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Inorganic Applications of X-Ray Photoelectron Spectroscopy

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Contents

I. Introduction

The principles of X-ray photoelectron spectroscopy (XPS or ESCA) have been covered in books by Siegbahn *et al.*[1,2] and Carlson.[3] Comprehensive reviews of the inorganic aspects of the field appeared in the 1972, 1973, and 1974 volumes of *Electronic Structure and Magnetism of Inorganic Compounds*[4] in the Chemical Society series of Specialist Periodical Reports and will presumably appear in future volumes of this publication. Reviews covering applications of XPS to coordination chemistry[5] and the equivalent cores approximation[6] were recently published. The XPS literature is classified and briefly summarized in biennial reviews by Hercules *et al.*[7] The purpose of this chapter is to describe recent XPS research involving problems of interest to inorganic chemists. Most of the chapter is devoted to methods for systematizing binding energy data and for deducing information about chemical bonding from the spectra. Some poorly understood phenomena and perplexing aspects of the technique are discussed to point out promising areas for future work.

II. Methods for Predicting Chemical Shifts

Chemists are interested in X-ray photoelectron spectroscopy mainly because the measured electron binding energy of an atomic core level is a function of the chemical environment of the atom. It has been shown that chemical shifts in the core binding energy of an atom in various compounds can be correlated with properties such as the nature of the groups bonded to the atom, atomic charges, thermodynamic data, and the electronic structures of the compounds. A correlation of binding energy with one of these properties can be of practical value in the case of a compound for which the property is unknown or uncertain. In that case an appropriate experimental binding energy of the compound can be used, with the aid of the established correlation, to estimate that property for the compound. In this section we shall discuss and evaluate the methods for predicting chemical shifts in binding energy which are of value to chemists.

A. Empirical Group Parameters

The very simple idea that chemical shifts in binding energy can be accounted for in terms of changes in substituent groups is the basis of a predictive method involving additive group shift parameters. The method may be represented by the equation

$$\Delta E_B = \sum_i \Delta E_{gr}(i) \qquad (1)$$

where ΔE_B is the binding energy shift and $\Delta E_{gr}(i)$ is the part of the shift due to the group i attached to the atom studied. A simple example will make the method clear. The absolute and relative (to CH_4) carbon

1s binding energies for CH_4, CF_4, CCl_4, and $CClF_3$ are given in Table 1. From the data for CF_4 and CCl_4 we can calculate group shift parameters of 2.76 and 1.38 eV for fluorine and chlorine atoms, respectively. Using these parameters, we calculate $\Delta E_B = 1.38 + 3 \times 2.76 = 9.66$ eV for $CClF_3$, in fair agreement with the experimental value. Obviously the method assumes that the binding energy of a chlorofluorocarbon is the weighted average of the binding energies of CF_4 and CCl_4. Separate sets of group shift parameters have been calculated by least squares treatments of a large number of carbon 1s,10,11) nitrogen 1s,12) silicon 2p,13) phosphorus 2p,12,14,15,16) and arsenic 3p12) binding energy data. In general, the experimental values can be reproduced by equation 1 with an average deviation of about 0.3 eV, which is approximately the experimental uncertainty in the binding energies. However, these results are not very impressive when one considers the large number of empirical parameters used. For example, in the correlation of 104 different nitrogen 1s binding energies,12) 57 group shift parameters were required. Of these parameters, 22 were determined from single binding energies and therefore automatically yielded perfect predictions.

Table 1. Carbon 1s Binding Energies

Compound	E_B, eV	ΔE_B, eV	Ref.
CH_4	290.71	0.00	8)
CF_4	301.76	11.05	8)
CCl_4	296.22	5.51	8)
$CClF_3$	300.13	9.42	8,9)

Lindberg *et al.*17) have shown that the carbon 1s shifts of some substituted benzenes are linearly correlated with the Hammett σ parameters of the substituents. However, Hammett parameters are of rather limited applicability; a given set of σ values can be used to correlate data only for similar chemical systems. It has recently been shown18) that a wider variety of core binding energy shifts can be correlated by the four-parameter relation

$$\Delta E_B = aF + bR \qquad (2)$$

in which the parameters a and b are characteristic of the class of molecule and atom to which the binding energies pertain and the parameters F and R are characteristic of substituent groups. For example, there are particular values of a and b which correspond to the carbon 1s binding energies of compounds of the type CH_3X, relative to methane. Similarly, there are particular values of F and R for the chloro group. Substitution of these values in equation 2 yields the relative binding energy for methyl chloride. Sixteen pairs of a and b values have been evaluated (corresponding to the core ionizations $\overset{*}{C}H_3X$, $\overset{*}{C}F_3X$, $O\overset{*}{C}X_2$, $\overset{*}{C}X_4$, $\overset{*}{C}H_2CHX$, $\overset{*}{F}X$, $\overset{*}{F}_3CX$, $\overset{*}{B}X_3$, $\overset{*}{Si}X_4$, $\overset{*}{Ge}X_4$, $\overset{*}{Sn}X_4$, $\overset{*}{P}X_3$, $\overset{*}{O}CX_2$, $\overset{*}{Cl}X$, $\overset{*}{Br}X$, and $\overset{*}{I}X$), and ten pairs of F and R values have been evaluated (corresponding to the substituents CH_3, CF_3, C_6H_5, SiH_3, GeH_3, OCH_3, F, Cl, Br, and I, in addition to H, the reference substituent). Forty-eight of these parameters are adjustable and were evaluated by a least-squares analysis of 92 experimental binding energies. The average deviation between the experimental and calculated ΔE_B values was ±0.2 eV.

The F and R parameters are qualitatively analogous to the "field" and "resonance" parameters, $\mathcal{F}$ and $\mathcal{R}$, of Swain and Lupton;[19)] that is, they measure the σ and π electronegativities, respectively, of substituents. However, the F and R values are more appropriate for correlating processes in which a localized positive charge develops than are the $\mathcal{F}$ and $\mathcal{R}$ values. Hence the F and R values correlate lone pair ionization potentials and proton affinities better than the corresponding $\mathcal{F}$ and $\mathcal{R}$ values do.

In principle, the empirical group parameter methods can be used to aid molecular structure determination, but their principal use to date has been in the determination of the nature of bonding and the electron distribution in compounds by interpretation of the magnitudes of the empirically evaluated parameters.

B. The Equivalent Cores Approximation

A core electron binding energy E_B can be considered as the energy of a chemical reaction. In the case of the carbon 1s binding energy of gaseous methane, the reaction is

$$CH_4 \longrightarrow CH_4^{+*} + e^- \qquad (3)$$

in which the asterisk indicates the absence of one of the carbon atom's 1s electrons. The heats of formation of CH_4 and e^- are well known, but we cannot directly obtain the heat of formation of CH_4^{+*} from ordinary thermodynamic data. However, we can do this if we apply the so-called "equivalent cores" approximation.[6,11,20-24)] According to this approximation, the hypothetical process in which an electron is transferred from the nucleus of a core-ionized atom to the core hole has an energy which is independent of the chemical environment of the core-ionized atom. For example, in the case of carbon 1s holes in CH_4 and CO_2, it is assumed that the following reactions have the same energy.

$$CH_4^{+*} \longrightarrow NH_4^{+} \qquad (3a)$$

$$CO_2^{+*} \longrightarrow NO_2^{+} \qquad (3b)$$

(In these reactions it is understood that the C and N atoms have the same mass numbers.) The approximation that reactions of this type have the same energy is equally valid if we convert the reactions into ordinary chemical reactions by adding $\frac{1}{2}N_2$ and $C_{(graphite)}$ to the left and right sides, respectively, of each reaction:

$$CH_4^{+*} + \tfrac{1}{2}N_2 \longrightarrow NH_4^{+} + C_{(graphite)} \qquad (4a)$$

$$CO_2^{+*} + \tfrac{1}{2}N_2 \longrightarrow NO_2^{+} + C_{(graphite)} \qquad (4b)$$

For such core replacement reactions the ordinary isotopic distributions of the elements can be assumed. It is assumed that the energy of any reaction like 4a or 4b is a constant, Δ_C. Note that if we add reactions as follows, 3a + 4a and 3b + 4b, we eliminate the core-ionized species:

$$CH_4 + \tfrac{1}{2}N_2 \longrightarrow NH_4^{+} + C_{(graphite)} + e^{-} \qquad (5a)$$

$$CO_2 + \tfrac{1}{2}N_2 \longrightarrow NO_2^{+} + C_{(graphite)} + e^{-} \qquad (5b)$$

The energies of reactions 5a and 5b are $E_B(CH_4) + \Delta_C$ and $E_B(CO_2) + \Delta_C$, respectively. Hence the constant Δ_C may be calculated from the reactions

$$\Delta_C = \Delta H_f^\circ(NH_4^+) - \Delta H_f^\circ(CH_4) - E_B(CH_4) \quad (6a)$$

$$\Delta_C = \Delta H_f^\circ(NO_2^+) - \Delta H_f^\circ(CO_2) - E_B(CO_2) \quad (6b)$$

In the general case of a molecule M(Z) containing an atom of atomic number Z which undergoes core ionization,

$$\Delta_Z = \Delta H_f^\circ[M(Z+1)^+] - \Delta H_f^\circ[M(Z)] - E_B[M(Z)] \quad (7)$$

Obviously for each type of core ionization (C 1s, O 1s, P 2p, etc.), there is a different value of Δ_Z. Carbon 1s binding energies and the corresponding calculated Δ_C values for some gaseous carbon compounds are given in Table 2. It can be seen that the various Δ_C values are fairly constant; the average value is -283.68 eV, and the average deviation from this value is ±0.17 eV. Hence we may write, for carbon 1s binding energies,

Table 2. Carbon 1s Binding Energies and Corresponding Values of the Energies of the Core Replacement Reactions, Δ_C

Cpd.	E_B, eV	Ref.	Δ_C, eV ($\Delta H_f^\circ[M(N)^+] - \Delta H_f^\circ[M(C)] - E_B$)
CHF_3	299.1	25)	-283.9
CO_2	297.71	26)	-283.69
HCN	293.5	27)	-283.9
C_2H_2	291.14	28)	-283.86
CH_4	290.88	8)	-283.49
C_2H_6	290.74	8)	-283.39
C_6H_6	290.42	17)	-283.46
$CH_3\overset{*}{C}CH$	290.40	28)	-283.71

$$E_B(\mathrm{C\ 1s}) = \Delta H_f^\circ(\mathrm{MN}^+) - \Delta H_f^\circ(\mathrm{MC}) + 283.68$$

Similar treatment of binding energies for gaseous compounds of boron, nitrogen, oxygen, phosphorus, and sulfur leads to the following relations.

$$\begin{aligned}
E_B(\mathrm{B\ 1s}) &= \Delta H_f^\circ(\mathrm{MC}^+) - \Delta H_f^\circ(\mathrm{MN}) + 186.9\\
E_B(\mathrm{N\ 1s}) &= \Delta H_f^\circ(\mathrm{MO}^+) - \Delta H_f^\circ(\mathrm{MN}) + 399.37\\
E_B(\mathrm{O\ 1s}) &= \Delta H_f^\circ(\mathrm{MF}^+) - \Delta H_f^\circ(\mathrm{MO}) + 529.62\\
E_B(\mathrm{P\ 2p_{3/2}}) &= \Delta H_f^\circ(\mathrm{MS}^+) - \Delta H_f^\circ(\mathrm{MP}) + 127.7\\
E_B(\mathrm{S\ 2p}) &= \Delta H_f^\circ(\mathrm{MCl}^+) - \Delta H_f^\circ(\mathrm{MS}) + 160.0
\end{aligned}$$

Obviously any one of these relations may be used to predict a core binding energy when the necessary heats of formation are known or may be used to predict an unknown heat of formation when the necessary binding energy and one heat of formation are known.

Application of the equivalent cores method to solid compounds is slightly more complicated, requires additional 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.20) The correlations were restricted, because of the nature of the assumptions involved, to molecular compounds or to compounds in which the core-ionized atoms are in anions.

A chemical shift in core binding energy corresponds, according to the equivalent cores approximation, to the energy of an ordinary chemical reaction. For example, the difference between the carbon 1s binding energies of CH_2Cl_2 and CH_4 is equated to the energy of the following reaction.

$$CH_2Cl_2 + NH_4^+ \longrightarrow NH_2Cl_2^+ + CH_4$$

Because the heat of formation of $NH_2Cl_2^+$ is not known, this chemical shift cannot be calculated from available thermodynamic data. However, quantum mechanical methods have been used to estimate the energy of this and similar reactions. These calculations are attractive for at least three reasons: (1) generally 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 having the same geometry, in accord with the fact that nuclei remain fixed during the photoelectric process. In Table 3 experimental carbon 1s binding energy shifts (relative to CH_4) for several compounds can be compared with the energies of the corresponding "equivalent-cores" chemical reactions calculated by various quantum mechanical methods. The agreement with experiment

Table 3. Some Carbon 1s Binding Energy Shifts Calculated Using the Equivalent Cores Approximation

Cpd.	ΔE_B, eV					
	Exptl.	Thermo.	CNDO/2 29)	MINDO/1 30)	MINDO/3 31)	ab initio
CH_4	0	0	0	0	0	0
CHF_3	8.2	7.8	1.68	----	10.78	9.31 32)
CF_4	11.05	11.3	2.00	----	14.48	12.64 32)
CO_2	6.83	6.6	----	2.33	4.88	5.6 33)
CH_3OH	1.6	----	----	0.56	2.09	----
CH_2Cl_2	3.1	----	1.62	----	-----	3.39 32)

improves, as expected, with increasing sophistication of the calculational method. The poorest agreement is obtained with the CNDO/2 method, and the best agreement is obtained with *ab initio* methods using Slater-type orbitals fitted by Gaussian functions. Although chemical shifts calculated by the semiempirical MO methods are in poor absolute agreement with the experimental values, the calculated values show fairly good linear correlations with the experimental values, particularly for compounds having similar structures.29)

C. Correlation with Atomic Charge

Simple electrostatic considerations lead to the conclusion that the energy required to remove a core electron from an atom should increase with increasing positive net atomic charge and decrease with increasing negative net atomic charge. This effect can be seen in the data of Table 4, where chemical shifts in the 1s binding energy of sulfur atoms with various charges (calculated by an SCF Hartree-Fock method1)) are listed. By interpolation of such data it is possible to calculate binding energy shifts for hypothetical fractionally-charged atoms. Over a small range

Table 4. Calculated Sulfur 1s Shifts

Species	ΔE_B, eV
S^-	-11.3
S	0
S^+	13.8
S^{2+}	29.8
S^{3+}	48.1

of atomic charge, binding energy is well represented as a linear function of atomic charge, as in the following equation,

$$E_B = kQ + \ell \tag{8}$$

where Q is the atomic charge and k and ℓ are constants. This same equation can also be derived by consideration of a simple shell model of the atom.1)

If one assumes that the core binding energy of an atom in a compound is dependent only on the atomic charge, one should expect equation 8 to serve as a basis for correlating binding energies in compounds. Indeed, many investigators have obtained fairly good correlations using equation 8 in combination with methods for estimating atomic charges. The method which has been most commonly used for estimating atomic charges is the Pauling34) method (or modifications of it), which 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 Δx is the difference between the electronegativities of the bonded atoms. For example, in this way Grim et al.35,36) found linear correlations between the calculated metal atom charges and the nickel $2p_{3/2}$ binding energies of some simple nickel(II) salts and the molybdenum $3d_{5/2}$ binding energies of compounds of molybdenum in a variety of oxidation states. Similarly Hughes and Baldwin37) found a linear correlation between molybdenum atom charges in various triphenylphosphine molybdenum complexes and the molybdenum $3d_{3/2}$ binding energies.

The potential energy of a core electron is not only affected by the charge of the atom of which it is a part, but is also affected by the charges of all the other atoms in the compound. That is, one must account for the work to remove the electron from the field of the surrounding charged atoms as well as from the atom which loses the electron. Both effects are accounted for by the so-called point-charge potential equation2)

$$E_B(A) = kQ_A + \sum_{i \neq A}(Q_i/R_i) + \ell \qquad (9)$$

in which Q_i are the charges of the atoms and R_i are their distances from the core-ionizing atom (atom A). When the more approximate equation (eq. 8) is used to correlate binding energies with atomic charge, good straight-line relationships are found only if the compounds involved have similar structures so that the omitted term, $\sum_{i \neq A}(Q_i/R_i)$, is either constant or approximately linearly related to Q_A. In general, very little improvement in correlations with equation 8 is achieved by the use of more sophisticated methods for estimating atomic charges. However, when equation 9 is used, it is important to use a good charge estimation procedure, and the resulting correlations are usually superior to the corresponding correlations with equation 8. Gray et al.13) have recently compared the correlations obtained for a set of silicon 2p binding energies using equations 8 and 9 with several different methods for estimating atomic charges.

In salts, rather small core binding energy shifts are observed for monatomic ions and for atoms in polyatomic ions when the counter-ions are changed. For example, in a series of sixteen potassium salts, the spread in K 2p binding energy (between the extremes of KCl and $K_2[Pt(NO_2)_4Cl_2]$) is only 1.7 eV.38) And both the N 1s and P 2p binding energies of many salts containing the bis(triphenylphosphine)iminium cation, $N[P(C_6H_5)_3]_2^+$, differ by only a few tenths of an eV39) The minor effect of crystal environment on chemical shift, illustrated by these results, is surprising when one considers the magnitude of the potential term of equation 9 as calculated using an appropriate Madelung function. In the case of simple salts such as KCl and LiF, if it is assumed that the ions bear unit charges, the chemical shifts calculated from the differences in the Madelung potentials differ greatly from the small observed chemical shifts. Citrin _et_ _al_.40) showed that the discrepancies can be markedly reduced by accounting for the mutual polarization of the ions. The inclusion of polarization effects is essentially equivalent to the use of covalent bonding with fractional atomic charges. In fact, Parry,41) by the solution of simultaneous equations (of the form of eq 9) has calculated atomic charges in several oxides of lead using theoretical k values.

Hamer and Walton42) have shown that it is possible to distinguish, within a single compound, chlorine atoms which are bonded to only one metal atom and chlorine atoms which act as bridges between two metal atoms. As expected from simple electrostatics and equation 9, bridging chlorines have a greater core binding energy than terminal chlorines. In Fig. 1a is shown the chlorine $2p_{1/2,3/2}$ spectrum of $Re_3Cl_9(pyz)_3$ (pyz = pyrazine), in which there are twice as many terminal chlorines as bridging chlorines. Deconvolution shows that the two sets of binding energies differ by ca 1.5 eV and that the doublet at lower binding energy is twice as intense as that at higher binding energy. Replacement of half of the terminal chlorines by other groups, as in the polymeric pyridine complex $[Re_3Cl_6(py)_3]_n$, yields a spectrum (Fig. 1b) in which the peaks due to terminal and bridging chlorines have a 1:1 intensity ratio. The diethyldithiocarbamate complex $Re_3Cl_3(SCN)_3(S_2CNEt_2)_3$, in which all the terminal chlorines have been replaced, gives a spectrum showing only the doublet due to the bridging chlorines.

Sometimes a simple qualitative interpretation of core binding energy data is sufficient to give a definitive answer to a problem involving atomic charge. Such was the case in the study of the ClF molecule by Carroll and Thomas.43) These investigators found that the fluorine core electrons are less bound in ClF than in F_2 and that the chlorine 2s electrons are more bound in ClF than in Cl_2. Now, in the case of a diatomic molecule it is certain that, in equation 9, the absolute magnitude of the kQ_A term will always be greater than that of the potential term (which in this case is simply $-Q_A/R$). Hence if we accept the validity of equation 9, we conclude that an increase in binding energy corresponds to an increase in positive charge and that a decrease in binding energy corresponds to an increase in negative charge. As we shall soon point out, this conclusion is valid only if the change in electronic relaxation energy associated with the core ionization is zero. In the case of the molecules under consideration, this is probably a good approximation.

Inasmuch as the atomic charges in F_2 and Cl_2 are zero, the binding energy data strongly indicate that, in ClF, the chlorine atom is positively charged and the fluorine atom is negatively charged. Thus the XPS data refute the work of Flygare et al.44,45) who, on the basis of the molecular Zeeman effect in ClF, came to the remarkable conclusion that the dipole moment corresponds to a positive charge on the fluorine and a negative charge on the chlorine.

The oxidation state of an atom in a compound is a quantity which is calculated according to a simple arbitrary recipe. If this recipe is agreed upon and understood, there should never be any argument as to the oxidation state of a particular atom in a compound. On the other hand, the charge of an atom is a quantity which must be calculated theoretically or somehow derived from experimental data. It is quite possible for an atom of a given element in a series of compounds to have the same oxidation state, and yet to have a wide range of atomic charges. Clearly attempts to determine oxidation states directly from core binding energies are potentially very risky. As we have seen, the relationship between binding energies and atomic charges is fairly straightforward, but the latter are related to oxidation states in a way which can be quite complicated. For example, it has been shown46) that the nickel $2p_{3/2}$ binding energies of the dicarbollide complexes of Ni(III) and Ni(IV) (in which the nickel atoms are coordinated to boron and carbon atoms of the polyhedral ligand $B_9C_2H_{11}{}^{2-}$) are lower than that of $[Ni(H_2O)_4Cl_2]\cdot 2H_2O$ (in which an Ni(II) atom is coordinated to relatively electronegative oxygen and chlorine atoms). Nevertheless, various workers have achieved reliable correlations of binding energy with oxidation state by restricting themselves to compounds with similar structures. Thus Chatt et al.[47)] showed that the rhenium $4f_{7/2}$ binding energies of $ReCl_2(PMe_2Ph)_4$, $ReCl_3(PMe_2Ph)_3$, and $ReCl_4(PMe_2Ph)_2$ are linearly related to the rhenium oxidation states. Schmidbaur et al.[48)] showed that compounds of gold in the +1, +2, and +3 oxidation states having similar structures show a similar correlation of the gold $4f_{7/2}$ binding energy with oxidation state. And Edwards[49)] found that the copper $2p_{3/2}$ binding energies of copper(I) carboxylates fall in the range 931.4-932.4 eV, whereas the range for copper(II) carboxylates is 934.0-934.4 eV.

D. Quantum Mechanical Calculations

Schwartz[50,51)] pointed out that the binding energy of a core electron is essentially equal to the potential felt at the core due to the nuclear charge and all the other electrons in the system. Chemical shifts can be related to a "valence electron potential", Φ_{val}, defined as

$$\Phi_{val} = -\sum_{A} P_i \left\langle r^{-1} \right\rangle_i + \sum_{i \neq A} (Q_i/R_i)$$

where P_i is the population in the ith valence orbital of atom A, $\left\langle r^{-1} \right\rangle_i$ is the radial expectation value for the orbital, and the second summation has the same significance that it has in equation 9. The valence electron potentials can be readily calculated by a semiempirical MO method such as CNDO/2 or Extended Hückel. Binding energies are then correlated by the relation

$$E_B = c\Phi_{val} + \ell' \qquad (10)$$

where c is an empirically evaluated parameter which helps to compensate for approximations of the semiempirical MO method used to evaluate Φ_{val}, and ℓ' represents the binding energy of the atom stripped of all valence electrons.

Ab initio calculations, that is, nonempirical LCAO SCF MO calculations, have been used in several different ways to calculate core binding energies and their shifts. We have already discussed the use of ab initio methods to calculate chemical shifts using the equivalent cores approximation. Such calculations have the advantage that they avoid hole-state calculations. However many direct hole-state calculations have been carried out. Often these calculations involve the assumption Koopmans' theorem$^{52)}$; that is, ionization potentials are assumed to be the same as the one-electron orbital energies of the parent neutral molecules. In this approximation, electronic relaxation and differences in correlation and relativitistic energies of molecules and ions are ignored. Differences in correlation and relativistic energies are expected to be less than about 1 eV for light atoms. However, electronic relaxation energies are considerably greater and pose a problem if absolute binding energies are calculated. A procedure which is theoretically more rigorous than the assumption of Koopmans' theorem is that in which ab initio calculations are carried out on both the molecule and its core-ionized state. An absolute binding energy, including relaxation energy, is then obtained by taking the difference between the calculated energies for these species. This procedure is often called the ΔSCF method. The difference between an absolute binding energy calculated in this way and the value calculated assuming Koopmans' theorem is essentially the electronic relaxation energy, E_R:

$$E_B \approx E_B(\Delta SCF) = E_B(KT) - E_R$$

In Table 5 we give some data of Hillier et al.[53)] to illustrate the

Table 5. Experimental and Calculated Binding Energies[53)]

	Experimental		Koopmans' Theorem		ΔSCF		Relaxn.
	E_B	ΔE_B	E_B	ΔE_B	E_B	ΔE_B	Energy
N 1s							
NH_3	405.6	0.0	422.2	0.0	405.3	0.0	16.9
N_2	409.9	4.3	428.3	6.1	411.6	6.3	16.7
$N\overset{*}{N}O$	412.5	6.9	432.2	10.0	413.0	7.7	19.2
$\overset{*}{N}NO$	408.5	2.9	428.5	6.3	410.0	4.7	18.5
CH_3CN	405.9	0.3	424.5	2.3	406.4	1.1	18.1
O 1s							
H_2O	539.4	0.0	558.6	0.0	539.3	0.0	19.3
O_2 $^4\Sigma$	543.1	3.7	563.8	5.2	543.5	4.2	20.3
O_2 $^2\Sigma$	544.2	4.8	565.2	6.6	544.2	4.9	21.0
CO	542.3	2.9	563.5	4.9	543.4	4.1	20.1
N_2O	541.2	1.8	562.2	3.6	541.2	1.9	21.0
CO_2	540.8	1.4	562.8	4.2	542.4	3.1	20.3
C_3O_2	539.7	0.3	562.9	4.3	540.6	1.3	22.3
H_2CO	538.5	-0.9	560.1	1.5	538.8	-0.5	21.3

magnitude of calculated relaxation energies and the general quality of results which are obtained from ab initio calculations. The data in Table 5 were obtained using contracted Gaussian type functions, the expansion parameters being determined by least-squares fit to double-zeta Slater-type orbitals. Several conclusions can be drawn. First, the Koopmans' theorem binding energies are considerably greater (by about 4%) than the experimental and ΔSCF values. Second, the ΔSCF binding energies are in good agreement with the experimental values, the average deviation being ±0.7 eV. Third, the chemical shifts calculated by either the Koopmans' theorem or the ΔSCF method are in fair accord with experiment, the ΔSCF values being much better in this respect than the Koopmans' theorem values. And fourth, relaxation energies for a core ionization can vary from one compound to another by as much as 2 or 3 eV.

E. Electronic Relaxation Energy

The principal stumbling block in the use of chemical shifts to study the nature of chemical bonding is the fact that the electronic relaxation energy is a variable. In other words, XPS does not directly give information about the ground state of a molecule. Thus Koopmans' theorem treatments and the unmodified point charge potential model (equation 9), which is based on the atomic charges of ground-state molecules, are in principle inadequate. Fortunately there are various ways of estimating relaxation energies or of avoiding their complications.

The electronic relaxation energy associated with the core ionization of a molecule can be divided into two parts:54)

$$E_R = E_R^{contr} + E_R^{flow} \qquad (11)$$

The term E_R^{contr} is the relaxation energy associated with the contraction of the local charge distribution on the atom which is undergoing core ionization. The term E_R^{flow} is the relaxation energy associated with the rest of the molecule, that is with the flow of electron density toward the core hole. It has been pointed out$^{54-57)}$ that E_R^{contr} is approximately a linear function of atomic charge (the more negative the charge, the greater the relaxation energy). Hence equation 11 can be rewritten as follows,

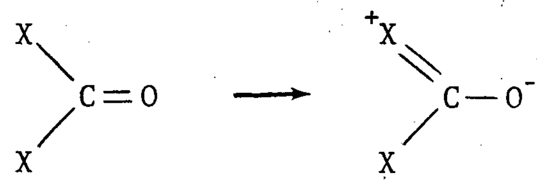
$$E_R = k'Q + E_R^{flow} + \ell_R \qquad (12)$$

where k' is a negative constant and ℓ_R is the relaxation energy due to orbital contraction around a neutral atom in the molecule. The simple point charge potential equation (equation 9) ignores relaxation energy. However, if we account for relaxation energy by subtracting the expression for E_R (as given by equation 12) from the right-hand side of equation 9, we see that the terms $-k'Q$ and $-\ell_R$ can be combined with the corresponding terms kQ_A and ℓ of equation 9, resulting in the expression

$$E_B(A) = (k - k')Q_A + \sum_{i \neq A} (Q_i/R_i) + (\ell - \ell_R) - E_R^{flow} \qquad (13)$$

Obviously whenever binding energy data are fit to equation 9, the empirically determined values of k and ℓ automatically take into account the "atomic" relaxation energy, E_R^{contr}. Equation 9 gives very good correlations for molecules which have similar structures, presumably because of the automatic accounting for E_R^{contr} and the fact that similar molecules have similar E_R^{flow} values and that $-E_R^{flow}$ is therefore absorbed into the constant ℓ.

When the simple point charge potential equation (eq. 9) is used to correlate binding energies for a wide variety of molecules having different types of structures, large discrepancies are often found between the calculated and experimental binding energies. Usually these discrepancies can be rationalized in terms of unusually large or small values of E_R^{flow}. For example, the carbon 1s binding energy of CO is much higher than one would predict from carbon compound correlations that do not take relaxation energy into account. This discrepancy is believed to be due to an unusually low relaxation energy for CO. In CO, the carbon atom is attached to only one other atom, whereas in almost all its other compounds carbon is attached to at least two other atoms. (One would expect the electron flow during relaxation to increase with an increase in the number of bonds, or avenues for electron flow.[58,59]) As another example of a discrepancy due to neglect of relaxation energy, we can cite the oxygen 1s binding energies of ketones and similar carbonyl compounds, which are usually much lower than predicted.[60] These core ionizations are believed to be accompanied by an extraordinarily large amount of relaxation, due to a shift of π electron density from the groups attached to the carbonyl group to the oxygen atom:



Such "π-donor relaxation" is of little importance in saturated oxygen compounds such as alcohols and ethers.

The point charge potential model (equation 9) and the valence electron potential model (equation 10) do not take account of electronic relaxation. They are based on the hypothetical "sudden" ejection of an electron, with the assumption that the energy of the process is dependent only on the initial ground-state charge distribution. However, data such as those in Table 5 and the success of the "equivalent cores" procedure (in which ground-state thermochemical data are used for excited states) indicate that the valence electron relaxation process is essentially complete in the time of the photoelectric process. Therefore if we wish to calculate accurately the binding energy by a hypothetical "sudden" process in which the valence electrons are assumed to remain fixed, we should not use the valence electron distribution of either the initial molecule or of the final core-hole ion. Use of the electron distribution of the initial molecule corresponds to the assumption of no relaxation energy (the absolute binding energy would be too high by an amount equal to the relaxation energy). Use of the electron distribution of the final ion corresponds to the inclusion of twice the appropriate relaxation energy (the absolute binding energy would be too low by an amount equal to the relaxation energy). However, a valence electron distribution between these two extremes, close to the average distribution, is appropriate.61) This procedure is equivalent to that achieved by quantum mechanical considerations by Liberman62) and Hedin and Johansson63) and is analogous to Slater's64) method for calculating excitation energies, in which one assumes occupation numbers half-way between those of the initial and final states. A logical name for the procedure of correlating binding energies with valence electron distributions half-way between those of the initial molecules and the core-ionized molecules is the "transition state" method. The equivalent cores approximation is used to calculate the electron distribution of the core-ionized molecule by simply replacing the core-ionized atom with the atom of the next element in the periodic table, plus a +1 charge. Alternatively, one can carry out the calculations directly for the transition state by using interpolated (pseudo-atom) calculational parameters (e.g., CNDO) for the atom which undergoes core ionization. These methods, or very similar methods, have been applied very successfully to a wide variety of compounds using the valence electron potential model combined with CNDO calculations[58,65)] and the point charge potential model combined with atomic charges estimated by the CHELEQ electronegativity equalization procedure[59,66)] or the CNDO/2 method.[67,68)]

III. Shake-up

The X-ray photoelectron spectrum of the core ionization of an atom in a molecule consists of peaks and bands corresponding to transitions to various excited states. None of these transitions corresponds to the formation of the Koopmans' theorem frozen-orbital ionic state, which is a completely hypothetical state. However, the center of gravity of the various peaks and bands lies at the energy corresponding to the hypothetical Koopmans' theorem transition. This relation may be expressed by the sum rule of Manne and Aberg,69)

$$E_{KT} = (\sum_j E_j I_j)/(\sum_j I_j),$$

where E_{KT} is the Koopmans' theorem energy, and E_j and I_j are the energies and intensities of the various transitions. The primary peak, which is usually the most intense peak in the spectrum, occurs at lower binding energy than the Koopman's theorem energy; the energy difference corresponds to the electronic relaxation energy. In general, the spectrum also contains several satellite peaks with binding energies higher than that of the primary peak which correspond to electronically excited core-hole ion-molecules. These "shake-up" transitions may be looked upon as combinations of core ionizations and molecular electronic excitations. A broad band in the very high binding energy region of the spectrum corresponds to "shake-off", i.e., to the loss of a valence electron as well as the core electron. For general discussions of the phenomena of shake-up and shake-off, the reader is referred to books by Siegbahn et al.2) and Carlson3) and a review article by Brisk and Baker.70)

If the primary peak is the only peak with a binding energy less than the Koopmans' theorem energy (this is usually the case), then an increase in the primary relaxation energy must be accompanied by an increase in the quantity $\sum_j (E_j - E_{KT})I_j$ for the shake-up and shake-off bands, where the intensities I_j are understood to be measured relative to the primary peak. This function would increase, for example, if the relative intensity of any shake-up peak increased. As a matter of fact, it may be stated as a rough rule of thumb that core electron spectra for which the electronic relaxation energy is high are usually accompanied by intense shake-up peaks. This generalization implies that the shake-off bands are similar in both position and intensity and that the energies of the shake-up peaks are of similar magnitude. As an illustration of this rule of thumb we may compare the C 1s and O 1s spectra of CO with those of C_3O_2 and transition metal carbonyls. When we go from CO to the more complicated molecules, the number of atoms which can act as sources of valence electron density during the electronic relaxation processes increases, and therefore it is reasonable to suppose that the relaxation associated with both the C 1s and O 1s ionizations increases. The shake-up peaks in the CO spectra71) are fairly weak, whereas those in the spectra of $C_3O_2$72) and the metal carbonyls73) are very intense.74,75)

The selection rules appropriate for a shake-up transition are of the monopole type.2,76) The intensity of a shake-up peak depends on the overlap integral between the lower state molecular orbital from which the electron is excited (in the neutral molecule) and the upper state molecular orbital to which the electron is excited (in the core-ionized molecule) Consequently one expects transitions of the type $\sigma_u \rightarrow \sigma_u$, $\sigma_g \rightarrow \sigma_g$,

$\pi_u \rightarrow \pi_u$, and $\pi_g \rightarrow \pi_g$ with g → u and u → g transitions forbidden.

As a first, trivial, example of the application of the overlap criterion, let us consider the possibility of a shake-up peak associated with the C 1s ionization of the terminal carbon atom in nitroethane and the $\pi \rightarrow \pi^*$ transition of the nitro group in that molecule. In this case the core ionization occurs in a region of the molecule remote from the molecular orbitals involved in the electronic transition. Hence the upper-state molecular orbital will be essentially unperturbed by the core ionization and it will be, as in the neutral molecule, orthogonal with the lower-state molecular orbital. Consequently the critical overlap integral is almost zero and no shake-up is observed for that transition.

As a second example, let us consider the O 1s and C 1s spectra of carbon suboxide, C_3O_2, shown in Figure 2. Strong satellites are seen 8.2 eV from the O 1s primary peak and about 7.9 eV from the more intense C 1s primary peak (the peak due the non-central carbon atoms). Gelius et al.[72,77)] believe that these satellites are due to the $1\pi_g \rightarrow 2\pi_g$ transition of C_3O_2, corresponding to the molecular orbitals schematically illustrated in Figure 3. In the C 1s spectrum, no satellite is seen in the region about 8 eV from the less intense primary peak, i.e. the peak due to the central carbon atom. The lack of a satellite in the C 1s spectrum of the central carbon atom would follow from the fact that neither the $1\pi_g$ nor the $2\pi_g$ molecular orbital has any magnitude at the central carbon atom. If the interpretation is correct, this is a case in which the overlap integral between the lower-state and upper-state molecular orbitals is exactly zero. On the other hand, Aarons et al.[74)] believe that the

8.2 and 7.9 eV satellites of the O 1s and non-central C 1s lines are due to the $2\pi_u \rightarrow 2\pi_g$ transition of C_3O_2. When one of the oxygen atoms or non-central carbon atoms in the $2\pi_g$ state of C_3O_2 is core-ionized, the state loses its g character and is no longer orthogonal with u states. Hence the latter assignment does not violate the $u \not\leftrightarrow g$ selection rule. However, when the central carbon atom in the $2\pi_g$ state is core-ionized, the state retains its g character and the shake-up transition is forbidden.

Pignataro[78,79] has observed bands centered about 5.5 eV from the main peaks in the C 1s and O 1s spectra of $Cr(CO)_6$. He has suggested that these are shake-up satellites corresponding to the ${}^1A_{1g} \rightarrow d^1T_{1u}$ metal→ligand charge transfer transition which appears at 5.5 eV in the ultraviolet absorption spectrum[80] of $Cr(CO)_6$ vapor. If this assignment is correct, it is another example in which the symmetry of a molecule is changed by a core-ionization, thus allowing an otherwise symmetry-forbidden transition to take place. A very weak satellite was observed about 5.8 eV from the primary peak in the Cr 3p peak of $Cr(CO)_6$. This peak is probably not a ${}^1A_{1g} \rightarrow d^1T_{1u}$ shake-up satellite because, in principle, such a satellite is strictly forbidden.

In general, the energy separation between a shake-up peak and the primary peak is not exactly equal to the corresponding electronic transition energy for the neutral molecule. And, in cases where a given electronic transition is represented by shake-up peaks in several core ionization spectra, the energy separations are usually slightly different. These differences can give information regarding the atomic orbital contributions to the relevant molecular orbitals.

The core ionization of an atom stabilizes all the valence electrons in the atom. Depending on whether the electronic transition shifts electron density to or from an atom, the energy separation for a shake-up peak of that atom will be less than or greater than the energy of the neutral molecule ionization.$^{81)}$ As an illustration of these effects, let us consider the shake-up spectra of formamide, H_2NCHO.$^{82)}$ The principal transitions involved are the $\pi_1 \rightarrow \pi_3{}^*$ and $\pi_2 \rightarrow \pi_3{}^*$ transitions. The π_1 molecular orbital consists of roughly equal amounts of carbon, nitrogen, and oxygen character, the π_2 molecular orbital has major contributions only from the nitrogen and oxygen atoms, and the $\pi_3{}^*$ molecular orbital has about twice as much carbon character as nitrogen or oxygen character. From the experimental data, given in Table 7, it can be seen that the energy of the band assigned to the $\pi_1 \rightarrow \pi_3{}^*$ transition is much lower in the carbon spectrum than in the nitrogen and oxygen spectra. This result is expected because the concentration of $\pi_3{}^*$ on carbon implies that a 1s hole on carbon stabilizes this orbital more than a 1s hole on nitrogen or oxygen would. The same sort of trend is expected in the case case of the $\pi_2 \rightarrow \pi_3{}^*$ peaks, but in this case the carbon peak is extremely

Table 7. Shake-up in the 1s Spectra of Formamide$^{73)}$

Transition	C 1s		N 1s		O 1s	
	ΔE	Intensity	ΔE	Intensity	ΔE	Intensity
Primary Peak	0	100	0	100	0	100
$\pi_2 \rightarrow \pi_3{}^*$	5?	<0.5	9.9	3.5	7.4	7.3
$\pi_1 \rightarrow \pi_3$	9.6	7.2	15.0	5.3	13.9	8.5

weak (as expected, because of the low π_2 density on the carbon atom) and there is considerable uncertainty as to the energy.

Relatively strong satellites, 5-10 eV from the main peaks, have been observed in the metal 2p spectra of 3d transition metal oxides and halides. These satellites are believed to correspond to ligand→(metal 3d) charge-transfer transitions.[76,83-85] Evidence for this assignment is found in the following facts. (1) Little satellite structure is found in the spectra of analogous cyanide complexes, except at excitation energies of 12-16 eV. The absence of high-intensity, low-energy shake-up peaks in the cyanide complexes is probably due to the fact that cyanide electrons are tightly bound and localized between the carbon and nitrogen atoms. The energy differences between metal 3d levels and filled CN^- levels are large. (2) Satellite structure is generally most intense for paramagnetic compounds and for compounds of weak-field ligands. In such cases the energy separation between the ligand and metal orbitals is likely to be small. A nice illustration of this phenomenon is shown by the Ni 2p spectra of the two isomers of bis(N-methylsalicylaldimine)-nickel(II), given in Figure 4.[35] The diamagnetic square-planar isomer shows practically no evidence of shake-up, whereas the paramagnetic octahedral isomer shows strong shake-up satellites. (3) As one goes to metals of higher Z, the intensities of the shake-up peaks increase. (4) Although shake-up peaks are present in the case of metal ions with vacant or partially filled 3d shells, they are absent in the case of ions with completely filled 3d shells.

Finally, we point out that occasionally one observes spectra in which the intensities of the shake-up lines are comparable to, or even greater than, those of the primary lines. For example, such was the case in the Fe 2p spectrum of a sample of $KFeS_2$, obtained by Binder[86).

IV. Multiplet Splitting

Core electron ejection normally yields only one primary final state (aside from shake-up and shake-off states). However, if there are unpaired valence electrons, more than one final state can be formed because exchange interaction affects the spin-up and spin-down electrons differently. If a core s electron is ejected, two final states are formed. If a core electron of higher angular momentum, such as a 2p electron, is ejected, a large number of multiplet states can result. In this case it is difficult to resolve the separate states, and the usual effect of unpaired valence electrons is (1) to broaden $2p_{1/2}$ and $2p_{3/2}$ peaks, and (2) to increase the energy separation between these peaks.76) The effect of spin on the width of the $2p_{3/2}$ line was studied by Main and Marshall.87) In a survey of 26 different 3d transition metal compounds, they found that all 14 diamagnetic compounds (including ions of d°, d^6 low spin, and d^{10} configurations) had $2p_{3/2}$ linewidths smaller than 2.5 eV and that 9 of the 12 paramagnetic compounds had linewidths greater than 2.5 eV. Several investigators have studied the effect of spin on the $2p_{1/2}$-$2p_{3/2}$ separation.88-90) It has been observed that the separation is 9.0-9.3 eV for most diamagnetic chromium compounds, 9.4-10.2 eV for most chromium(III) compounds,88) 15.1 ± 0.3 eV for diamagnetic cobalt(III) complexes and 16.0 ± 0.3 eV for cobalt(II) complexes.89,90)

Small perturbations of the $2p_{1/2}$-$2p_{3/2}$ separations in the spectra of paramagnetic 3d transition metal compounds can be interpreted in terms of changes in the covalency of the metal ligand bonds. A decrease in the exchange interaction (leading to a decrease in the multiplet splitting or broadening and a decrease in the $2p_{1/2}$-$2p_{3/2}$ separation) is attributed to a delocalization of the unpaired electron density from the metal atom to the ligand atoms. For example, consider the Cr 2p data in Table 8.$^{88)}$ In the complexes with "hard" ligands such as oxide and fluoride, the spin-orbit splitting is distinctly higher than it is in complexes with "soft" ligands such as urea and thiocyanate. The splitting approximately follows the nephelauxetic series of ligands,$^{91)}$ and it appears that in complexes such as $K_3[Cr(NCS)_6]$ the metal d orbitals are sufficiently expanded to preclude measurable interaction with the 2p core electrons. An apparently discordant fact, however, is the observation that the multiplet splitting of the Cr 3s line in $K_3[Cr(CNS)_6]$ is approximately of the same magnitude as, or slightly greater than, that in Cr_2O_3.$^{92)}$

Table 8. Spin-Orbit Separation for Some Chromium(III) Compounds$^{88)}$

Compound	$2p_{1/2}$-$2p_{3/2}$ sepn., eV
K_3CrF_6	10.2
$NaCrO_2$	9.9
Cr_2O_3	9.7
$Cr(NH_3)_6Cl_3$	9.7
$CrCl_3$	9.6
$Cr(urea)_6Cl_3$	9.4
$K_3[Cr(NCS)_6]$	9.2

Because of the 1/r dependence, the exchange interaction rapidly decreases with an increase in the difference between the principal quantum numbers of the impaired electrons and the core vacancy. Thus multiplet splitting is negligible in the 1s spectra of paramagnetic transition metal compounds. On the other hand, shake-up intensity is essentially independent of the core level involved. Hence one can distinguish between shake-up and multiplet satellites by changing the principal quantum number of the core electron ionized.$^{76)}$

V. Some Studies of Metal-Ligand Interactions

A. Nitrosyl complexes

Nitrosyl complexes are of two types, depending on the orientation of the NO group with respect to the metal atom. In a "linear" complex, the M-N-O bond angle is near 180°, and the ligand is often considered to be the NO^+ ion; in a "bent" complex, the M-N-O bond angle is around 125°, and the ligand is often looked upon as the NO^- ion. In nitrosyl complexes it is obviously reasonable to look for a correlation between the N 1s binding energy and the type of coordination. Unfortunately there is only a very weak correlation, if any, of this type, although there is a strong correlation between the electron density on the metal atom and the N 1s binding energy.93,94) The N 1s binding energy is relatively low (in the range 399-401 eV) when the metal is in an extraordinarily low oxidation state, and relatively high (in the range 401-403 eV) when the metal is in a normal or high oxidation state. For example, the N 1s binding energies of $Ru(PPh_3)_3H(NO)$ and $Ru(PPh_3)_2Cl_3(NO)$ are 398.9 and 401.4 eV, respectively, although the NO groups are linear in both complexes.94) Su and Faller found that the difference between the O 1s and N 1s binding energies shows a remarkable correlation with the orientation of the NO group.94) In the case of linear nitrosyls, the O 1s - N 1s difference is 132 ± 2 eV; in the case of bent nitrosyls the difference is 128 ± 2 eV. The direction of this effect (i.e., the fact that the difference for the linear nitrosyls is greater than that for the bent nitrosyls) does not seem to have a simple explanation. Perhaps the effect is due to a much greater relaxation energy associated with the O 1s ionization in the bent nitrosyls than in the linear nitrosyls.

B. Carbon Monoxide as a Ligand

1. Metal Carbonyls

The transition metal carbonyls represent a large and important class of compound. In a series of these compounds, the interaction of the carbon monoxide ligand with the metal atom can vary significantly. One cause for this variation is change in the degree of back-bonding, i.e., in the extent to which dπ electron density is transferred from the metal atom to the oxygen atom of the CO ligand:

$$^{-}M{-}C{\equiv}O^{+} \longleftrightarrow M{=}C{=}O$$

Because of the changes in formal charge which accompany back-bonding, one would expect the O 1s binding energy to be correlated with back-bonding. With this in mind, we have listed, in Table 9, the O 1s binding energies of a variety of metal carbonyls, all determined in the gas phase.[95)] As an aid in looking for a correlation, we have also listed two other quantities which are expected to be functions of the degree of back-bonding in the CO ligand. One is the multiplicity-weighted average of the C-O stretching frequencies, $\langle\nu_{CO}\rangle$, listed for each compound for which all the required frequencies are known.[96-108)] The quantity $\langle\nu_{CO}\rangle$ is expected to decrease with increasing back-bonding. The other quantity is the sum of n_V (the number of valence electrons in the free metal atom) and n_{CO} (the number of CO ligands and their

Table 9. Correlation of Oxygen 1s Binding Energies of Carbonyl Complexes with Back-Bonding

Carbonyl Cpd.	E_B(O 1s), eV	$\langle \nu_{CO} \rangle$, cm^{-1}	Ref.	$(n_V + n_{CO})$
$C_6H_6Cr(CO)_3$	538.23	1938	96	10
$C_7H_7V(CO)_3$	538.6	1935	97	10
$C_5H_5V(CO)_4$	538.7	1963	98	10
$C_5H_5(CH_3)Mo(CO)_3$	538.8	1971	99	10
$C_5H_5Mn(CO)_3$	538.85	1974	100	11
$Mn_2(CO)_{10}$	538.89	2017	100	12
$C_7H_8Fe(CO)_3$	539.09	2004	101	12
$CH_3(OCH_3)CCr(CO)_5$	539.1	1984	102	12
$C_4H_6Fe(CO)_3$	539.29	2005	103	12
$W(CO)_6$	539.52	2017	100	12
$Mo(CO)_6$	539.61	2021	100	12
$CH_3Re(CO)_5$	539.64	2033	104	12
$Cr(CO)_6$	539.66	2018	100	12
$HMn(CO)_5$	539.84	2039	105	12
$CH_3Mn(CO)_5$	539.87	2032	106	12
$V(CO)_6$	539.9			11
$CH_3COMn(CO)_5$	539.92	2038	107	12.5
$Fe(CO)_5$	540.01	2035	100	13
$Ni(CO)_4$	540.11	2066	100	14
$Cl_3SiMn(CO)_5$	540.31	2058	108	13

equivalent[a)] per metal atom in the compound). The quantity n_V changes in much the same way as the effective nuclear charge on the metal atom and, other things being equal, would be expected to be inversely related to the dπ donor ability of the atom. The quantity n_{CO} is a measure of the competition among ligands for dπ electron density and also would be expected to be inversely related to the dπ donor ability of the metal atom in the compound. Hence the sum $(n_V + n_{CO})$ should decrease with increasing back-bonding.

From Table 9 it can be seen that the three quantities E_B(O 1s), $\langle \nu_{CO} \rangle$, and $(n_V + n_{CO})$ are closely correlated. We conclude that the O 1s binding energy of a carbonyl can be used to estimate the degree of dπ→pπ back-bonding: the lower the binding energy, the lower the degree of back-bonding. The one compound which appears to be out of line with respect to the correlation of E_B(O 1s) with $(n_V + n_{CO})$ is $V(CO)_6$. Perhaps the high binding energy in this case is due to the fact that the vanadium atom is one electron short of the krypton effective atomic number. This electron deficiency would be expected to make the vanadium atom a relatively poor dπ donor.

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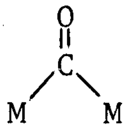
a) In the case of carbonyls containing ligands other than CO, it was assumed that the following ligands are equivalent, as π acceptors, to the indicated number of CO groups: C_7H_7, 2; C_5H_5, C_6H_6, C_4H_6, C_7H_8 (tetrahapto), $SiCl_3$, $CH_3(CH_3O)C$, 1; CH_3CO, 0.5. Although these assumptions are somewhat <u>ad hoc</u>, it can be seen that they are chemically reasonable.

There are two principal modes of coordination of the carbon monoxide ligand in transition metal carbonyls: terminal coordination, to a single metal atom, and bridging coordination, to two or more metal atoms. The O 1s spectrum of $Co_4(CO)_{12}$, shown in Figure 5, can be readily deconvoluted into two peaks corresponding to these two types of carbonyl groups.109) This spectrum is useful for determining the relative chemical shifts for the two types because (1) the groups are attached to identical cobalt atoms, and thus shifts due to changes in the metal and other ligands are avoided, and (2) the $Co_4(CO)_{12}$ molecule contains terminal and bridging carbonyl groups in a 3:1 abundance ratio, and thus the deconvoluted peaks can be readily assigned on the basis of their relative intensities. From the spectrum one concludes that the O 1s binding energy of the terminal carbonyl group is 1.25 eV higher than that of the bridging carbonyls groups. This result is qualitatively in accord with what one might expect, assuming greater back-bonding in the bridging carbonyl groups. It is also the result expected on the basis of simple valence bond formulas in which the terminal carbonyl group is represented with no back-bonding and the bridging carbonyl group is represented by a simple keto structure.



2. Adsorption of CO on Metal Surfaces

The chemisorption of carbon monoxide on a metal surface involves metal-ligand interactions which are similar to those in metal carbonyls as well as interactions which are peculiar to the surface. For example, Yates, Madey, and Erickson110,111) have interpreted the O 1s spectrum of CO adsorbed on tungsten in terms of six different types of adsorbed carbon monoxide: "virgin," α_1, α_2, β_1, β_2 and β_3. The virgin CO, for which E_B(O 1s) = 536.0 eV, is identified with carbon monoxide coordinated to two or more metal atoms and is structurally analogous to bridging CO groups in molecular carbonyls. This species is formed during adsorption at low temperatures and low surface coverage. The α_1 and α_2 forms (E_B(O 1s) = 538.7 and 537.3 eV, resp.) are identified with weakly-bound carbon monoxide, coordinated through the carbon atom to only one metal atom. The α_2 form is supposed to have more back-bonding from the tungsten than the α_1 form. Presumably this difference in the nature of the metal-ligand bonding arises from adsorption on different surface sites, such as terrace sites (where the metal d electrons are delocalized and relatively unavailable for back-bonding) and step sites (where the metal d electrons are localized and relatively available for back-bonding). It is significant that the O 1s spectrum of CO adsorbed on a tungsten (100) single crystal surface could not be readily resolved into more than one peak in the α-CO region, whereas the spectrum of CO adsorbed on polycrystalline tungsten was deconvoluted to give α_1 and α_2 peaks. The binding energies of the α forms and virgin forms are qualitatively in agreement with the values found for the analogous terminal and bridging carbonyl groups of molecular carbonyls. The β_1, β_2, and β_3 forms (E_B(O 1s) in the range 534.5-537.1 eV) are identified with carbon monoxide in which both the carbon and oxygen atoms are directly bonded to the tungsten metal. The

E_B(O 1s) of the β_2 form (∿ 534.5 eV) is close to that observed for species which form in the adsorption of O_2 and CO_2 on tungsten. It has been suggested that these coincidences in O 1s binding energy reflect a limiting condition for the oxygen of CO, O_2, and CO_2. Perhaps in each case complete molecular fragmentation (dissociative sorption) occurs to form chemisorbed oxygen atoms, with E_B(O 1s) ≈ 534.5 eV.

Some interesting results have been obtained in XPS studies of the adsorption of CO on a single crystal surface on which 5/6 of the surface platinum atoms were on terraces (the 111 plane) and 1/6 of the surface atoms were at step and kink sites, as shown in Figure 6.[112)] The initial adsorption of carbon monoxide was dissociative, as evidenced by the appearance in the C 1s spectrum of a "carbide" or "carbon atom" peak with a binding energy of 283.8 eV. The intensity of the C 1s peak corresponded to that expected for quantitative adsorption at the step and kink sites. The ratio of the C 1s to O 1s peak intensities was slightly greater than expected for a 1:1 ratio of C and O atoms, suggesting that some of the oxygen atoms reacted with CO to form gaseous CO_2. Increasing exposure of the surface to CO caused the growth of a second C 1s peak with a binding energy of 286.7 eV. This binding energy is equal to that found for CO adsorbed on an unstepped Pt(111) surface and corresponds to associatively adsorbed CO groups on the terraces. The fact that associative adsorption occurs on platinum terraces and that dissociative adsorption occurs at platinum steps and kinks may be related to the relative electron densities at these sites. At steps and kinks, the electron density is presumably high enough to cause effective reduction of the atoms to "carbide" and "oxide" ions.

Exposure of the clean stepped platinum surface to oxygen caused saturation of the step and kink sites (no adsorption occured on a 111 surface under identical conditions). The oxygen atom-saturated surface was then exposed to varying amounts of carbon monoxide. Both "carbide" carbon and CO carbon C 1s peaks formed, with a one-to-one correspondence between the growth of carbide and the decrease of surface oxygen atoms. These data are consistent with three possible reaction schemes:

$$\mathrm{O(ad)} + \mathrm{CO(ad)} \longrightarrow \mathrm{CO_2(g)} \qquad \text{(i)}$$

$$\mathrm{O_2(g)} + \mathrm{CO(ad)} \longrightarrow \mathrm{CO_2(g)} \qquad \text{(ii)}$$

$$\mathrm{O(ad)} + \mathrm{CO(g)} \longrightarrow \mathrm{CO_2(g)} \qquad \text{(iii)}$$

The first scheme was ruled out by showing that, at room temperature, a surface formed by very brief exposure of the oxygen-saturated surface to carbon monoxide is stable after removal of the carbon monoxide from the reaction chamber. In other words, no further surface carbide formed by lateral reactions of adsorbed carbon monoxide with surface oxygen atoms. The second scheme was ruled out by showing that exposure of the surface formed in the latter experiment to oxygen had no effect. Consequently the third scheme is believed to represent the mechanism of oxidation of carbon monoxide at the step and kink sites of platinum.

C. Olefins as Ligands

1. Olefin Complexes

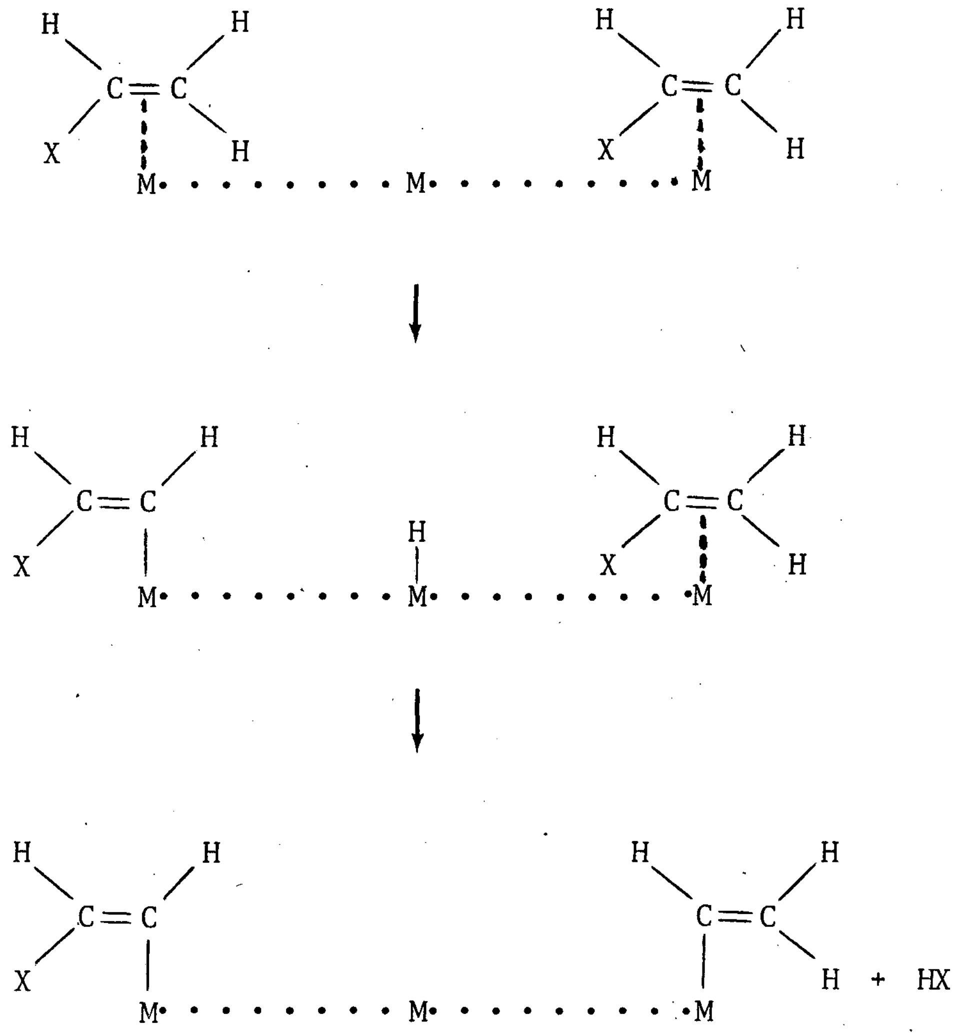
The bonding of an olefin to a metal atom is usually described as a synergistic combination of σ donor bonding and π back-bonding. Studies of the metal core binding energies of olefin complexes are consistent with this bonding description; indeed, the results suggest that more charge is transferred in the back-bonding than in the donor bonding. Thus Cook *et al.*113) have shown that the Pt $4f_{7/2}$ binding energy of $(C_2H_4)Pt(PPh_3)_2$ is 0.6 eV higher than that of $Pt(PPh_3)_4$. By making the reasonable assumption that the platinum atom in the tetrakis(phosphine) complex has a zero charge, they concluded that the platinum atom in the olefin complex is positively charged. Zakharova *et al.*114) found that, on going from K_2MCl_4 to the 1,5-hexadiene complex $C_6H_{10}MCl_2$, the metal core binding energy increased by 0.4 eV for M = Pd and by 1.5 eV for M = Pt. The greater increase in the case of the platinum complexes was explained by the greater ability of the platinum atom to participate in back-bonding.

The Pt $4f_{7/2}$ binding energy changes by no more than 0.2 eV in the series of complexes $(C_2R_4)Pt(PPh_3)_2$, where R = H, Cl, F, Cn, and C_6H_5.113,115) This essential constancy of the platinum binding energy has been taken as evidence that the Lewis basicity of the bis(triphenylphosphine)platinum(0) moiety is so strong that the substituent groups on the olefin play a minor role in determining charge transfer from the metal to ligand antibonding orbitals. In a series of complexes (olefin)-$Ni[P(O\text{-}o\text{-}tolyl)_3]_2$ a slight trend in the Ni $2p_{3/2}$ binding energy (total change: 0.4 eV) was observed: C_2H_4 < acrylonitrile < maleic anhydride.116) By contrast, the Ir $4f_{7/2}$ binding energy of olefin complexes of Vaska's complex, $Ir(CO)Cl(PPh_3)_2$, changed significantly on going from one olefin to another.115,117) For example, a 1.0 eV increase was observed on going from the C_2F_4 complex to the $C_2(CN)_4$ complex. It was inferred that Vaska's complex has a relatively low basicity and that metal to ligand charge transfer is significantly determined by the nature of the adduct.

2. Adsorption of Olefins on Metal Surfaces

Mason and coworkers have used XPS as an analytical tool for studying the reactions of haloalkenes on a platinum (100) surface.118-120) In Figure 7 the results of several sets of experiments are presented graphically.119) The data show that the low-coverage chemisorptions of vinyl chloride and vinyl fluoride proceed without the appearance of any XPS peak for the halogen. The halogen peak appears only after about 0.4 monolayer coverage, and beyond that point the halogen and carbon peak intensities increase in proportion to the known relative cross-sections for these atoms. Similar results were found for 1,1-difluoroethylene. It is concluded that these molecules are dissociatively adsorbed at low coverages (with the loss of hydrogen halide to the gas phase), and associatively adsorbed at high coverages. The olefins 1,2-difluoroethylene and trifluorochloroethylene were found to adsorb associatively at all coverages. Evidence that the dehydrohalogenation involved in the dissociative sorptions is intermolecular rather than intramolecular was found in a study of the sequential adsorption of two different olefins. When the initial associative adsorption of trifluorochloroethylene was followed by the adsorption of ethylene, dehydrohalogenation took place.

A mechanism which has been offered to explain these and other data is shown in the following scheme.



The initial step corresponds to the metallation of a metal-hydrogen bond. The rate of metallation of a haloalkene (which is essentially an electrophilic attack by the metal on the bond) depends on the electron density in the C-H bond. Obviously electron-withdrawing substituents such as halogen atoms would be expected to reduce the rate of metallation. We can rationalize the data for the reactions on platinum (100) by assuming that a halogen atom directly attached to the carbon of a C-H bond reduces the rate of metallation to a negligible value.

The change in the nature of the adsorption with increasing coverage (dissociative followed by associative) has been explained by a statistical consideration of the reaction mechanism shown above.120) Associative adsorption is expected to occur at vacant sites for which all adjacent olefin binding sites are occupied by earlier dissociation products (or carbon monoxide, as shown by Figure 6b), because dissociative adsorption (formation of vinyl and hydride species, followed by hydride migration to another alkene) requires two adjacent vacant sites.

VI. Mixed Valence Compounds

For the purposes of this discussion, a mixed valence compound is defined as a compound containing two or more metal atoms with an average oxidation state which is either (1) non-integral or (2) unusual for the metal and intermediate between two well-known oxidation states of the metal. Compounds of this type have received much study in recent years.121) One of the important properties to be determined for a mixed valence compound is the extent of electronic coupling between the metal atoms. Do the metals atoms have the same, average, oxidation state (corresponding to a delocalization of the metal valence electrons), or do they have different oxidation states (corresponding to localized valence electrons)? Before answering this question, one must decide what lifetime for a particular valence electronic state is the upper limit for a delocalized system and is the lower limit for a localized system. Then, to answer the question, one must employ a physical measurement which has a time scale of the same magnitude as that of the chosen lifetime.122) For example, if Mössbauer spectroscopy shows the presence of two different kinds of iron atoms in a mixed valence compound, one knows that the lifetime of the state must be longer than about 10^{-7} s. If infrared spectroscopy shows that the metal atoms of a mixed valence compound are structurally equivalent, one knows that the lifetime of any electronic state in which the atoms are nonequivalent must be less than about 10^{-13} s (the time required for a bond vibration). If the lifetime were longer, atoms would shift so as to trap the compound in the state with nonequivalent atoms.

X-Ray photoelectric ionization is believed to take place in a time interval of about 10^{-18} s. Therefore separate XPS peaks are possible for atoms if the lifetime of the asymmetric electronic state is greater than about 10^{-18} s, whether or not the atoms are structurally equivalent. We may represent the ground state of a localized mixed valence compound (involving two metal atoms differing in oxidation state by one unit) by the following formula, where the dot represents the extra valence electron: $\mathrm{M}\text{—}\dot{\mathrm{M}}$. The two possible XPS transitions can then be represented as follows, where the asterisk indicates core ionization,

$$\mathrm{M}\text{—}\dot{\mathrm{M}} \longrightarrow [\overset{*}{\mathrm{M}}\text{—}\dot{\mathrm{M}}]^{+} + e^{-}$$
$$\mathrm{M}\text{—}\dot{\mathrm{M}} \longrightarrow [\mathrm{M}\text{—}\overset{\bullet *}{\mathrm{M}}]^{+} + e^{-}$$

The first transition would be expected to be of higher energy than the second from simple atomic charge considerations. Because the two atoms are of equal abundance, the two peaks have essentially equal intensities. Unfortunately, the observation of two XPS peaks does not rule out the possibility of delocalized valence electrons in the ground state. Two transitions are expected even in that case because of polarization of the excited state by the core ionization.123) The ground state of a delocalized mixed valence compound can be crudely represented by the formula $\mathrm{M}\overset{\bullet}{\text{—}}\mathrm{M}$, where the intermediate position of the dot indicates that the odd valence electron is equally shared by the two metal atoms. The two XPS transitions can then be represented as follows,

$$\mathrm{M}\overset{\bullet}{\text{—}}\mathrm{M} \longrightarrow [\overset{*}{\mathrm{M}}\text{—}\dot{\mathrm{M}}]^{+} + e^{-}$$
$$\mathrm{M}\overset{\bullet}{\text{—}}\mathrm{M} \longrightarrow [\mathrm{M}\text{—}\overset{\bullet *}{\mathrm{M}}]^{+} + e^{-}$$

Notice that the excited states are similar to those formed from the localized ground states. Again the first transition is of higher energy than the second. Hush has made a theoretical study of these transitions.123) He concluded that, in the case of symmetrical delocalized mixed valence complexes, the two XPS peaks will occur at energies

$$\tfrac{1}{2}[E_B(\mathrm{unocc}) + E_B(\mathrm{occ})] + \tfrac{1}{2}\Delta[\alpha \pm (1+\alpha^2)^{1/2}]$$

where Δ is the difference between the orbital energies in the excited state and $\alpha = 2|J|/\Delta$, where J is the electronic interaction integral. He similarly concluded that the relative intensities of the two peaks will be

$$\frac{I(\mathrm{low}\ E_B)}{I(\mathrm{high}\ E_B)} = \left(\frac{1 + (1+\alpha^2)^{1/2} + \alpha}{1 + (1+\alpha^2)^{1/2} - \alpha}\right)^2$$

There may be some profit in looking upon the low- and high-energy transitions of a symmetrical delocalized complex as primary core ionization and shake-up transitions, respectively. According to this interpretation, the intensities of the two peaks will not, in general, be equal. The intensity of the "shake-up" peak would be expected to be proportional to the overlap between the wave functions of the metal valence electron in the delocalized ground state and in the excited, core-ionized state. The half-width of the "shake-up" peak would be expected to be greater than that of the "primary" peak because the excited core-ionized state would probably have a more strained geometry than the unexcited state.

It must be admitted that, with our present understanding of these compounds and their core-ionization phenomena, the interpretation of two-peak XPS spectra for mixed valence compounds is necessarily somewhat ambiguous. Considerable further study will be required before we are able to extract the information inherent in such spectra. Nevertheless, let us consider several examples of 2-peak spectra which have been described in the literature. The Mössbauer spectrum of biferrocene(II,III) picrate (which has the structure given in Figure 8) shows the existence of two distinctly different types of iron atoms, indicative of a localized ground state.124) The Fe $2p_{3/2}$ spectrum is consistent with this result; two peaks of approximately equal area, separated by 3.4 eV, are observed.124) The higher energy peak, corresponding to Fe(III), is much broader than the lower energy peak probably because of unresolved multiplet splitting. Crystal structure studies of Cs_2SbCl_6 have shown that the Sb(III) and Sb(V) atoms occupy sites which are slightly different. In accord with this result, the Sb $3d_{5/2}$ spectrum shows two peaks of equal intensity and half-width, separated by 1.8 eV.125) The physical properties of the ruthenium(II,III) complex ion $(NH_3)_5Ru(pyr)Ru(NH_3)_5^{5+}$ do not unequivocally indicate whether the ion is localized or delocalized.126,127) Citrin128) has observed two Ru $3d_{5/2}$ peaks, separated by 2.8 eV, for this complex. As we have pointed out, such a result does not prove that the extra Ru valence electron is localized. In fact, Hush123,127) has shown that Citrin's data, as well as the near-infrared electronic transition and the vibrational spectra, can be interpreted in terms of a delocalized complex.

The appearance of only one XPS peak for a mixed valence compound is consistent with a delocalized ground state (and excited state).

Biferrocenylene(II,III) picrate, whose structure is shown in Figure 8, probably fits in this category. The Mössbauer spectrum of the complex indicates only one kind of iron atom, and the Fe $2p_{3/2}$ spectrum consists of only one peak with a weak shoulder at higher binding energy.$^{129)}$ It should be recognized, however, that even in the case of a localized system in which two XPS peaks are expected, if the chemical shift between the two peaks is less than the resolution of the spectrometer, only one peak will be observed.

VII. Acknowledgements

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Figure Captions

Fig. 1. Chlorine 2p spectra of (a) $Re_3Cl_9(pyz)_3$ and (b) $[Re_3Cl_6(py)_3]_n$ showing deconvolutions into two Cl $2p_{1/2,3/2}$ doublets; bridging and terminal chlorine components are distinguished by the labels b and t. Reproduced with permission from Ref. 42.

Fig. 2. The O 1s and C 1s regions of the X-ray photoelectron spectrum of C_3O_2, showing the shake-up satellites. Reproduced with permission from Ref. 77.

Fig. 3. The π molecular orbitals of C_3O_2. The atomic orbital contributions are shown only for one plane.

Fig. 4. The Ni 2p regions of the X-ray photoelectron spectra of the isomeric forms of bis(N-methylsalicylaldimine)nickel(II). A, square planar isomer; B, octahedral polymer. Reproduced with permission from Ref. 35.

Fig. 5. The O 1s spectrum of gaseous $Co_4(CO)_{12}$. The left-hand peak is due to CO formed in the decomposition of the $Co_4(CO)_{12}$. The $Co_4(CO)_{12}$ band has been deconvoluted into two peaks with relative areas of 3:1. Reproduced with permission from Ref. 109.

Fig. 6. A model of a platinum surface on which 5/6 of the atoms are on terraces (the 111 plane) and 1/6 of the atoms are at step and kink sites. Reproduced with permission from Ref. 112.

Fig. 7. Plots of halogen XPS peak area vs carbon 1s peak area for vinyl halides adsorbed on a platinum 100 surface. (a) Vinyl chloride. The solid line corresponds to the ratio (0.78) of the Cl 2p and C 1s emission intensities in the gas phase spectrum. (b) Open circles correspond to vinyl fluoride data. The solid line corresponds to the ratio (2.27) of the F 1s and C 1s emission intensities in the gas phase spectrum. The crosses correspond to preadsorption of 0.3 monolayer of CO; the squares to preadsorption of 0.6 monolayer of CO. Reproduced with permission from Ref. 119.

Fig. 8. Structures of the biferrocenylene(II, III) cation (a) and the biferrocene(II, III) cation (b). Reproduced with permission from Ref. 5.

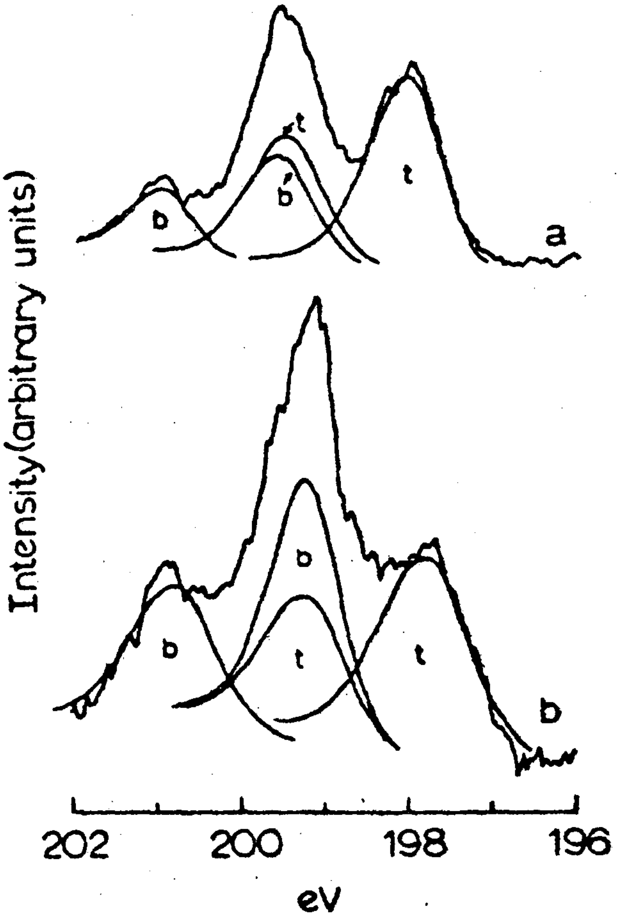

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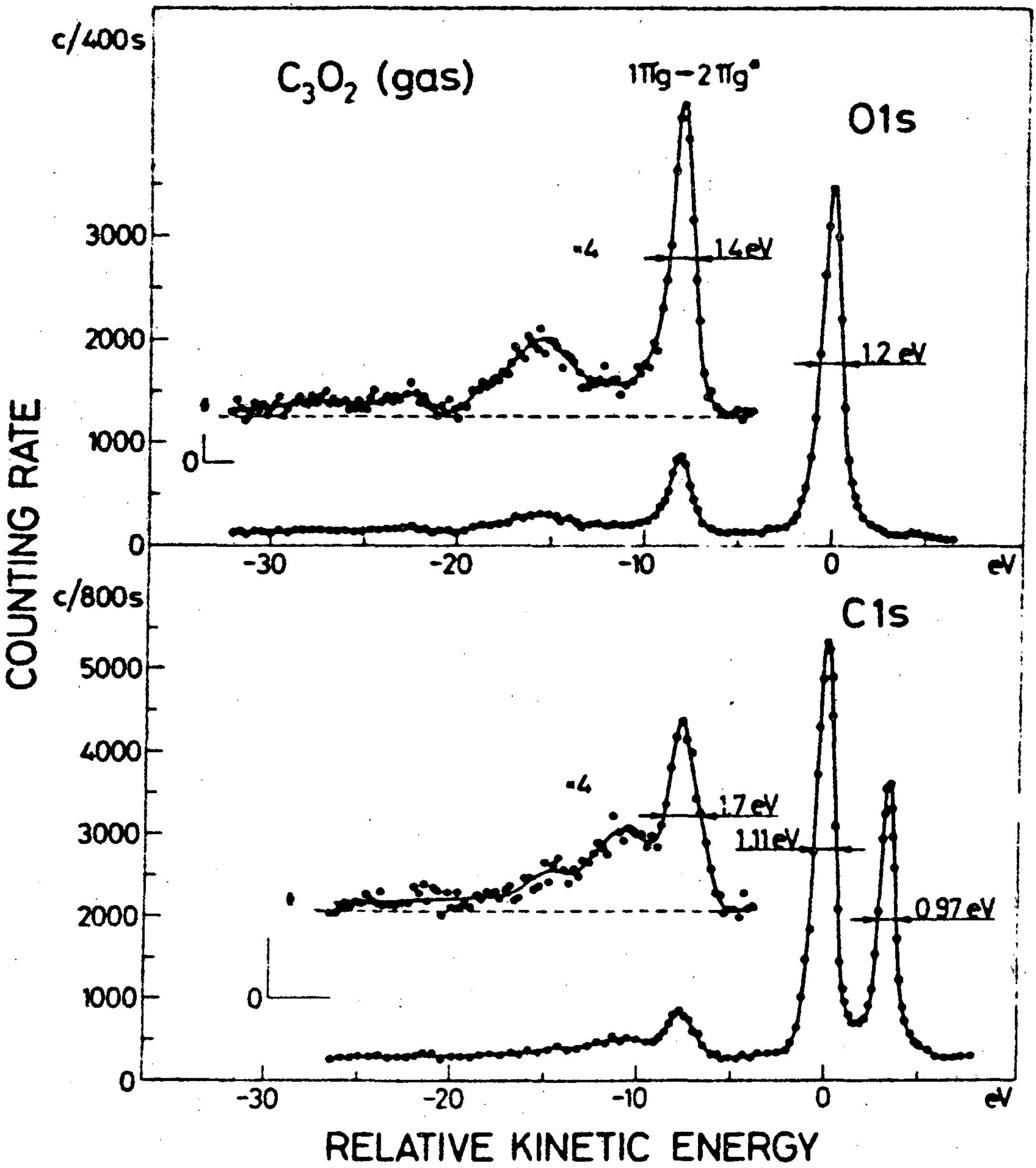
Fig. 1



~~XBL 769-10666~~

Fig. 2

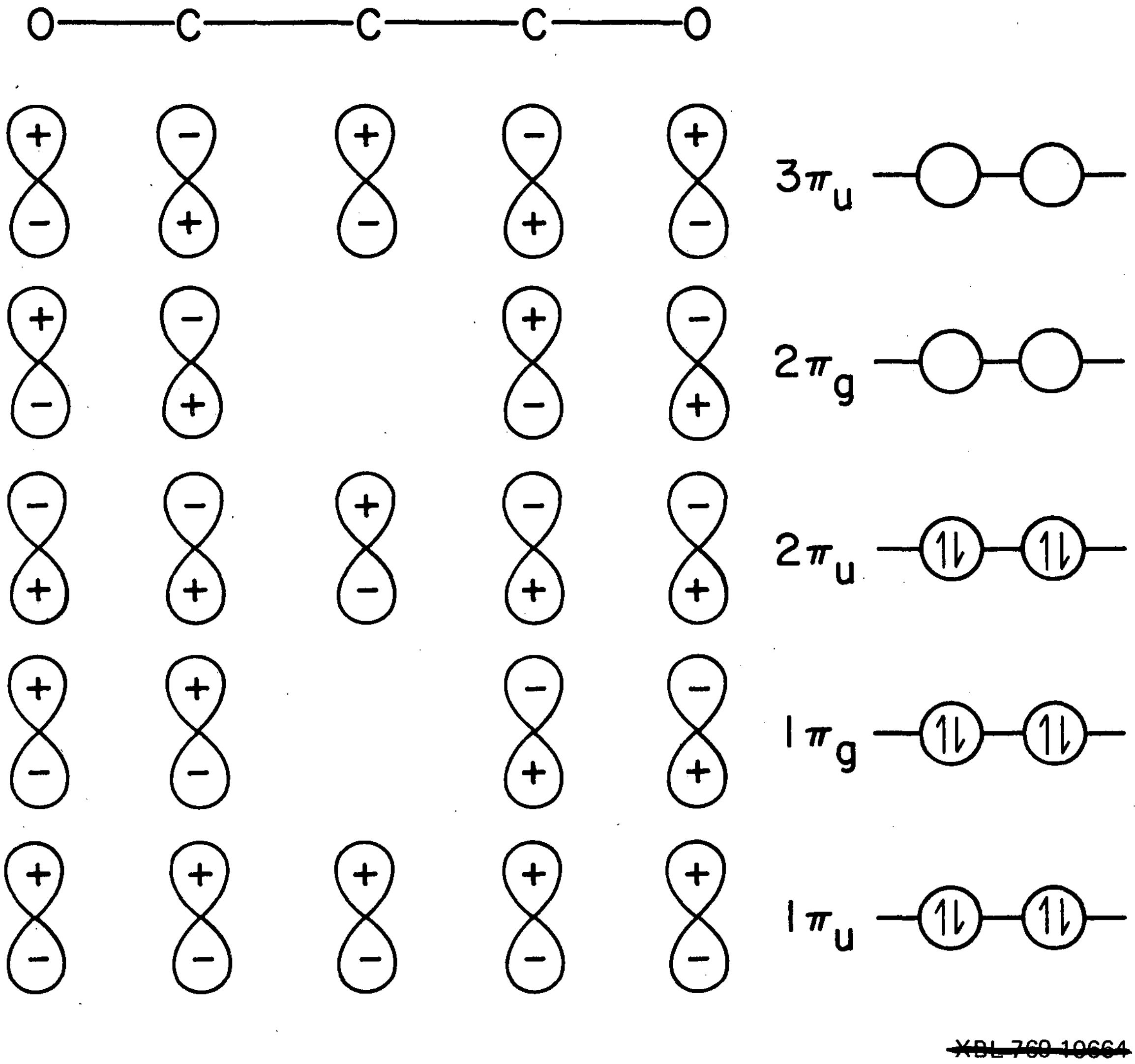


Fig. 3

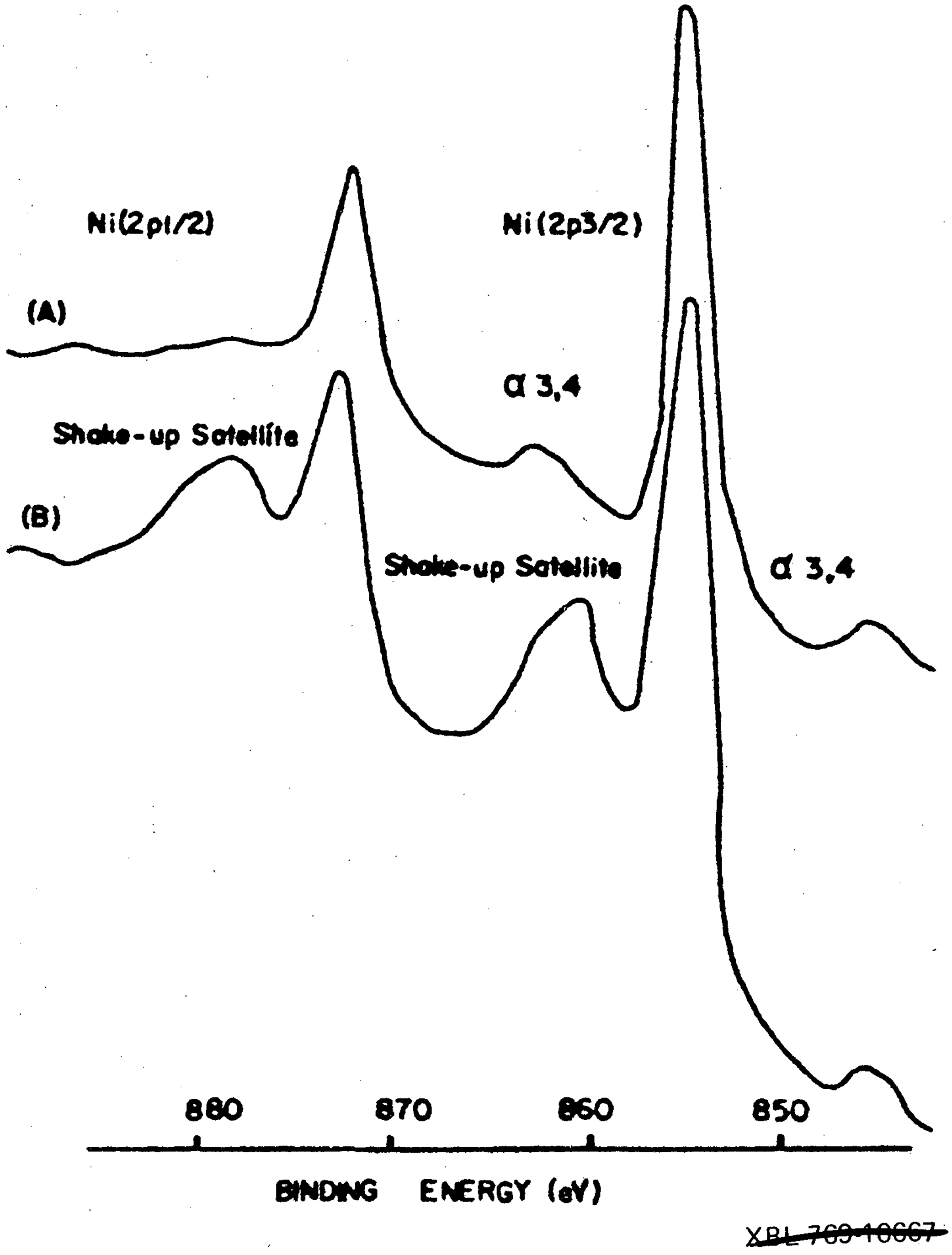
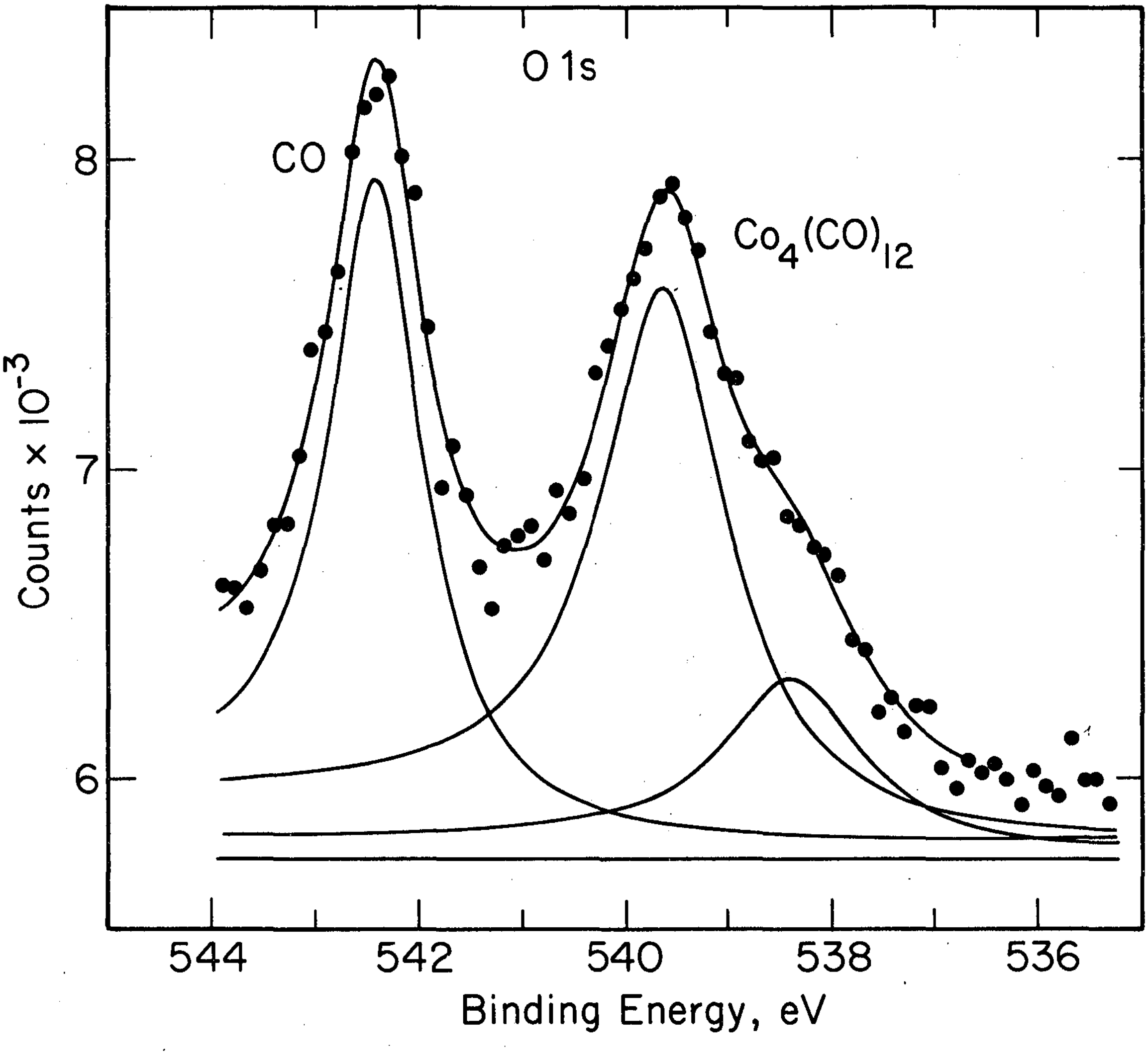
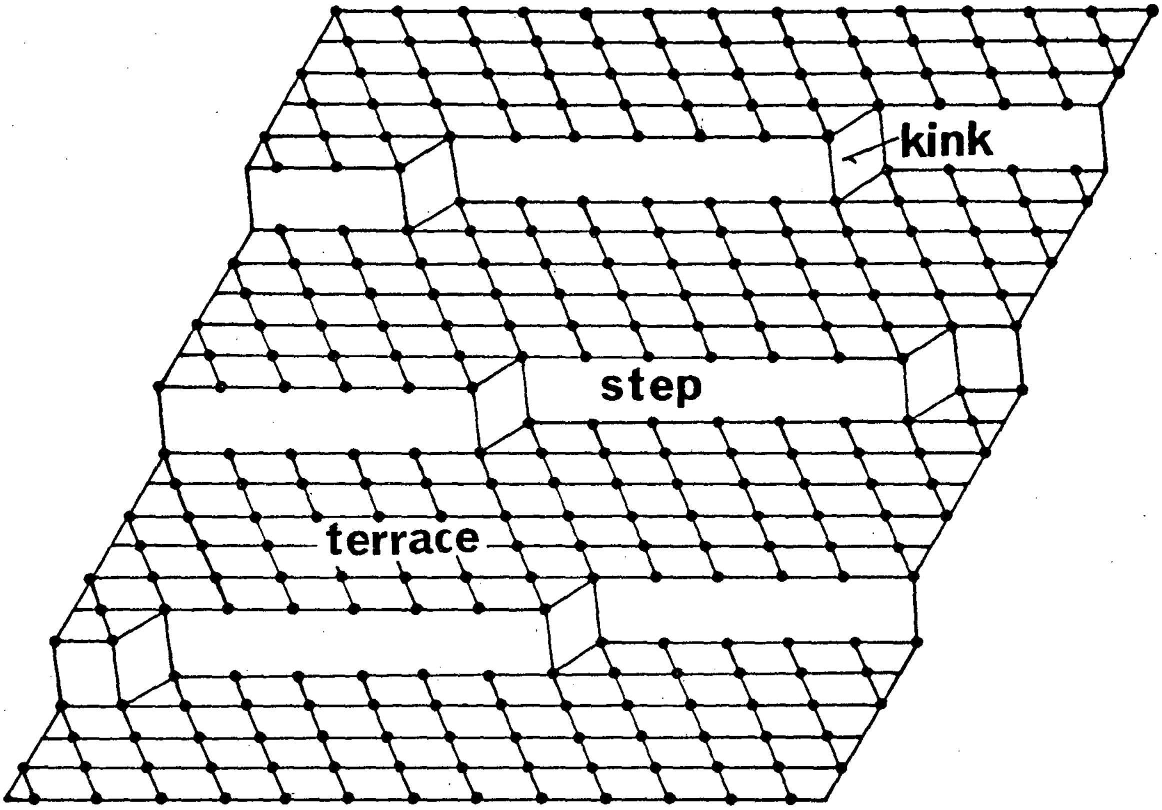

Ni(2p1/2)
Ni(2p3/2)
(A)
α 3,4
Shake-up Satellite
(B)
Shake-up Satellite
α 3,4
880
870
860
850
BINDING ENERGY (eV)
~~XBL 769-10667~~

Fig. 4



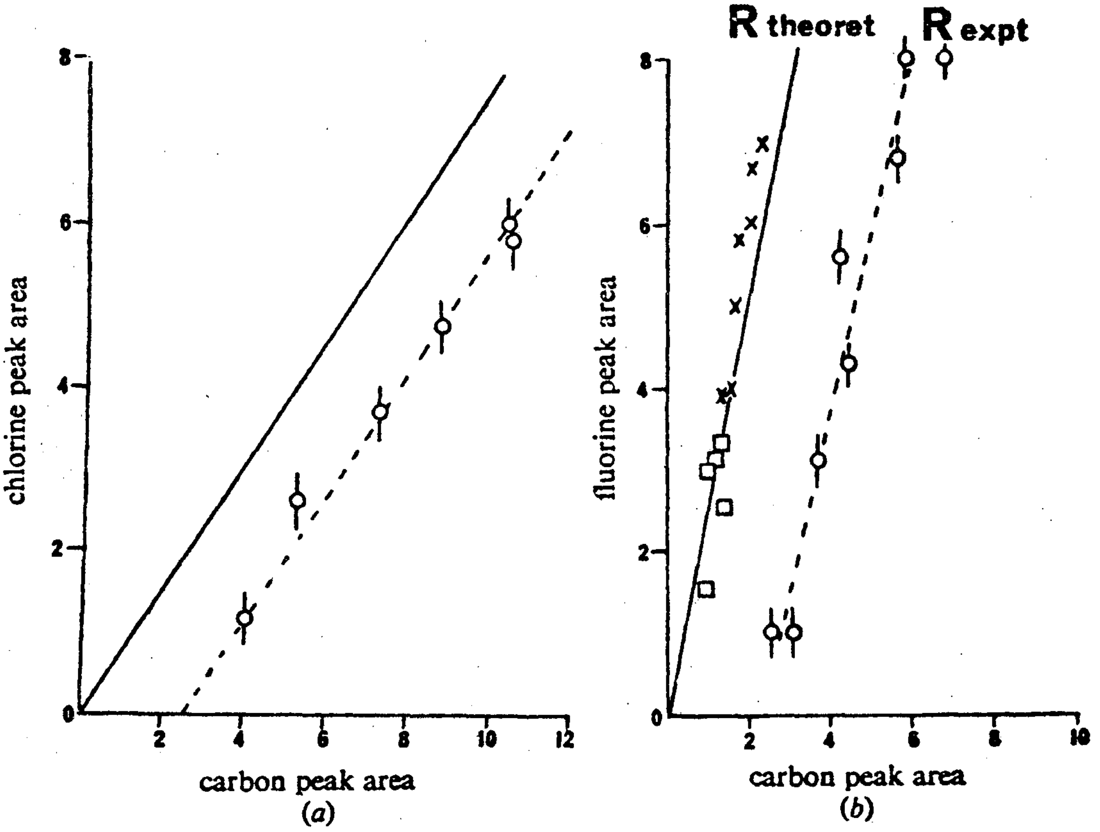
XBL 763-707

Fig. 5



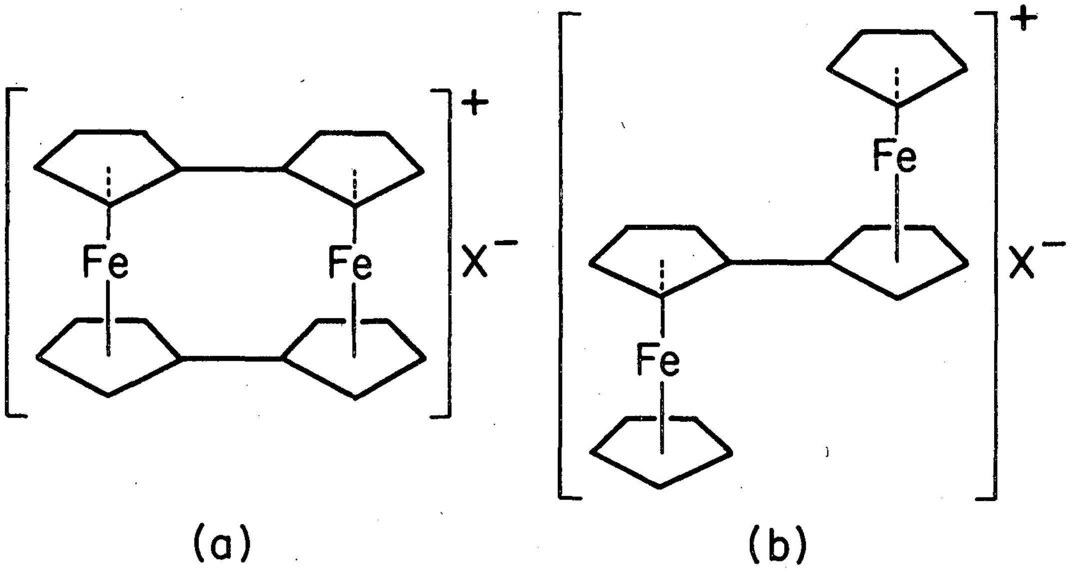
XBL 769-10663

Fig. 6



~~XBL 769-10665~~

Fig. 7



(a) (b)

XBL 737-6511

Fig. 8

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