:



Equivalent-cores representation of ClF<sub>3</sub> in which an axial fluorine has lost a 1s electron:



As a rough but reasonable approximation, we may assume that only one orbital of the chlorine atom (a 3p orbital) is involved in bonding to the axial ligands and that the 3s and two 3p orbitals of the chlorine atom are used for the lone pairs and for bonding to the equatorial ligand. We also assume that, in each case, the bonding between the neon atom and the  $\text{ClF}_2^+$  ion is negligibly weak. Therefore the relative energies of the neon-containing cations are essentially the relative energies of the linear and bent form of  $\text{ClF}_2^+$ . Inasmuch as the linear  $\text{ClF}_2^+$  contains only two half-bonds, whereas the bent  $\text{ClF}_2^+$  contains two full bonds, it is clear that the linear ion has the higher energy. Hence one predicts correctly that the binding energy of the equatorial fluorine is higher than that of the axial fluorines. The experimental values<sup>19</sup> are 694.76 and 692.22 eV, respectively, corresponding to a 2.54 energy difference between the two  $\text{ClF}_2\text{Ne}^+$  ions.<sup>20</sup>

Quantum mechanical methods for estimating chemical shifts, using the equivalent cores approximation, are attractive for at least three reasons: (1) in general, only closed-shell calculations are required, (2) the difference in energy between two isoelectronic species can be calculated more accurately than the absolute energy of either species, and (3) the calculations can be made for isoelectronic species with identical geometries, corresponding to a photoelectric process in which the nuclei remain fixed. The CNDO/2<sup>16,21</sup> and MINDO/1<sup>22</sup> methods have given calculated binding energy shifts which are linearly correlated with the experimental shifts but which are in poor quantitative agreement with the experimental shifts. The poor quantitative agreement is probably due to the failure of the semiempirical methods to give accurate energies for the ionic species. On the other hand, ab initio calculations have generally given very good results.<sup>23-25</sup>

In comparisons of experimental data with predictions based on Koopmans' theorem, hole-state calculations, and equivalent core calculations, the best results are consistently obtained with the equivalent cores calculations. The only poor result by the latter method was obtained for the carbon 1s shifts between CO and transition metal carbonyl complexes.<sup>26</sup> This result was probably due to the inadequacy of the computational methods used for the relatively complicated transition metal carbonyl complexes.

### C. Other Aspects of the Method

1. Relaxation Energy. - When a core electron is ejected from an atom in a molecule, the other electrons in the molecule tend to migrate toward the positive hole. In the early days of X-ray photoelectron spectroscopy, it was not known with certainty whether or not this electronic relaxation is complete in the time required for the ejected electron to leave the vicinity of the molecule - that is, it was not known whether or not the measured binding energy corresponds to the difference in energy between the ground state and a relaxed hole state. The equivalent cores thermodynamic method for estimating chemical shifts involves the use of thermodynamic data for ordinary ground-state ("relaxed") chemical species. Therefore we may conclude that, at least to the accuracy with which chemical shifts can be predicted by the equivalent cores method, measured binding energies do correspond to the formation of electronically relaxed hole states.<sup>11</sup>

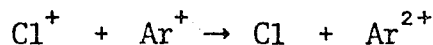
Three-dimensional perspective plots of electron density, obtained from ab initio calculations, permit a qualitative visualization of the

electronic relaxation accompanying core electron ejection. In Figure 4 is shown a plot of the difference in electron density between the ground-state carbon monoxide molecule and the same molecule with an oxygen 1s hole.<sup>27</sup> The two atoms lie on the grid plane; surfaces above the plane correspond to regions where electron density decreases upon ionization, and surfaces below the plane correspond to regions where electron density increases upon ionization. It can be seen that considerable electron density is lost from a shell immediately around the nucleus and that smaller amounts of electron density are lost from the internuclear region and from the outer periphery of the oxygen atom. Most of the increase in electron density occurs in the valence shell of the oxygen atom. Figure 5 is a plot of the valence electron density of  $\text{CO}^{7+}$  less the valence electron density of  $\text{CF}^+$ . The changes are rather small except in the region of the 1s shell. If the  $\text{O}^{7+}$  and  $\text{F}^{7+}$  cores were exactly equivalent, the surface of Fig. 5 would be perfectly flat.

2. Comparison with the Potential Model. - Binding energy shifts are largely caused by changes in the electrostatic potential experienced by core electrons on going from one molecule to another. On this basis, Basch<sup>28</sup> and Schwartz<sup>29</sup> developed a quantum mechanical potential model for correlating chemical shifts. Shirley<sup>30</sup> has pointed out that, to a certain approximation, the potential model and the equivalent cores thermodynamic method are based on the same assumption. However the potential model derived by Schwartz involves ground state potentials, whereas the thermodynamic method takes electronic relaxation into account; hence the two methods are not equivalent. As we shall

later show, the potential model can be modified to include relaxation energy - but by an application of the equivalent cores approximation!

3. Calculations for Monatomic Ions. - Core binding energies for gaseous ions have not yet been measured. However, quantum mechanical calculations can give binding energies for gaseous atoms and ions which, although somewhat uncertain on an absolute scale, can be used to calculate accurate chemical shifts. Thus Siegbahn et al.<sup>31</sup> have calculated the 1s binding energy shifts for several ions of sulfur and chlorine. However, the same chemical shifts can be very easily obtained by the equivalent cores method using optical spectroscopic data.<sup>4</sup> For example, the chemical shift between  $\text{Cl}^+$  and Cl is taken as the difference between the second ionization potential of argon and the first ionization potential of chlorine:



In Table I the calculated chemical shifts, both with and without inclusion of electronic relaxation energy, may be compared with the corresponding equivalent-cores values. As expected, the values calculated including relaxation energy are in better agreement with the equivalent-cores values. The average deviation between corresponding values (omitting the  $\text{S}^{6+}$  and  $\text{Cl}^{7+}$  values, which are in poor agreement) is  $\pm 0.25$  eV. This good agreement is surely not fortuitous and attests to the general accuracy of both methods.

Table I.

## Calculated 1s Shifts for Gaseous Ions

Atom	Q	SCF-HFS Calcns. <sup>31</sup>		Equiv.-Cores Calc.
		Without Relaxation	With Relaxation	
S	-1	-9.2	-11.3	-10.9
	0	0	0	0
	+1	12.3	13.8	13.4
	+2	27.1	29.8	29.9
	+3	44.0	48.1	48.4
	+4	62.9	68.5	68.9
	+6	109.1	115.0	119.4
Cl	-1	-10.3	-12.4	-12.1
	0	0	0	0
	+1	13.4	14.9	14.6
	+2	29.2	32.2	31.7
	+3	47.2	51.5	51.6
	+5	89.2	96.4	96.6
	+7	141.0	148.4	153.1



4. Vibrational Excitation of Molecules. - The thermodynamic equivalent cores method for predicting chemical shifts for molecules involves an approximation not required in the case of monatomic ions. Although the photoelectric process forms hole-state molecule-ions with geometries the same as those of the ground-state molecules, thermodynamic data for the equilibrium geometries of the isoelectronic species are used in the calculations. In general, the equilibrium geometries of the isoelectronic species are different. For example, the equilibrium bond distances in  $\text{CN}^-$ ,  $\text{CO}$ , and  $\text{N}_2$  are 1.14, 1.128, and 1.098 Å, respectively. From the potential energy-bond distance data for  $\text{CO}$  and  $\text{N}_2$  we calculate that, because of the neglect of the strain energy of the excited states, the thermodynamic equivalent cores method is in error by about 0.04 and 0.13 eV in the case of the nitrogen 1s and carbon 1s binding energies of  $\text{CN}^-$ , respectively.<sup>11</sup> Because most of the bond distance changes accompanying the core ionization of a given element are in the same direction, errors of this type tend to cancel when binding energy shifts are calculated. However, Shaw and Thomas<sup>32</sup> point out a case in which the error may be fairly serious. The fluorine 1s shift between  $\text{HF}$  and  $\text{F}_2$  corresponds to the following reaction.



Calculations<sup>33</sup> indicate that the equilibrium bond length of  $\text{HNe}^+$  differs from that of  $\text{HF}$  by about 7%, whereas the bond length of  $\text{NeF}^+$  differs from that of  $\text{F}_2$  by about 16%. From the calculated potential energy curve for  $\text{NeF}^+$ , one calculates that  $\text{NeF}^+$  with a bond distance equal to that of  $\text{F}_2$  would be 0.7 eV above its ground state energy. It

should be noted that the calculated bond distances of  $\text{NeF}^+$ , as well as the potential energy curve, are quite uncertain. Unfortunately the energy of formation of  $\text{NeF}^+$  is not known with enough certainty to permit a meaningful comparison of the equivalent cores estimate with the experimental chemical shift. However Shaw and Thomas did find essentially perfect agreement between the equivalent cores estimate and the experimental shift in the case of the fluorine 1s shift between HF and the gaseous  $\text{F}^-$  ion.

Probably the most important effect of the change in equilibrium geometry accompanying core ionization of a molecule is the broadening of the photoline. Spectra for molecules frequently show asymmetric lines under high resolution. This asymmetry has been attributed to Franck-Condon transitions between ground and hole states having different geometries.<sup>34,35</sup> For example, highly accurate calculations<sup>36</sup> for methane have shown that the loss of a carbon 1s electron should cause a reduction in the equilibrium C-H bond distance of 0.05 Å. This displacement is sufficient to cause the appearance of two excited vibrational bands in the spectrum and accounts for the asymmetry of the XPS line. Application of the equivalent cores approximation would have made the calculations much simpler and would probably have given results of comparable accuracy. The equilibrium bond distance of  $\text{NH}_4^+$  is 0.057 Å shorter than that of  $\text{CH}_4$ , and accurate potential energy-bond distance data are available for both species.

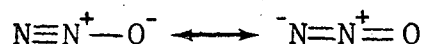
The equivalent cores approximation, in combination with appropriate potential energy data, has been used to account quantitatively for the fact that the carbon 1s line of CO is much broader (FWHM 0.82 eV) than

the nitrogen 1s line of  $N_2$  (FWHM 0.46 eV).<sup>34,35</sup> In each case, the equivalent cores stand-in for the hole-state ion is  $NO^+$ . The equilibrium bond distance of  $NO^+$  is 0.066 Å shorter than that of CO and 0.036 Å shorter than that of  $N_2$ . The fact that the very small difference in bond distance between CO and  $N_2$  causes a large difference in the line width is due to the fact that vibrational broadening is quadratically, not linearly, related to the relative displacement of the potential curves.

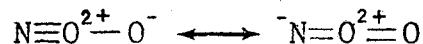
In general, a core ionization causes a contraction of the valence electron cloud in the immediate vicinity of the atom, corresponding to a reduction of both the atomic size and the equilibrium bond distances. This contraction of the equilibrium distances is favored when the atom which undergoes core ionization is negatively charged and hence has an easily contracted electron cloud. Thus we can account for the fact that the carbon 1s line of  $CH_4$  is broader than that of  $CF_4$ , that the sulfur 2p line of the terminal sulfur atom in the  $S_2O_3^{2-}$  ion is broader than that of the central sulfur atom in that anion, and that the nitrogen 1s line of  $NH_4^+$  is broader than that of  $NO_3^-$ .<sup>34</sup> However it is important to recognize that this correlation of atomic charge with line width is valid only when the formal bond orders of all the bonds in the molecule are unchanged upon ionization of the core. Two examples in which the latter condition is not fulfilled are discussed in the following paragraphs.

When a core electron is lost from the terminal nitrogen atom of

$N_2O$ , the equilibrium N-N bond distance probably increases and the equilibrium N-O bond distance probably decreases. This conclusion is reached by consideration of the equilibrium bond distances in  $N_2O$  ( $r_{N-N} = 1.129 \text{ \AA}$  and  $r_{N-O} = 1.187 \text{ \AA}$ ) and  $NO_2^+$  ( $r_{N-O} = 1.154 \text{ \AA}$ ). The same conclusion may be reached by consideration of the valence-bond resonance structures for these isoelectronic species. In  $N_2O$ , the N-N bond order is between 2 and 3 and the N-O bond order is between 1 and 2 because of the predominance of the resonance structures



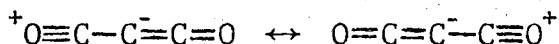
In  $O=N^+=O$ , the N-O bond order is exactly 2. Thus we conclude that the ionization of the terminal nitrogen atom of  $N_2O$  produces an ion in a strained configuration (in a steep region of the potential energy surface) and that the photoline should be vibrationally broadened. On the other hand, core ionization of the middle nitrogen atom of  $N_2O$  produces a species for which we may write the following resonance structures, using the equivalent-cores approximation



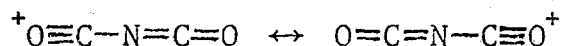
The relative weights of these structures are probably similar to those for the analogous structures of  $N_2O$ . For this reason, and also because the middle nitrogen atom is positively charged and not subject to much contraction, the core-hole ion is produced in a relatively unstrained state and the photoline for the middle nitrogen atom is not expected to be strongly vibrationally broadened. Indeed, these predictions are in accord with the facts: the FWHM of the terminal nitrogen line

is 0.70 eV; that for the middle nitrogen atom is 0.59 eV.<sup>34</sup>

The carbon 1s spectrum of C<sub>3</sub>O<sub>2</sub> consists of a relatively broad line corresponding to the outer carbonyl carbon atoms and a relatively narrow line corresponding to the middle carbon atom.<sup>37</sup> The ground state of the molecule can be represented by the valence bond structure O=C=C=O, with small contributions from the resonance structures



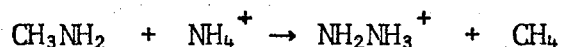
The ion formed by core ionization of the middle carbon atom can be represented, using the equivalent-cores approximation, by the structure O=C=N<sup>+</sup>=C=O. However, because of the greater electronegativity of the nitrogen atom, the contribution of the resonance structures



is somewhat greater than the contribution of the analogous structures in the ground state. This change in the weighting of the resonance structures tends to increase the equilibrium C-C bond lengths. However this tendency is counteracted by the tendency for the middle carbon atom (which is more negatively charged than the outer ones) to contract and shorten the equilibrium C-C bond distances. The result is a negligible change in the equilibrium C-C distances, a slight shortening of the equilibrium C-O distances, and a relatively narrow photoline. The ion formed by ionization of an outer carbon atom can be represented mainly by the structure O-C=C=N<sup>+</sup>=O. However, because of electrostatic interactions, the contribution of the resonance structure <sup>+</sup>O≡C-C≡N<sup>+</sup>-O<sup>-</sup> is probably greater, and that of the resonance structure O=C=C<sup>-</sup>-N<sup>+</sup>≡O<sup>+</sup> is probably less, than

the contributions of the analogous structures in the ground-state  $C_3O_2$  molecule. The outer carbon atoms of  $C_3O_2$  are relatively positively charged and would not tend to contract much on core ionization. Hence the ionization produces the ion in a strained configuration, causing a vibrationally broadened line.

5. Estimation of Chemical Reaction Energies. - Instead of using thermodynamically derived chemical reaction energies to estimate core binding energy shifts, the procedure can be reversed, and binding energy shifts can be used to estimate thermodynamic data.<sup>11,16</sup> In this way one can use chemical shift data to calculate the energies of a wide variety of unusual species. For example, the carbon 1s chemical shift between  $CH_4$  and  $CH_3NH_2$  corresponds to the energy of the following reaction.<sup>38</sup>



In this reaction, the heats of formation are known for all the species except  $NH_2NH_3^+$ . By combining the known heats of formation with the experimental binding energy shift, we calculate  $\Delta H_f^\circ = 169$  kcal/mol for  $NH_2NH_3^+$ . From this value and the known heats of formation of  $N_2H_4$  and  $H^+$ , we calculate the proton affinity of hydrazine to be 221 kcal/mol.

The absorption spectrum of  $N_2$  in the 30-Å region shows lines corresponding to the excitation of 1s electrons to outer-shell orbitals of the nitrogen molecule.<sup>39</sup> By using the equivalent-cores approximation, these excited levels have been interpreted as the ground state and excited levels of the NO molecule. Similar interpretations have been

made for energy loss spectra for 2500-eV electrons in  $N_2$ ,<sup>40</sup>  $CO$ ,<sup>40</sup>  $CH_4$ ,<sup>41</sup>  $NH_3$ ,<sup>41</sup> and  $H_2O$ .<sup>41</sup> From the measured energies for the latter three species, it was possible to estimate the heats of formation of the  $NH_4$ ,  $OH_3$ ,<sup>and</sup>  $H_2F$  radicals.<sup>41</sup>

### III. Correlation With Atomic Charge

#### A. Atomic Charge and the Potential Model

It was early recognized that a core binding energy of an atom should be related to the effective charge of the atom. From simple electrostatic considerations, one would expect that the energy for removing an electron from an atom would be inversely related to the valence electron density on the atom; that is, that binding energy would increase with increasing positive atomic charge and decrease with increasing negative atomic charge. Consideration of a simple shell model of the atom leads to the linear relation<sup>31</sup>

$$E_B = kQ + \ell \quad (4)$$

where  $E_B$  is the binding energy for a particular core level in an atom,  $Q$  is the charge of the atom, and  $k$  and  $\ell$  are empirical constants. Many sets of binding energy data can be correlated using this equation. When the compounds involved have closely related structures and similar types of bonding, fairly good correlations are obtained using even extremely crude methods for estimating atomic charges. When the compounds involved differ markedly in structure and bonding, relatively poor correlations are obtained and little improvement in the correlation is obtained by using more sophisticated methods for estimating atomic charges.

In general, to obtain a good correlation of binding energy with atomic charge, one must take account of the electrostatic potential due to the charges on all the other atoms in the compound. In other



words, one must consider not only the work to remove the electron from the atom which loses the core electron, but also the work to remove the electron from the field of the surrounding charged atoms. This can be accomplished by using the so-called potential model equation<sup>7</sup>

$$E_B = kQ + V + \ell \quad (5)$$

where  $V$  is the coulomb potential energy at the hypothetical vacated site of the atom in the midst of the other atoms of the compound. This equation gives good results when (a) a reasonably good method for estimating atomic charges is used and (b) the electronic relaxation energies of the compounds are very similar in magnitude. When one correlates compounds for which the relaxation energies differ significantly, the equation must be modified to include a term that accounts for the differences in relaxation energy:<sup>4,2</sup>

$$E_B = kQ + V + \ell + E_R \quad (6)$$

## B. Solid Compounds

1. Approximate Correlations. - The Pauling method<sup>4,3</sup> for estimating atomic charges involves the assumption that the partial ionic character of a bond is given by the relation

$$I = 1 - e^{-0.25(\Delta x)^2}$$

where  $\Delta x$  is the difference between the electronegativities of the bonded atoms. Many investigators have used this method, or modifications of it, to calculate atomic charges for the correlation of binding energies according to equation 4. For example, Matienzo et al.<sup>4,4</sup> found a good

correlation between the calculated charge on nickel atoms in some simple salts of nickel(II) and the corresponding nickel  $2p_{3/2}$  binding energies. A plot of their data is shown in Figure 6. The success of this correlation is probably partly due to the facts that the nickel ions in most of the compounds are similarly coordinated (octahedrally) and the ligands are relatively simple. Hughes and Baldwin<sup>45</sup> found a good correlation between molybdenum atom charges in a variety of triphenylphosphine molybdenum complexes and the molybdenum  $3d_{3/2}$  binding energies. A plot of their data is given in Figure 7. In this case the good correlation is probably attributable to the fact that the compounds are all neutral complexes with similar coordination numbers.

Remarkably small chemical shifts are observed for monatomic ions and for atoms in polyatomic ions upon going from one salt to another by changing the counter-ion. For example, in a series of sixteen different potassium salts, the overall spread in the K 2p binding energy (between KCl and  $K_2[Pt(NO_2)_4Cl_2]$ ) is only 1.7 eV.<sup>46</sup> Both the N 1s and P 2p binding energies of a wide variety of salts containing the bis(triphenylphosphine)-iminium cation,  $N[P(C_6H_5)_3]_2^+$ , differ by only a few tenths of an electron volt.<sup>47</sup> The F 1s binding energies in  $UF_4$  and LiF differ by only 1.7 eV.<sup>48</sup> The minor effect of crystal environment on chemical shift, illustrated by these data, is particularly surprising when the changes in the theoretical point-charge lattice potentials are considered. In the case of simple salts such as KCl and LiF, if it is assumed that the ions bear unit charges, chemical shifts between two different salts of the same cation or between two different salts of the same anion should be readily calculable from

the appropriate sums of  $Q/r$  terms for the other ions in the lattice. However the calculated differences in these Madelung potentials differ greatly from the observed chemical shifts. Citrin et al.<sup>49</sup> have shown that the discrepancies can be markedly reduced by considering the mutual polarization of the ions. That is, the use of unit point charges is not valid. The inclusion of polarization effects is essentially equivalent to the use of fractional atomic charges combined with the calculation of chemical shifts by means of equation 5. However calculations which take these effects into account are quite complicated, particularly for more complicated compounds, and most investigators do not attempt to account for chemical shifts in ionic compounds using equation 5.

The fact that small chemical shifts are observed for an atom in an ion on going from one salt to another in spite of large differences in the calculated Madelung potentials illustrates what appears to be a general rule: by a combination of the effects of crystal packing and charge transfer by polarization, a given ion achieves approximately the same potential energy in all its salts. This rule applies even to ions which occupy structurally different sites within the same crystal. For example, Hayes and Edelstein found no apparent broadening of the F 1s line of  $\text{LaF}_3$  even though the solid contains crystallographically different fluoride ions for which the simple point charge lattice potentials differ by more than 3 eV.<sup>48</sup>

In some complexes, it is possible to distinguish bridging and terminal ligand atoms. Thus Hamer and Walton<sup>50</sup> have observed separate peaks for bridging and terminal chloride ions in cluster complexes of rhenium(III) and molybdenum(II).

2. Internal Referencing. - The comparison of core binding energies of atoms in different solid compounds is fraught with difficulty. In the case of nonmetallic samples, one does not know what the effective Fermi levels are, and therefore one cannot put the binding energies on the basis of a common reference level. The usual, probably poor, solution to the problem is to assume that the work functions of all the samples are identical. Nonmetallic samples are also subject to an unknown amount of electrostatic charging, and although various techniques have been devised to minimize errors due to this effect, absolute values of binding energies for solids are always uncertain to some extent because of this charging. Both the work function problem and the electrostatic charging problem can be completely avoided by measuring chemical shifts between core levels of atoms in the same sample. Several studies based on such internal referencing are discussed in the following paragraphs.

The topic of "mixed valence compounds" has become very popular in recent years.<sup>51</sup> X-Ray photoelectric ionization is believed to take place in a time interval of about  $10^{-18}$  sec; therefore separate binding energy peaks are possible for atoms of different oxidation states in structurally equivalent sites if the lifetime of a given electronic configuration is greater than about  $10^{-18}$  sec. The higher the barrier to electron exchange between the equivalent sites, the longer the lifetime of a given state. R. E. Connick<sup>52</sup> has pointed out to the author that in all mixed valence compounds one would expect electron transfer processes between atoms to be slower than the X-ray photoelectric process. This conclusion is based in part on the fact that the kinetic

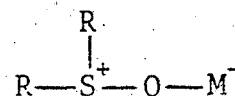
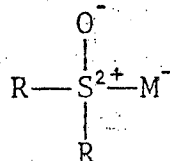
energy of a valence electron is of the order of 10-20 eV, whereas the kinetic energy of the ejected core electron is usually much higher. If this is true, then one should always observe two core lines for a mixed valence system except in cases of poor resolution.

The antimony 3d spectrum of  $\text{Cs}_2\text{SbCl}_6$  shows two peaks, separated by 1.80 eV, presumably identifiable with the +3 and +5 oxidation states.<sup>53</sup> The fact that the antimony atoms are not all of +4 oxidation state is a particularly interesting result. In this salt, the Sb atoms occupy sites which are almost, but not exactly, identical.<sup>54</sup>

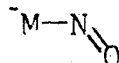
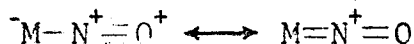
Citrin<sup>55</sup> obtained the ruthenium core spectra shown in Figure 8 for salts containing the ions  $[(\text{NH}_3)_5\text{Ru}(\text{pyr})\text{Ru}(\text{NH}_3)_5]^{4+,5+,6+}$  and  $[\text{Cl}(\text{bipy})_2\text{Ru}(\text{pyr})\text{Ru}(\text{bipy})_2\text{Cl}]^{2+,3+,4+}$  (pyr = pyrazine; bipy = bipyridine). In these symmetric complexes the ruthenium oxidation states can be represented as [II, II], [II, III], and [III, III]. The chemical shift between the [II, II] and [III, III] peaks is greater in the case of the pentaammine complexes than in the case of the bipyridine complexes, presumably because of greater ruthenium valence electron delocalization in the bipyridine [II, II] complex than in the pentaammine [II, II] complex. Both of the [II, III] complexes show separate peaks for the two different oxidation states. In the case of the pentaammine complexes, the separation between the [II, III] peaks is less than that between the [II, II] and [III, III] peaks. This result is probably caused by the delocalization of the extra electron of the [II, III] complex principally on the pyrazine molecule coordinated to both ruthenium atoms. In the case of the bipyridine [II, III] complex, in which the extra electron

density can be delocalized onto the bipyridine ligands attached to the ruthenium(II) atom, the peak separation is essentially the same as that between the corresponding [II, II] and [III, III] peaks.

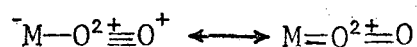
Su and Faller<sup>56,57</sup> have shown that the geometric aspects of the bonding of sulfoxides (R<sub>2</sub>SO) and nitrosyl (NO) groups to metal atoms can be correlated with differences in the binding energies of different atoms in the ligands. In the case of sulfoxide complexes, which contain either metal-oxygen or metal-sulfur bonds, the absolute S 2p<sub>3/2</sub> and O 1s binding energies show very little correlation with the mode of bonding.<sup>56</sup> However, the difference between the O 1s and S 2p<sub>3/2</sub> binding energies does show a marked correlation, as shown by the data plotted in Fig. 9. When the metal is bonded to the oxygen atom of the sulfoxide, the O 1s - S 2p<sub>3/2</sub> difference is ~365.8 eV, whereas when the metal is bonded to the sulfur atom of the sulfoxide, the difference is ~365.0 eV. This type of correlation is reasonable in view of the formal charges on the oxygen and sulfur atoms in the two geometries:



In the case of nitrosyl complexes, which can be "linear" (that is with the metal-N-O bond angle near 180°) or "bent" (with the bond angle near 120°), the O 1s binding energy minus the N 1s binding energy is in the range of 132±1 eV for linear nitrosyls and 128±2 eV for bent nitrosyls.<sup>57</sup> It is difficult to rationalize these data on the basis of the formal charges in the two valence bond structures as one would ordinarily write them:



From the formal charges in these structures one might have predicted that the O 1s - N 1s difference would be greater for the bent nitrosyls rather than for the linear nitrosyls. Perhaps the observed behavior is due to an extraordinarily large relaxation energy for the nitrogen atom in the linear nitrosyls. By applying the equivalent cores approximation, we may represent the N 1s ionized state of the linear complex as follows:



The left-hand structure, which has adjacent atoms with positive formal charges, would be very unstable, and there would be a strong tendency for electron density to flow from the other ligands through the metal d orbitals to make the right-hand structure dominant. This electron flow corresponds to a large (negative) relaxation energy and a low N 1s binding energy.

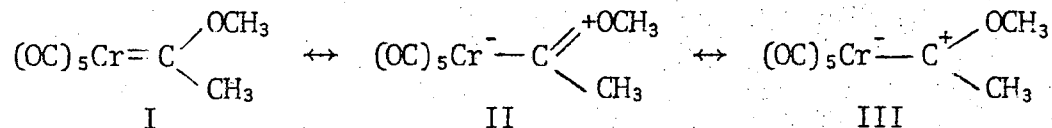
### C. Gases

1. Qualitative Interpretation of Chemical Shifts. - It is often possible to interpret core binding energy data in terms of valence electron distribution without direct recourse to a theoretical method for calculating binding energies. Such interpretation is usually at least implicitly based on a relation such as equation 6. However, by the appropriate choice of reference binding energies the changes in the potential term,  $V$ , and the relaxation energy term,  $E_R$ , can be assumed to be very small. Thus shifts in binding energy can be directly, although qualitatively, related to changes in atomic charge.

There has been considerable discussion regarding the nature of the bonding in transition metal carbene complexes.<sup>58</sup> A carbene complex



in which the carbene carbon atom is bonded to a heteroatom with nonbonding electrons, such as  $(OC)_5CrC(OCH_3)CH_3$ , may be represented as a resonance hybrid of the following structures, I-III:



Carbon-13 nmr data,<sup>59</sup> the strongly electrophilic reactivity behavior of the carbene carbon atom,<sup>60</sup> and other chemical and physical data<sup>58</sup> have been interpreted as evidence for the importance of structure III, that is, as evidence for an exceptionally positive charge on the carbene carbon atom. However, the C 1s spectrum of the gaseous molecule shows that the binding energies of all three carbon atoms of the  $C(OCH_3)CH_3$  group are lower than the binding energy of the carbonyl carbon atoms.<sup>61</sup> Therefore one concludes that the carbene carbon atom is not exceptionally positively charged. This conclusion is based on the reasonable assumption that the potential term and electronic relaxation energy for the carbene carbon atom are essentially the same as those for the carbonyl carbon atoms. The data underscore the facts that nmr chemical shifts of carbon atoms bound to transition metals are very difficult to interpret<sup>62</sup> and that chemical reactivity data do not always correlate well with the properties of ground-state molecules. In this study, the C 1s spectrum was obtained for a gaseous sample rather than a solid sample to avoid the spurious C 1s line due to hydrocarbon contamination which is generally observed in the spectra of solid samples.

The study of the core binding energies of an isoelectronic series of compounds has the advantage that the nature of the bonding in such

compounds changes in a fairly systematic way with changes in the atomic numbers of the atoms. To a good approximation, the electronic relaxation energy for an atom of a particular element in a series of isoelectronic, isostructural compounds can be assumed to be constant. Therefore chemical shifts can be ascribed to changes in atomic charge and potential. Consider the five series of isoelectronic compounds listed in Table II.<sup>63</sup> In the first four series, halogen atoms or methyl groups are replaced with oxygen atoms as the atomic number of the central atom is increased stepwise. The last series of compounds is generated by the hypothetical stepwise transfer of protons from one of the fluorine nuclei of  $\text{SiF}_4$  to the silicon nucleus of that molecule. It is reasonable to assume that, on progressing down through any one of the five series, the charge of the central atom increases. This increase in charge of the central atom would be expected to cause increased electron withdrawal from a given type of ligand atom and is probably responsible for the increase in the oxygen, chlorine, and carbon binding energies within each series.

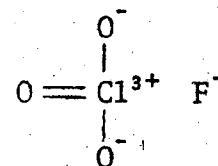
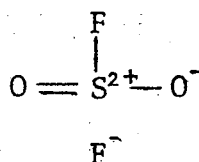
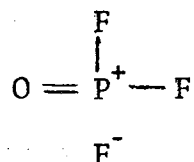
Notice, however, that the fluorine 1s binding energies do not follow the predicted trend. In both the fourth and fifth series, the fluorine binding energies increase to a maximum value and then decrease. The increase between  $\text{SiF}_4$  and  $\text{POF}_3$  is probably caused by the dominating effect of the increased positive charge and electronegativity of the central atom. The decrease in fluorine binding energy between  $\text{SO}_2\text{F}_2$  and  $\text{ClO}_3\text{F}$  and between  $\text{POF}_3$  and  $\text{SNF}_3$  is apparently due to an increase in the negative charge of the fluorine atoms. This increase in negative charge tends to decrease the binding energy; clearly this

TABLE II  
Oxygen 1s, Chlorine 2p<sub>3/2</sub>, Carbon 1s, and Fluorine 1s Binding Energies<sup>63</sup>

Compound	E <sub>B</sub> , eV			
	O 1s	Cl 2p <sub>3/2</sub>	C 1s	F 1s
TiCl <sub>4</sub>		205.66		
VOCl <sub>3</sub>	538.73	205.93		
CrO <sub>2</sub> Cl <sub>2</sub>	538.89	206.01		
MnO <sub>3</sub> Cl	539.43	207.28		
SiCl <sub>4</sub>		206.77		
POCl <sub>3</sub>	537.80	207.16		
SO <sub>2</sub> Cl <sub>2</sub>	539.34	207.32		
Si(CH <sub>3</sub> ) <sub>4</sub>			289.61	
P(CH <sub>3</sub> ) <sub>3</sub> O	535.88		290.57	
S(CH <sub>3</sub> ) <sub>2</sub> O <sub>2</sub>	537.67		291.58	
SiF <sub>4</sub>				694.56
POF <sub>3</sub>	538.9			695.4
SO <sub>2</sub> F <sub>2</sub>	540.3			695.4
ClO <sub>3</sub> F	541.0			694.0
SiF <sub>4</sub>				694.56
POF <sub>3</sub>				695.4
SNF <sub>3</sub>				695.0

effect is greater than and opposed to the effect of the increase in potential caused by the increase in positive charge on the central atom.

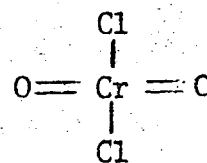
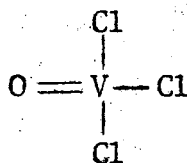
The increase in the negative charge of the fluorine atoms can be explained by the dominating effect of a large increase in the extent of hyperconjugation. Hyperconjugation (sometimes called 'no-bond resonance') corresponds to the contribution of resonance structures of the following type.



This type of bonding transfers some of the negative formal charge of oxygen atoms to fluorine atoms. On going from  $\text{POF}_3$  to  $\text{ClO}_3\text{F}$ , the number of oxygen atoms which can transfer negative charge increases from one to three and the number of fluorine atoms which can accept negative charge decreases from three to one. Consequently, the fluorine atoms acquire an increasing amount of negative formal charge in this series. The effect on the actual charge of the fluorine atoms is most marked between  $\text{SO}_2\text{F}_2$  and  $\text{ClO}_3\text{F}$ . On going from  $\text{POF}_3$  to  $\text{SNF}_3$ , the hyperconjugation increases markedly because of the increased donor character (decreased electronegativity) of the nitrogen atom compared with that of the oxygen atom.

The effect of hyperconjugation on atomic charges is more apparent in the fluorine compounds than in the chlorine and methyl compounds because of the greater electronegativity of fluorine atoms and the corresponding greater ability of fluorine atoms to accept negative charge. It is possible that hyperconjugation occurs even in methyl

compounds such as  $P(CH_3)_3O$  and  $S(CH_3)_2O_2$ , but that the effect is not strong enough to cause a reversal in the carbon binding energies like that observed in the fluorine binding energies. Hyperconjugation is probably not significant in transition metal compounds such as  $VOCl_3$  and  $CrO_2Cl_2$ . Such compounds, in which metal inner d orbitals are importantly involved in the bonding, can be represented by structures such as the following



The relatively small increases in oxygen 1s binding energies observed for the first series of compounds in Table II are consistent with this interpretation.

2. The "Transition State" Method. - Explicit inclusion in equation 6 of the relaxation energy term,  $E_R$ , can be obviated by using modified values of  $Q$  and  $V$  corresponding to a hypothetical "transition state" molecule which has a valence electron distribution halfway between that of the initial molecule and that of the core-ionized molecule.<sup>64-66</sup>

$$E_B = kQ + k\Delta Q^* + V + \Delta V^* + l$$

Here  $\Delta Q^*$  and  $\Delta V^*$  are the changes in  $Q$  and  $V$  on going from the initial to the transition state.

Hence

$$E_R = k\Delta Q^* + \Delta V^* = k(Q_f - Q - 1)/2 + (V_f - V)/2 \quad (7)$$

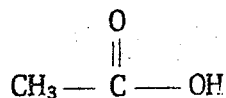
where  $Q_f$  and  $V_f$  are the values of  $Q$  and  $V$  for the core-ionized molecule. These values can be estimated using the approximation of equivalent cores.

A method similar to the transition state method described above has been used by Davis and Shirley,<sup>64,67</sup> in combination with the CNDO method, to calculate relaxation-corrected binding energy shifts for compounds of carbon, nitrogen, and oxygen. The correlation of nine nitrogen compounds was significantly better with the inclusion of the relaxation energy (standard deviation 1.30 eV) than without inclusion of the relaxation energy (standard deviation 2.35 eV). The improvements of the correlations of the carbon and oxygen compounds was not as marked. Shirley<sup>68</sup> has also shown that the transition state method, combined with calculated or experimental data for ground-state atoms, can be used to estimate relaxation energies for the core ionization of atoms. Howat and Goscinski<sup>69</sup> have shown that calculations for the transition state method can be simplified by calculating, for each molecule, the charge distribution for the hypothetical transition state rather than for both the ground state and the core-ionized state. They used "pseudo-atom" interpolated CNDO parameters for the atom which undergoes core ionization.

Jolly and Perry<sup>65,66</sup> have used the transition state method and the CHELEQ electronegativity equalization procedure for calculating atomic charges to correlate the binding energies of a wide variety of gaseous molecules. Equation 6 was used for the correlations; the  $E_r$  values were obtained from equation 7. The binding energies included 64 carbon 1s, 20 nitrogen 1s, 24 oxygen 1s, 28 fluorine 1s, 11 silicon 2p, 13 phosphorus  $2p_{3/2}$ , 16 sulfur  $2p_{3/2}$ , 16 chlorine  $2p_{3/2}$ , 8 germanium  $3p_{3/2}$ ,

10 bromine  $3d_{5/2}$ , and 5 xenon  $3d_{5/2}$  binding energies. The least-squares evaluated  $k$  values, the corresponding correlation coefficients, and the standard deviations (with and without inclusion of  $E_R$ ) are listed in Table III. The correlations, as measured by the standard deviations and the correlation coefficients, are quite good and attest the usefulness of the CHELEQ method. By comparison of the standard deviation with and without  $E_R$  it can be seen that, in most cases, inclusion of the relaxation energy markedly improved the correlation.

The calculation of the atomic charges of a molecule by the CHELEQ method requires that one first write a single valence bond structure for the molecule.<sup>65,66</sup> In the case of a molecule for which there is more than one satisfactory valence bond structure, a suitable resonance hybrid structure must be written. Inasmuch as the transition state correlations involve the calculation of atomic charges for the core-ionized molecules as well as the ground-state molecules, resonance structures for the core-ionized molecules must be considered when appropriate. For example, although the structure



is a satisfactory representation of the ground-state acetic acid molecule, the analogous structure for the molecule in which the carbonyl oxygen atom has lost a 1s electron is inadequate. By applying the equivalent cores approximation, we see that two resonance structures are important:



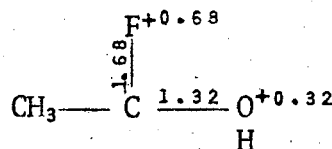
Table III

Parameters of Potential Model Correlations<sup>66</sup>

Element	k	Correl. coeff.	Std. dev.	Std. dev., no E <sub>R</sub>
C	30.50	0.972	0.62	0.81
N	30.69	0.987	0.60	1.01
O	25.50	0.896	0.73	0.59
F	27.95	0.934	0.34	0.26
Si	17.29	0.964	0.47	0.51
P	19.28	0.953	0.89	1.33
S	18.63	0.983	0.70	0.74
Cl	18.24	0.988	0.44	0.52
Ge	15.87	0.984	0.34	0.47
Br	13.32	0.993	0.31	0.38
Xe	12.06	0.992	0.39	0.37



It is not possible to predict the relative weights of these resonance structures, and therefore the carbonyl oxygen binding energy of acetic acid could not be included in the data used to obtain the oxygen  $k$  and  $l$  values. However, using equation 6 and the oxygen  $k$  and  $l$  values obtained from compounds with unambiguous valence structures, one can calculate the weighting of the resonance structures which gives perfect agreement between the experimental and calculated values of the carbonyl oxygen binding energy of acetic acid. The resonance hybrid structure for the core-ionized molecule, calculated in this way, is



where the numbers next to the bonds are the bond orders. Similar treatment of the oxygen binding energies of other carbonyl compounds yields analogous resonance hybrid structures for the core-ionized molecules.<sup>70</sup> The order of the bond between the core-ionized oxygen atom (or fluorine atom, in the equivalent cores approximation) and the carbon atom can be taken as a measure of the  $\pi$ -donor character of the groups attached to the carbonyl group. These calculated bond orders for various carbonyl compounds are listed in Table IV. The lower the bond order, the more negative  $E_R$  and the greater the combined  $\pi$  donor characters of the groups bonded to the carbonyl group.

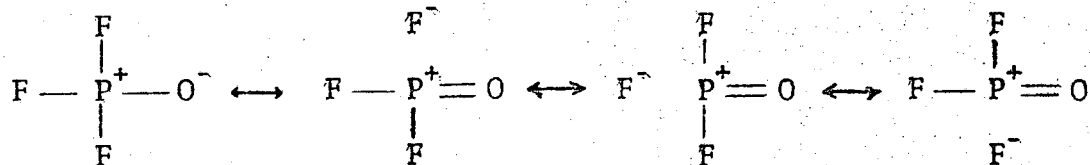
The question of hyperconjugation in molecules such as  $\text{POF}_3$  can be attacked by the transition-state method in combination with CHELEQ charge calculations. Let us assume that the ground state of  $\text{POF}_3$  can be

Table IV

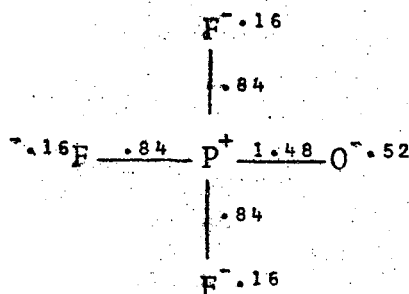
## Calculated C-O Bond Orders in C 1s-Ionized Carbonyl Compounds

Compound	C-O Bond Order
H <sub>2</sub> CO	2.0
CH <sub>3</sub> CHO	1.79
(CH <sub>3</sub> ) <sub>2</sub> CO	1.70
Cl <sub>2</sub> CO	1.70
CH <sub>3</sub> CO <sub>2</sub> H	1.68
F <sub>2</sub> CO	1.64
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO	1.58
(CH <sub>3</sub> O) <sub>2</sub> CO	1.40

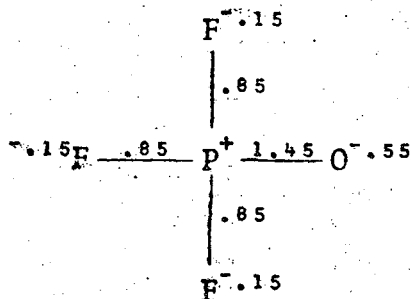
represented as a resonance hybrid of the structures



and that the oxygen 1s and fluorine 1s core-hole ions of  $\text{POF}_3$  can be represented by resonance hybrids with exactly the same weightings of the individual resonance structures. Then one obtains agreement between the experimental oxygen binding energy and the value calculated from equation 6 (using the appropriate  $k$  and  $l$  values) if one assumes the resonance hybrid structure<sup>70</sup>



The analogous calculation, using the fluorine binding energy, yields the following resonance structure.



The fact that both binding energies give essentially the same resonance hybrid structure gives credence to the assumptions involved.

Acknowledgement. - This work was supported by the National Science Foundation (Grant GP-41661x) and the Energy Research and Development Agency.

References

- (1) A. Hammett and A. F. Orchard, Electronic Structure and Magnetism of Inorganic Compounds, 1, 36(1972); S. Evans and A. F. Orchard, ibid., 2, (1973); A. Hammett and A. F. Orchard, ibid., 3, 218(1974).
- (2) W. L. Jolly, Coord. Chem. Rev., 13, 47(1974).
- (3) H. W. B. Skinner, Proc. Roy. Soc. (London), A135, 84(1932). Also see E. M. Baroody, J. Opt. Soc. Am., 62, 1528(1972).
- (4) We have used modern values for the atomic energy levels, taken from C. E. Moore, "Atomic Energy Levels," Vol. I, NSRDS-NBS 35, National Bureau of Standards, Washington, D.C., Dec. 1971, and "Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra," NSRDS-NBS 34, National Bureau of Standards, Washington, D.C., Sept. 1970.
- (5) Obtained from data in ref. 4, giving weights of 1 and 3 to the  $1s2s^1S$  and  $1s2s^3S$  states of  $Li^+$ .
- (6) D. B. Adams and D. T. Clark, J. Electron Spectr. Rel. Phen., 2, 201 (1973); D. B. Adams, J. Electron Spectr. Rel. Phen., 4, 72(1974).
- (7) K. Siegbahn et al., "ESCA Applied to Free Molecules," North-Holland Publ. Co., Amsterdam, 1969.
- (8) Adams and Clark<sup>6</sup> assumed that an ion of configuration  $(1s^22s^1)$  is a core as far as the 2p electrons are concerned. Making this very poor assumption, they concluded that the equivalent cores approximation is invalid for calculating 2s binding energies for second row elements.
- (9) S. P. Kowalczyk, L. Ley, F. R. McFeely, R. A. Pollak, and D. A. Shirley, Phys. Rev., B8, 3583(1973).

- (10) P. E. Best, J. Chem. Phys., 47, 4002(1967); P. E. Best, J. Chem. Phys., 49, 2797(1968).
- (11) W. L. Jolly and D. N. Hendrickson, J. Amer. Chem. Soc., 92, 1863(1970).
- (12) W. L. Jolly, J. Amer. Chem. Soc., 92, 3260(1970).
- (13) J. M. Hollander and W. L. Jolly, Acc. Chem. Res., 3, 193(1970).
- (14) P. Finn, R. K. Pearson, J. M. Hollander and W. L. Jolly, Inorg. Chem., 10, 378(1971).
- (15) P. Finn and W. L. Jolly, J. Amer. Chem. Soc., 94, 1540(1972).
- (16) W. L. Jolly, in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland Publ. Co., Amsterdam, 1972, pp. 629-645.
- (17) R. L. Martin and D. A. Shirley, J. Amer. Chem. Soc., 96, 5299(1974).
- (18) D. W. Davis and J. W. Rabalais, J. Amer. Chem. Soc., 96, 5305(1974).
- (19) R. W. Shaw, T. X. Carroll, and T. D. Thomas, J. Amer. Chem. Soc., 95, 5870(1973).
- (20) The energy difference between the  $\text{ClF}_2^+$  ions is actually greater than 2.54 eV because the equatorial neon atom is weakly bonded to the chlorine atom and the axial neon atom is probably completely nonbonded. If we restrict the chlorine 3s orbital to the lone pairs, then the linear forms of  $\text{ClF}_2^+$  lacks an octet whereas the bent form has a complete octet.
- (21) D. T. Clark and D. B. Adams, Nature Phys. Sci., 234, 95(1971).
- (22) D. C. Frost, F. G. Herring, C. A. McDowell and I. S. Woolsey, Chem. Phys. Letters, 13, 391(1972).
- (23) D. T. Clark and D. B. Adams, J. Chem. Soc. Faraday II, 68, 1819 (1972); J. Electron Spectro. Rel. Phen., 1, 302(1972); also see Discuss. Faraday Soc., 54, 43(1972).

- (24) D. B. Adams and D. T. Clark, Theoret. Chim. Acta, 31, 171(1973).
- (25) L. J. Aarons and I. H. Hillier, J. Chem. Soc. Faraday II, 69, 1510 (1973).
- (26) J. A. Connor, M. B. Hall, I. H. Hillier, and W. N. E. Meredith, J. Chem. Soc. Faraday II, 70, 1677(1973).
- (27) J. Cambray, J. Gasteiger, A. Streitwieser, and P. S. Bagus, J. Amer. Chem. Soc., 96, 5978(1974).
- (28) H. Basch, Chem. Phys. Letters, 5, 337(1970).
- (29) M. E. Schwartz, Chem. Phys. Letters, 6, 631(1970).
- (30) D. A. Shirley, Chem. Phys. Letters, 15, 325(1972).
- (31) K. Siegbahn et al., "ESCA; Atomic, Molecular and Solid-State Structure Studied by Means of Electron Spectroscopy," Almqvist and Wiksells AB, Uppsala, 1967.
- (32) R. W. Shaw and T. D. Thomas, Chem. Phys. Letters, 22, 127(1973).
- (33) J. F. Liebman and L. C. Allen, J. Amer. Chem. Soc., 92, 3539(1970).
- (34) U. Gelius, J. Electron Spectr. Rel. Phen., 5, 985(1974).
- (35) U. Gelius, S. Svensson, H. Siegbahn, E. Basilier, A. Faxälv, and K. Siegbahn, Chem. Phys. Letters, 28, 1(1974).
- (36) W. Meyer, J. Chem. Phys., 58, 1017(1973).
- (37) U. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, Chem. Phys. Letters, 11, 224(1971).
- (38) J. S. Jen and T. D. Thomas, J. Electron Spectr. Rel. Phen., 4, 43(1974).
- (39) M. Nakamura et al., Phys. Rev. 178, 80(1969).

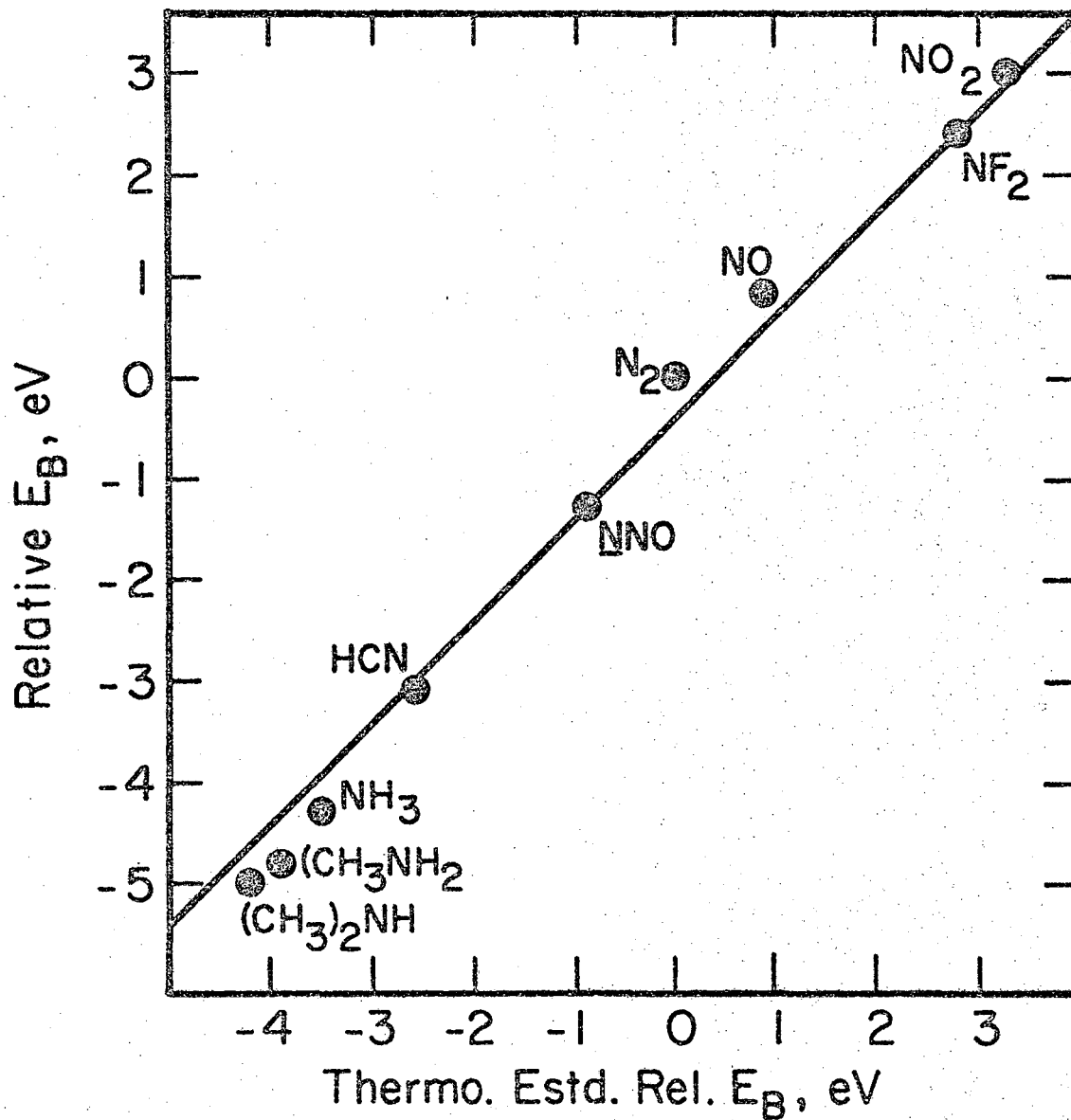
- (40) G. R. Wight, C. E. Brion, and M. J. Van der Wiel, J. Electron Spectr. Rel. Phen., 1, 457(1972/3).
- (41) G. R. Wight and C. E. Brion, Chem. Phys. Letters, 26, 607(1974).
- (42) U. Gelius, Physica Scr., 9, 133(1974).
- (43) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell Univ. Press, Ithaca, N. Y., 1960. Also see 2nd ed., 1940, pp. 65-66.
- (44) L. J. Matienzo, L. I. Yin, S. O. Grim, and W. E. Swartz, Inorg. Chem., 12, 2762(1973).
- (45) W. B. Hughes and B. A. Baldwin, Inorg. Chem., 13, 1531(1974).
- (46) W. E. Moddeman, J. R. Blackburn, G. Kumar, K. A. Morgan, M. M. Jones, and R. G. Albridge, in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland, Publ. Co., Amsterdam, 1972, pp. 725-32.
- (47) W. E. Swartz, J. K. Ruff, and D. M. Hercules, J. Amer. Chem. Soc., 94, 5227(1972).
- (48) R. G. Hayes and N. Edelstein, in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland Publ. Co., Amsterdam, 1972, pp. 771-779.
- (49) P. H. Citrin, R. W. Shaw, A. Packer, and T. D. Thomas, in "Electron Spectroscopy," D. A. Shirley, ed., North-Holland Publ. Co., Amsterdam, 1972, pp. 691-706; also see J. Chem. Phys., 57, 4446(1972).
- (50) A. D. Hamer and R. A. Walton, Inorg. Chem., 13, 1446(1974).
- (51) M. B. Robin and P. Day, Advances Inorg. Chem. Radiochem., 10, 247(1967).
- (52) R. E. Connick, University of California, Berkeley, private discussion with author.
- (53) P. Burroughs, A. Hamnett, and A. F. Orchard, J. Chem. Soc. Dalton, 565(1974). Also see C. K. Jørgensen, Chimia, 25, 213(1971) and M. J. Tricker, I. Adams, and J. M. Thomas, Inorg. Nucl. Chem. Letters, 8, 633(1972).



- (54) A. T. Jensen and S. E. Rasmussen, Acta Chem. Scand., 9, 708(1955).
- (55) P. H. Citrin, J. Amer. Chem. Soc., 95, 6472(1973).
- (56) C.-C. Su and J. W. Faller, Inorg. Chem., 13, 1734(1974).
- (57) C.-C. Su and J. W. Faller, J. Organomet. Chem., 84, 53(1975).
- (58) D. J. Cardin, B. Cetinkaya, M. J. Doyle and M. F. Lappert, Chem. Soc. Rev., 2, 99(1973); F. A. Cotton and C. M. Lukehart, Prog. Inorg. Chem., 16, 487(1972).
- (59) L. F. Farnell, E. W. Randall, and E. Rosenberg, Chem. Commun., 1078 (1971); G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, Inorg. Chem., 12, 1071(1973).
- (60) A. Davison and D. L. Reger, J. Amer. Chem. Soc., 94, 9237(1972).
- (61) W. B. Perry, T. F. Schaaf, W. L. Jolly, L. J. Todd, and D. L. Cronin, Inorg. Chem., 13, 2038(1974).
- (62) J. Evans and J. R. Norton, Inorg. Chem., 13, 3043(1974).
- (63) S. C. Avanzino, W. L. Jolly, M. S. Lazarus, W. B. Perry, R. R. Rietz, and T. F. Schaaf, Inorg. Chem., 14, 0000(1975).
- (64) L. Hedin and A. Johansson, J. Phys. B, Ser. 2, 2, 1336(1969); W. L. Jolly, Discuss. Faraday Soc., 54, 13(1972); D. W. Davis and D. A. Shirley, Chem. Phys. Lett., 15, 185(1972).
- (65) W. L. Jolly and W. B. Perry, J. Amer. Chem. Soc., 95, 5442(1973).
- (66) W. L. Jolly and W. B. Perry, Inorg. Chem., 13, 2686(1974).
- (67) D. W. David and D. A. Shirley, J. Electron Spectr. Rel. Phen., 3, 137 (1974).
- (68) D. A. Shirley, Chem. Phys. Lett., 16, 220(1972).
- (69) G. Howat and O. Goscinski, Chem. Phys. Lett., 30, 87(1975).
- (70) T. F. Schaaf and W. L. Jolly, unpublished data and calculations, 1975.

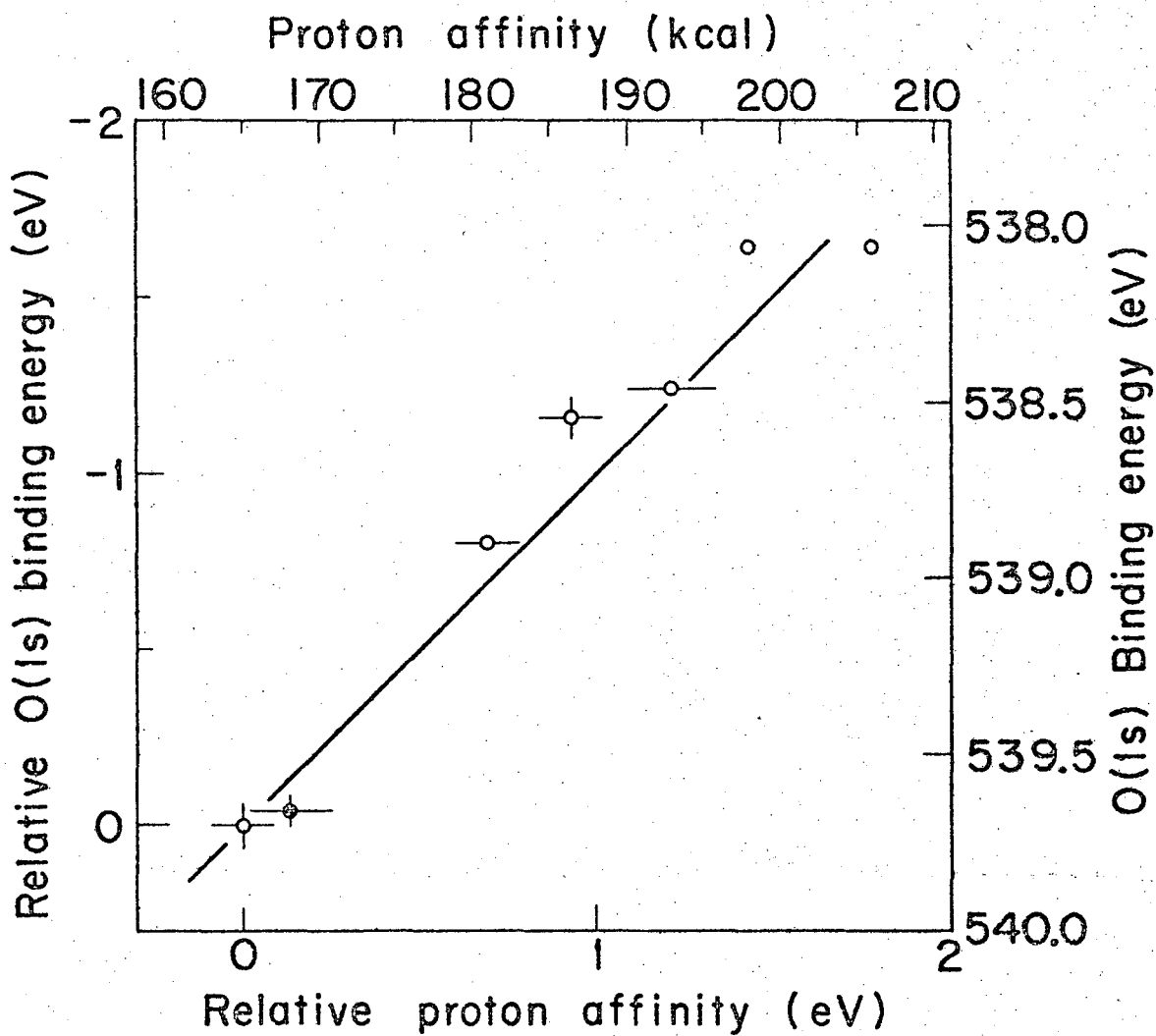
Figure Captions

- Fig. 1. Plot of nitrogen 1s binding energies vs. thermodynamically estimated energies. (Reproduced from Ref. 16).
- Fig. 2. Oxygen 1s binding energies vs. proton affinities for simple alcohols (open circles) and  $\text{CF}_3\text{CH}_2\text{OH}$  (filled circle). (Reproduced from Ref. 17.)
- Fig. 3. Nitrogen 1s binding energies vs. proton affinities for  $\text{NH}_3$  and amines. (Reproduced from Ref. 17.)
- Fig. 4. Electron density difference plot,  $\text{CO} - \text{CO}^{++}$ , derived from the molecule and ion SCF wave functions. The vertical axis is in electrons per cubic atomic units. (Reproduced from Ref. 27.)
- Fig. 5. Valence electron density difference plot,  $\text{CO}^{++} - \text{CF}^+$ , derived from SCF wave functions. The vertical axis is in electrons per cubic atomic units. (Reproduced from Ref. 27.)
- Fig. 6. Relative nickel  $2p_{3/2}$  binding energies vs. estimated nickel atom charges for some simple nickel(II) compounds. (Reproduced from Ref. 44.)
- Fig. 7. Molybdenum  $3d_{3/2}$  binding energies vs. estimated molybdenum atom charges for some molybdenum complexes. (Reproduced from Ref. 45.)
- Fig. 8. X-Ray photoelectron spectra of  $[(\text{NH}_3)_5\text{Ru}(\text{pyr})\text{Ru}(\text{NH}_3)_5]^{4+,5+,6+}$  and  $[\text{Cl}(\text{bipy})_2\text{Ru}(\text{pyr})\text{Ru}(\text{bipy})_2\text{Cl}]^{2+,3+,4+}$  salts. The C 1s electron binding energies in both systems have been assigned as 284.4 eV for purposes of comparison. (Reproduced from Ref. 55.)
- Fig. 9. Core binding energies, and their differences, for some sulfoxide complexes. (Reproduced from Ref. 56.)



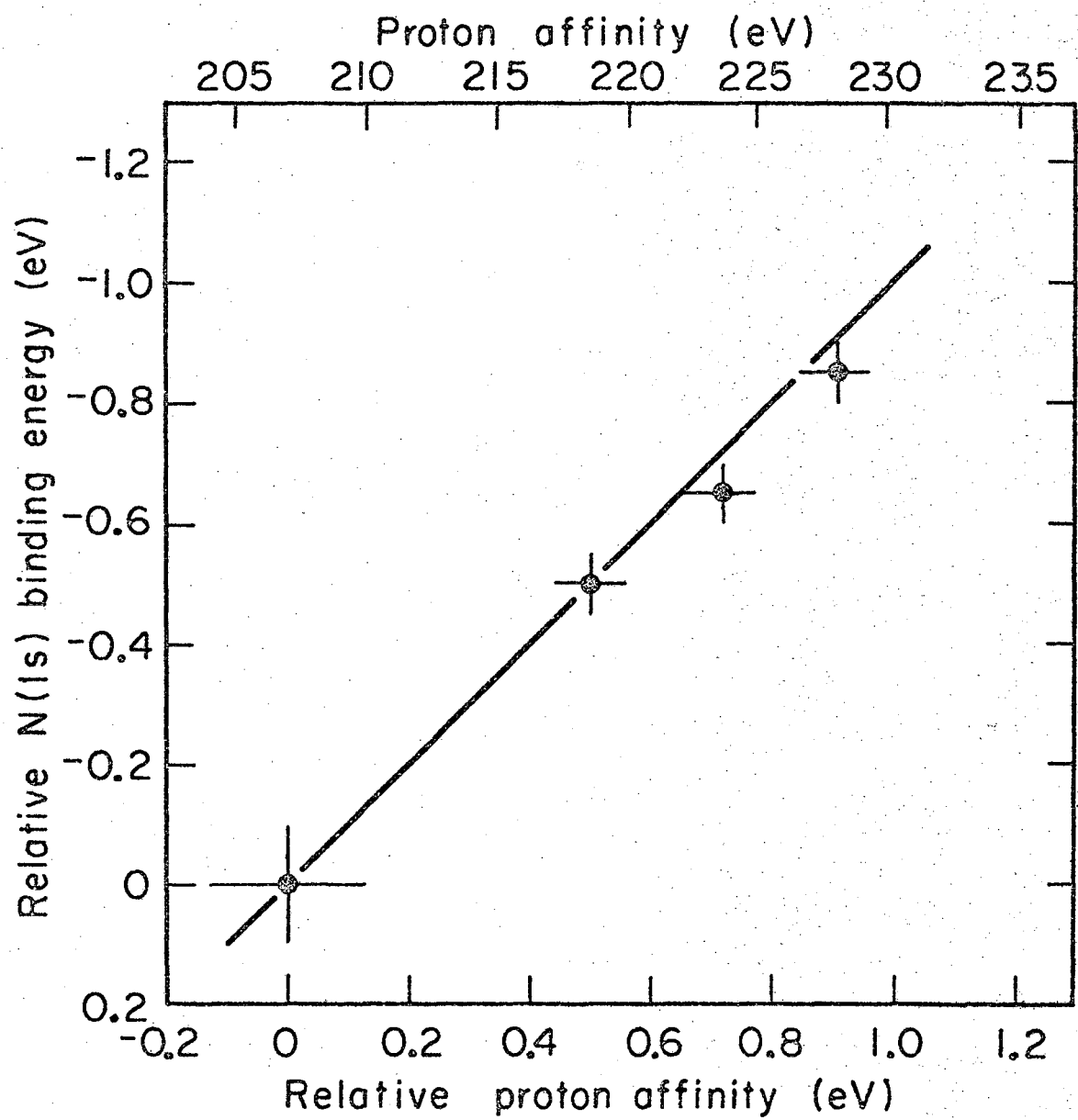
XBL 718-7208

Fig. 1



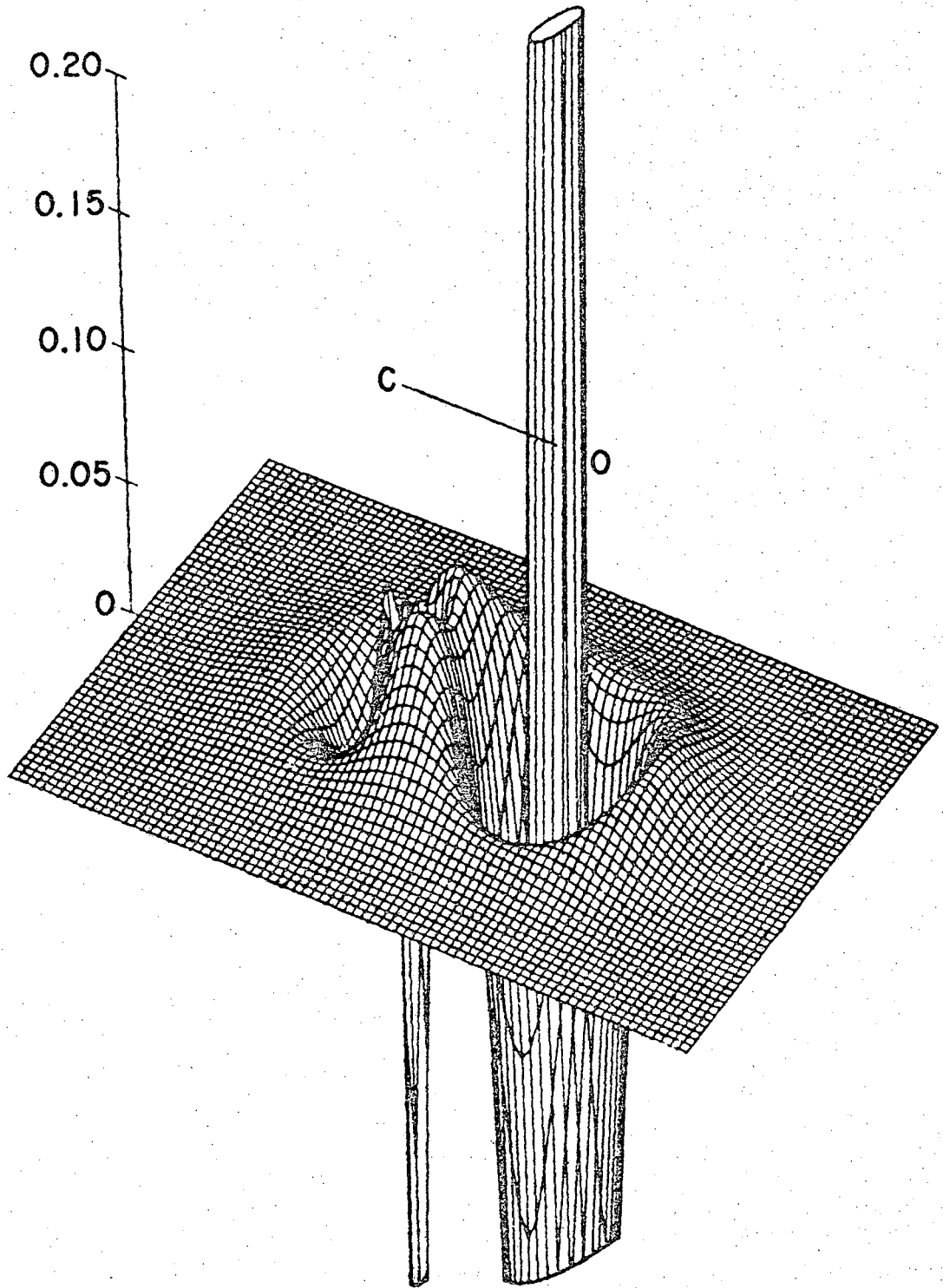
XBL 7312 - 7033

Fig. 2



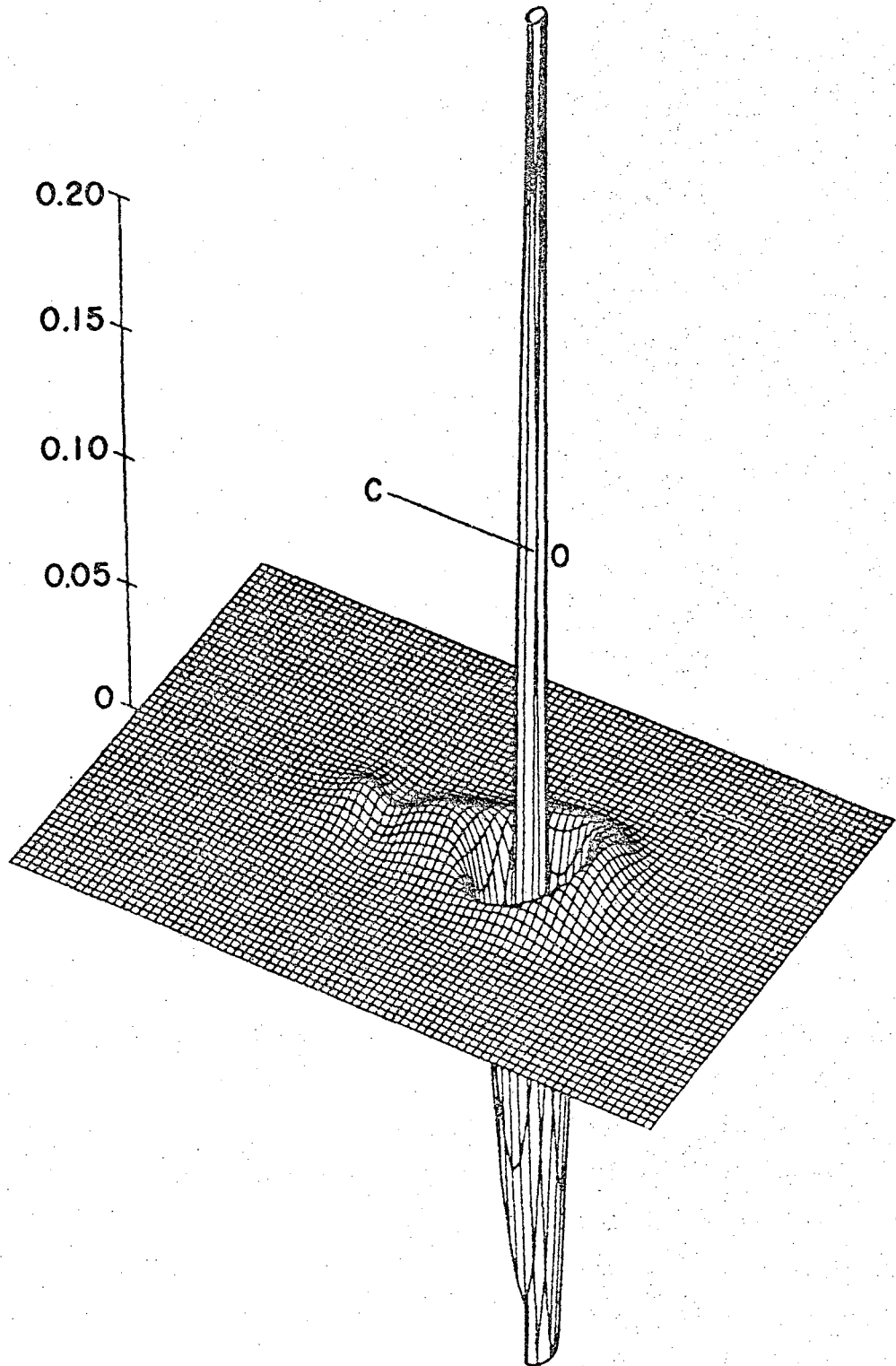
XBL7312-7032

Fig. 3



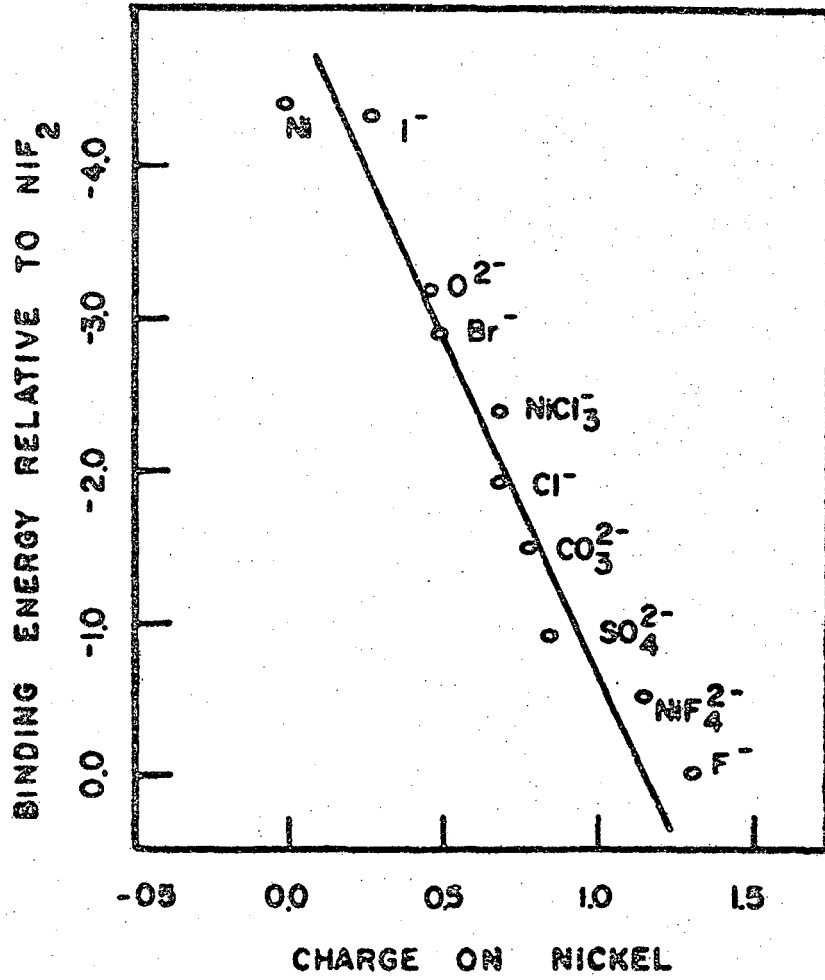
XBL 752-318

Fig. 4



XBL 752-322

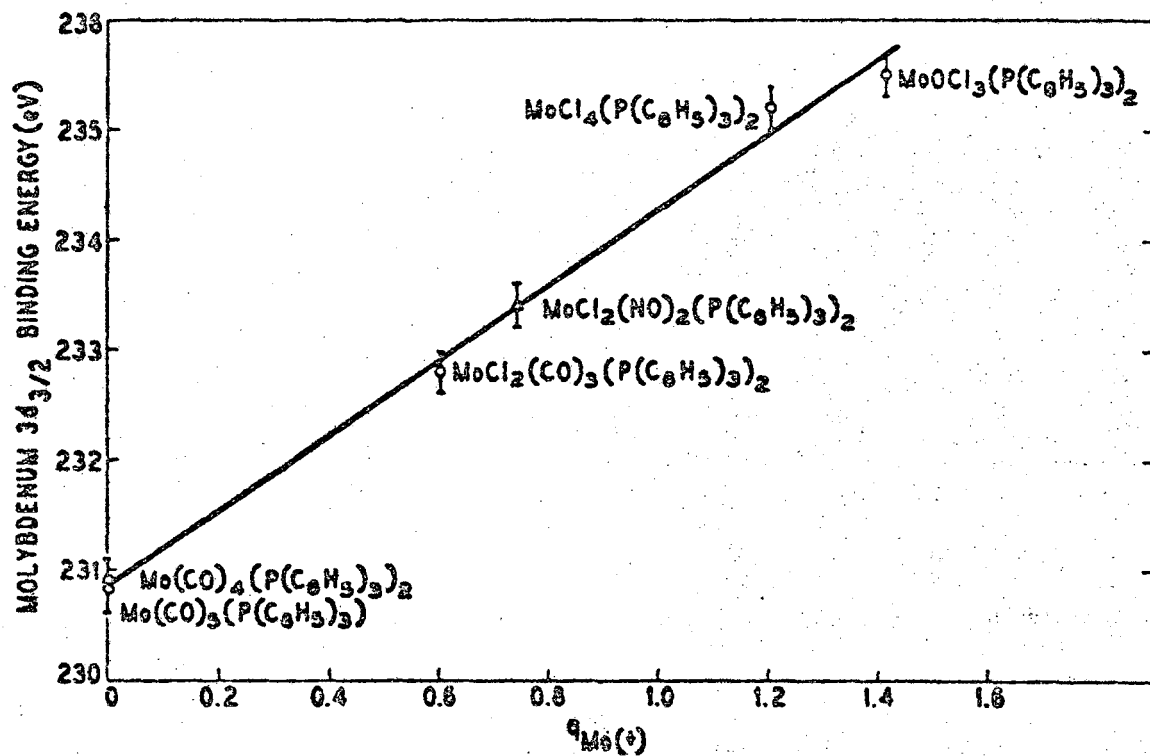
Fig. 5



XBL 752-317

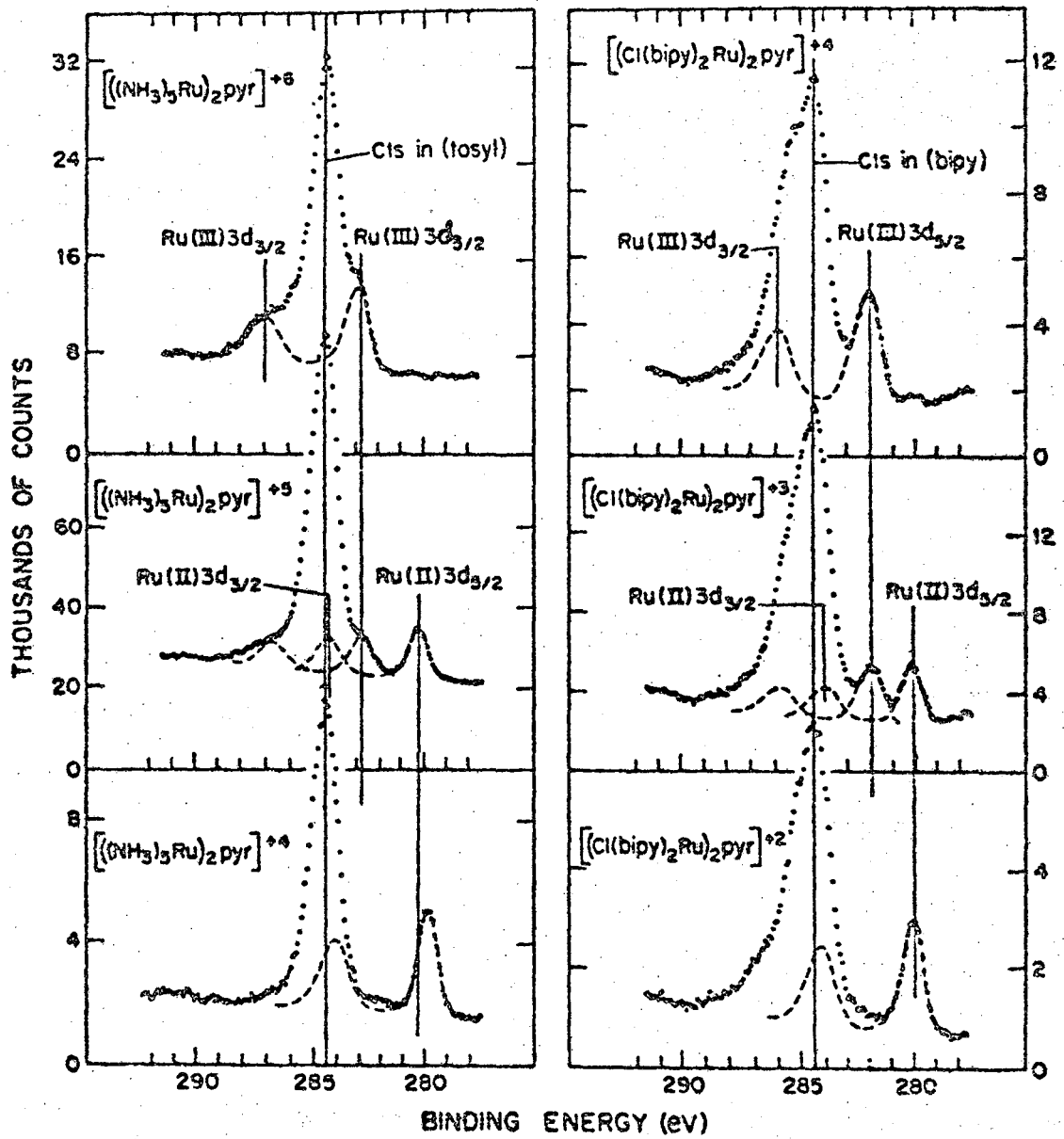
Fig. 6





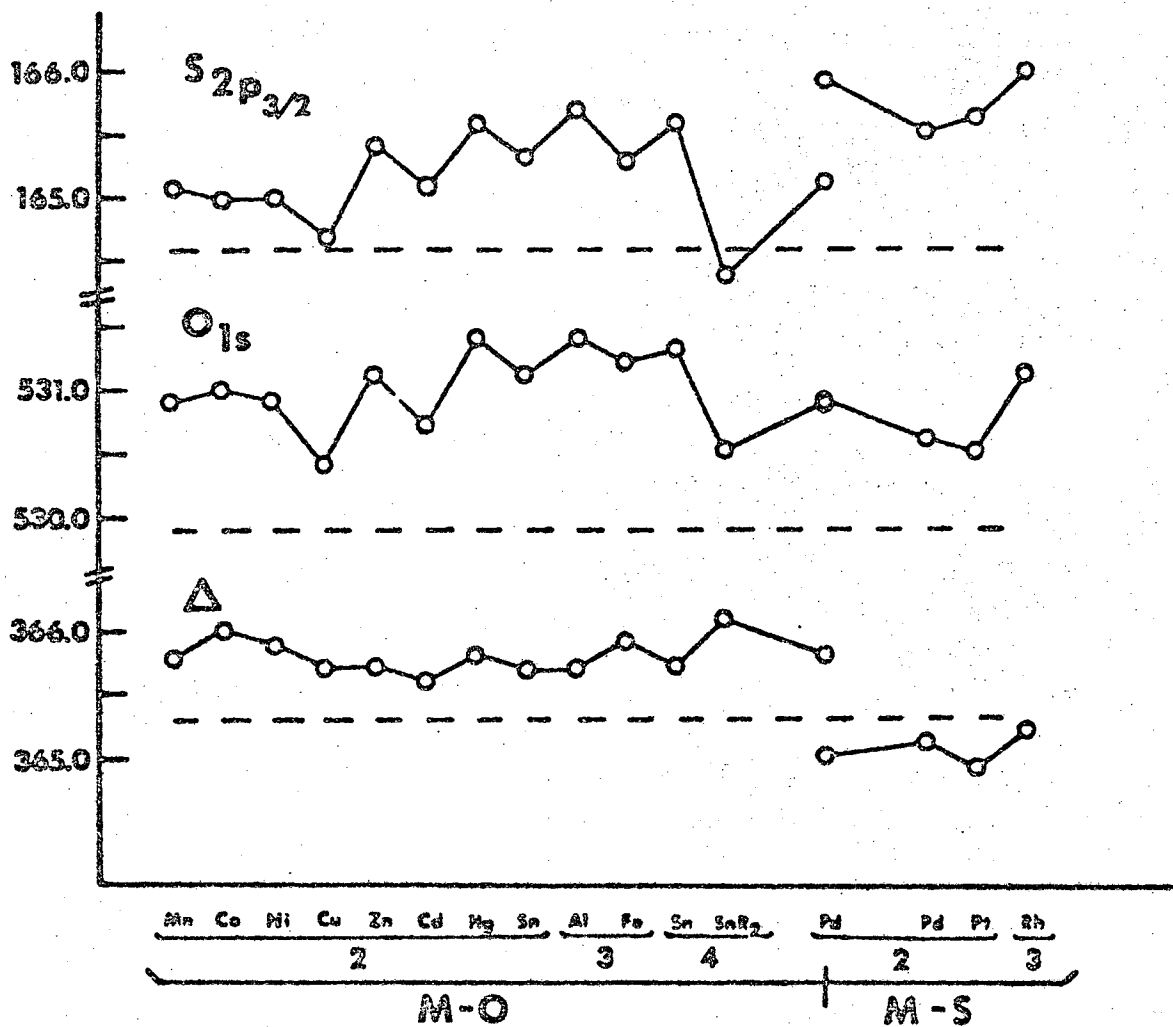
XBL 752-319

Fig. 7



XBL 752-320

Fig. 8



XBL 752-321

Fig. 9

## LEGAL NOTICE

*This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.*

TECHNICAL INFORMATION DIVISION  
LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
BERKELEY, CALIFORNIA 94720