Coordination Chemistry Reviews, 13 (1974) 47–81

THE APPLICATION OF X-RAY PHOTOELECTRON SPECTROSCOPY TO INORGANIC CHEMISTRY

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(Received August 5th, 1973)

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A. INTRODUCTION

X-Ray photoelectron spectroscopy (also called ESCA and XPS) involves the determination of the energy distribution of electrons emitted from X-ray-irradiated compounds. In principle all the electrons of a compound, from the atomic cores to the valence levels, can be studied; however, the technique is used principally for the study of core electrons. X-Ray photoelectron spectroscopy has applications in many scientific disciplines, including all the classical branches of chemistry, biochemistry, solid-state chemistry and physics, the study of surface phenomena, and geology. The books by Siegbahn et al.[1,2] are highly recommended for a general introduction to the field. The several review articles[3-6] which have been written on this topic have been aimed at audiences of physical chemists or chemical physicists. In this review I have restricted the discussion to matters of interest to inorganic and organometallic chemists, with emphasis on applications to transition metal complexes. The coverage is not intended to be complete; literature data have been cited only as far as necessary to illustrate the important points.

B. EXPERIMENTAL PROBLEMS

(i) Solids

Most X-ray photoelectron spectrometers are designed only for the study of solid samples. The study of solid compounds involves experimental problems which should be familiar not only to specialists in this field but also to any chemists who wish to interpret experimental data. The problems are those of the sample work function, the electric charging of the sample, the effective escape depth of the photoelectrons, surface impurities, and sample decomposition.

(a) Work function

If the sample is metallic and in contact with the spectrometer, we may reasonably assume that the Fermi levels of the sample and the spectrometer material are the same. By convention, the binding energy of an electron is the energy required to raise the electron to the Fermi level. To raise the electron to the gaseous zero-velocity state in the spectrometer chamber, a further amount of energy – the work function of the spectrometer material – must be provided. Any further energy provided by the X-ray photon appears as kinetic energy. Thus, energy conservation for the photoemission process is given by the relation

$$E_{h\nu} = E_{\mathrm{B}} + E_{\mathrm{k}} + \phi_{\mathrm{sp}} \qquad (1)$$

where $E_{h\nu}$ is the X-ray energy, E_{B} is the binding energy of the electron in a particular level of the compound, E_{k} is the photoelectron kinetic energy, and ϕ_{sp} is the work function of the spectrometer material. An electron energy analyzer scans the kinetic energy spectrum and yields the E_{k} values of discrete photolines. The value of ϕ_{sp} is either known or is assumed to be constant for a given system, and the binding energies E_{b} are calculated using eqn. (1). In most work the quantity ϕ_{sp} is treated as an empirical parameter to be determined by calibration with a substance of known binding energy. It is assumed that the sample and the reference substance have the same Fermi levels. In the case of a sample which is ordinarily electrically insulating, free charge carriers are formed during X-ray irradiation. If the electrical conductivity of the sample is adequate and if contact between the sample and the spectrometer or reference substance is good (big ifs) we may again assume that the Fermi levels are the same.

A consequence of the foregoing considerations, even if the assumptions regarding Fermi levels are correct, is that the measured binding energies for various solids have no common basis of comparison. They are based on different reference levels – i.e. the Fermi levels of the various solids. The binding energies could be put on a comparable basis by adding to each binding energy the work function of the corresponding solid, but unfortunately the work functions of insulating solids are unknown. Consequently, it is standard practice to assume that the work functions of all solid compounds of a given element are equal and to compare the binding energies as if they were based on the same reference level for the electron. Now, it is known that work functions for metals can differ by several electron volts and that even for a given metal, the work function can vary by several tenths of an electron volt depending on the crystal face[7]. Therefore, we might expect that shifts in measured binding energies (based on Fermi levels) would differ from the corresponding shifts in absolute binding energies (based on the free gaseous electron level) by as much as several volts. However, trends in the available data seem to indicate that errors due to the assumption of equal work function are usually not as serious as that. Nevertheless, all binding energy comparisons for insulators are subject to this unknown uncertainty.

(b) Charging

When an insulating sample in contact with the spectrometer is irradiated with X-rays, the ejection of electrons can cause the sample to have excess positive charge if the conductivity of the sample is inadequate to permit electrical equilibration. In other words, the Fermi level of the sample may be lower than that of the spectrometer because of the electric charging. The error in binding energy due to this effect can amount to many volts and varies with the X-ray flux. Various techniques have been used to reduce or to eliminate this charging effect. In early work[1,8] the carbon 1*s* peak due to an organic film on the surface of most samples was taken as a reference standard. Some workers[9-11] used as a reference the carbon 1*s* peak of the Scotch tape used in mounting the powdered sample. These methods were based on the somewhat dubious assumption that the organic material and the sample, being in contact, were at electrostatic equilibrium. Other workers have ground the sample with graphite (a fair electrical conductor) in order to provide a carbon 1*s* reference line in a standard material electrostatically equilibrated with the sample[12-14] Probably the most reliable method for providing a reference material with a Fermi level the same as that of the sample is to vacuum sputter a thin layer of metallic gold on the sample[15-22]. The gold adheres to the surface of the sample in small clumps or islands which are close enough together to ensure that all regions of the sample surface are in electrostatic equilibrium with the gold and yet which are far enough apart not to cover up the sample. The gold $4f_{7/2}$ peak is used as a reference. Even if various compounds treated in this way are charged to different extents relative to the spectrometer, their calculated binding energies, relative to the gold standards, can be compared without any error due to charging.

A directly measured difference in binding energy between different atoms *of the same compound* has no uncertainty due to work function (because the same Fermi level is involved in each binding energy measurement) or due to charging effects (because the charging error is the same for each measurement). If, in a series of compounds under study, there exists a common chemical group containing an atom or atoms which may reasonably be expected to have the same binding energy in all the compounds, a core binding energy peak for that atom (or group of atoms) may be used as an internal reference. Such internal referencing has been accomplished using the carbon 1*s* peak of ligands such as organophosphines[9,23-26], ethylenediamine[14], and *N,N'*-ethylenebis (benzoylacetonimine)[27]. Care must be taken when comparing binding energies calculated by different investigators, because a wide variety of values have been taken as the standard values for reference materials.

(c) Escape depth and surface impurities

To obtain a peak in a photoelectron spectrum, the photoelectrons must emerge from the solid without suffering any inelastic scattering. Because the X-rays normally used are the Al or Mg K_α X-rays (1487 and 1254 eV, respectively), the photoelectrons must have energies less than these amounts, and the mean free paths of the electrons are very short. Table 1 summarizes the results of several studies on the escape depth of photoelectrons. All the data indicate that X-ray photoelectron spectra of solids yield information regarding only the outer layers, near the surfaces, of the samples. The most important implication of this fact is that photoelectron spectra are very sensitive to surface impurities. Many materials, when exposed to air, have surface coatings which are entirely different in composition from the bulk materials. The overall chemical analysis of the sample is of no significance in such cases. Thus, the spectra of many metals which have been handled in air are actually the spectra of the corresponding oxides or, in the case of relatively noble metals, the combined spectra of the oxides and metals. Materials which can react with water (either by hydrolysis or by a redox reaction) must be handled under strictly anhydrous conditions, and even then the spectra should be viewed with suspicion. Some spectrometers have provision for cleaning the surface of the sample by argon ion bombardment in an electric discharge. Such preliminary treatment is often effective for obtaining spectra characteristic of the bulk sample rather than a surface contaminant.

(d) Sample decomposition

Finally, it should be recognized that many compounds undergo decomposition in the X-ray flux of the spectrometer. Such decomposition is extremely likely for any compound which is thermodynamically unstable. When decomposition is significant, the spectrum may correspond to the decomposition product rather than to the original compound. Sometimes decomposition can be recognized by a change in color of the sample upon irradiation. In other cases it is possible to observe a change in the recorded spectrum as a function of time in the spectrometer; such behavior is strong evidence for decomposition.

TABLE 1

Mean escape depths, λ, for various materials and photoelectrons

Material	E_k (eV)	λ (Å)	Ref.
C	920	15	28
C	1169	18	28
Ag	362	8	29
W	1455	13	30
WO_3	1450	26	30
Au	1405	22	31

(ii) Gases

Obviously the aforementioned difficulties associated with work functions, electric charging, and surface impurities are of no concern in the study of gaseous samples. Even sample decomposition is seldom a problem because the irradiated gas is present only in a steady state; it is constantly being pumped away and replenished from a reservoir. The theoretical interpretation of binding energies for gaseous molecules is much simpler than for solid samples. In view of the many advantages of working with gases, it is surprising that relatively few X-ray photoelectron spectrometers are designed for the study of gases[2, 32]. Pressures of the order of $10^{-2}-10^{-1}$ torr are adequate; hence, any solid or liquid with a room-temperature vapor pressure of that magnitude or greater can be studied as a vapor. The next big breakthrough in this field will be the construction of a spectrometer with which one can routinely study high-temperature vapors. Such an instrument would increase the number of vapor species which can be studied by more than an order of magnitude. A start has been made in this direction. Khodeyev et al.[33] have studied the spectra of Bi and Bi_2 at 800°C in a molecular beam.

C. CHEMICAL SHIFT

The main value of X-ray photoelectron spectroscopy to chemists lies in the fact that the measured core electron binding energies are a function of the chemical environment of the atoms. A striking illustration of the chemical structure dependence of binding energy is seen in the spectrum of the nitrogen 1*s* levels of *trans*-dinitrobis(ethylenediamine) cobalt(III) nitrate[34], $[Co(en)_2(NO_2)_2]NO_3$, shown in Fig. 1. This salt contains three structurally distinguishable types of nitrogen atoms, in an abundance ratio of 4 : 2 : 1, and the three peaks in the spectrum with approximately this intensity ratio correspond to these types of nitrogen atoms. It should be pointed out that the clean-cut separation of the peaks in this spectrum is a consequence of the markedly different chemical environments of the nitrogen atoms in coordinated ethylenediamine, coordinated nitrite

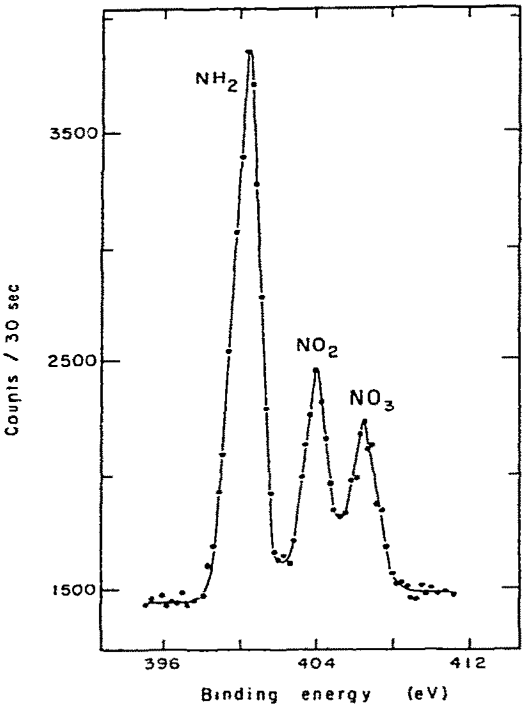

Fig. 1. Nitrogen 1*s* photoelectron spectrum of *trans*-$[Co(NH_2CH_2CH_2NH_2)_2(NO_2)_2]NO_3$. (Reproduced with permission from ref. 34.)

ion, and nitrate ion. Peaks due to atoms with relatively subtle structural differences are often difficult or impossible to resolve. For example, only one peak is found in the nitrogen 1*s* spectrum of $[Co(NH_3)_5Cl]Cl_2$, even though this complex contains two types of NH_3 groups, in an abundance ratio of 4 : 1.

(i) Correlation of chemical shift with atomic charge

(a) Simple correlations

It was realized early that a core binding energy of an atom should be related to the effective charge of the atom[1, 35]. From simple electrostatic considerations, one would expect that the energy for removing an electron from an atom would increase as the charge on the atom became more positive. Indeed, this type of relationship has generally been observed. Plots of the core binding energy for a given type of atom against estimated atomic charge show approximately linear correlations[1,8,34]. Obviously one would expect to find a connection between core binding energy shifts and any other atomic property which depends on electron density. Thus, linear correlations have been observed between core binding energies and Mössbauer chemical shifts[19,36,37] for compounds of tin and iron and between core binding energies and nuclear quadrupole resonance frequencies[23] for compounds of chlorine. Because, for a particular stereochemistry, metal–halogen vibrational stretching frequencies generally increase with increase in metal charge, roughly linear correlations have been found between rhodium $3d_{5/2}$ binding energies in various halide complexes and the corresponding infrared Rh–Cl frequencies[38]. A rough linear correlation has been observed between heavy metal core binding energies for various phosphine complexes and the optical electronegativity values[9]. A plot of metal core binding energies for platinum compounds against the corresponding binding energies for the analogous palladium compounds yields an approximate straight line of unit slope[39] Such a correlation is expected because of the close similarity in chemical properties of platinum and palladium.

(b) The potential model

It is now recognized that, in a correlation of binding energy with atomic charge, one should take account of the electrostatic potential due to the charges on all the other atoms in the compound[2, 40]. In other words, one must consider not only the work to remove the electron from the charged atom which actually loses the 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

$$E_B = kQ_i + V + l \tag{2}$$

In this equation, E_B is the binding energy for a particular core level for a particular atom (the "ionizing atom"), Q_i is the charge of the ionizing atom, V is the coulomb potential energy at the hypothetical vacated site of the ionizing atom in the midst of the other charged atoms of the molecule, and k and l are empirical constants determined by fitting binding energy data to calculated Q_i and V values. The energy V is calculated from the relation $V = \Sigma(Q/r)$, in which Q is the charge of an atom, r is its distance from the ionizing atom, and the sum is carried out over all the atoms except the ionizing atom. The constants k and l can be determined by a least-squares fitting of a straight line to a plot of $E_B - V$ vs. Q_i.

In qualitative discussions of core binding energy shifts, it is usually assumed that an increase in the binding energy of an atom corresponds to an increase in the atomic charge. When dealing with compounds of similar structure, this assumption is reasonable. However, eqn. (2) tells us that the simple relation is not necessarily true: it is possible for a change in the potential term, V, to be of opposite sign and of greater magnitude than the corresponding change in the term kQ_i. In careful work, atomic charges should be estimated and eqn. (2) should be used.

The potential model equation is only as good as the method used to calculate the atomic charges. When applied to gaseous molecules, only fair correlations have been obtained with this equation using Pauling charges[41], whereas good correlations have been obtained using CNDO charges[2, 42, 43] and charges calculated by an electronegativity equalization procedure[44].

The ejection of a core electron from a compound is accompanied by a relaxation process in which valence electrons flow toward the ionizing atom[45–48]. The measured binding energies include the corresponding relaxation energies. The fact that the potential model equation, which neglects this factor and uses initial-state charges, is successful in correlating binding energies is evidence that the relaxation energies of most molecules are almost equal.

In application of the potential model equation to solid compounds, evaluation of V requires the determination of an almost infinite sum of Q/r terms. In the case of a simple binary compound, V is essentially a Madelung potential which can be calculated using a known Madelung constant. In the case of a crystal consisting of a lattice of neutral molecules, V can be considered as the sum of a molecular term and a lattice term. If the molecules are relatively non-polar, it is probably a reasonable approximation to neglect the lattice term. In the case of a complex salt in which the ionizing atom is part of a polyatomic ion, V can be considered as the sum of a "local ion" term and a lattice term. The "local ion" term includes only the (Q/r) values for atoms in the complex ion containing the ionizing atom, and the lattice term includes the Q/r values for all other atoms in the compound. We have found, in the case of such complex salts; that if we neglect the lattice term while including the "local ion" term, we obtain a much poorer correlation than we obtain by complete neglect of V. Preliminary work indicates that it is possible to obtain improved correlations by including both the "local ion" term and a lattice term calculated on the assumption that all the other ions are integral point charges[49].

A remarkably small chemical shift is observed for an atom in an ion upon going from one salt to another in which only the counter-ion is changed[48]. For example, in a series of sixteen different potassium salts, the extreme spread[50] in the K 2p binding energy (between KCl and $K_2[Pt(NO_2)_4Cl_2]$) is only 1.7 eV. The F 1s binding energy[51] shifts by only 0.9 eV on going from UF_4 to LiF. The N 1s and P 2p binding energies in the bis(triphenylphosphine)iminium cation[25], $N[P(C_6H_5)_3]_2^+$, shift by only a few tenths of an electron volt as the anion is changed through the series F^-, Cl^-, Br^-, I^-, OCN^-, SCN^-, NO_3^-, N_3^-, $V(CO)_6^-$. These results may be explained as follows. First, the reduced Madelung constant is practically the same for all crystal structures[52]. That is, the proportionality constant relating the potential of an ion of charge Q in a lattice to the expression Q/R, where R is the interionic distance, is essentially independent of the lattice structure. Second, an increase in R, causing a decrease in the absolute value of the electrostatic potential, is usually compensated by an increase in the polarizability of the counter-ion[53].

(ii) The determination of oxidation state

(a) Definitions

Some confusion has arisen in the literature regarding the meanings of the expressions *oxidation state*, *atomic charge*, and *formal charge*. Therefore, a brief review of these concepts is appropriate. The *oxidation state* of an atom is a quantity which is determined by arbitrary convention. Once the rules of the convention are defined and understood, there should be no argument as to the oxidation state of each element in a compound* For example, the oxidation state of chromium in the complex $Cr(CN)_5NO^{3-}$ is +1 if we choose to consider the cyano groups as CN^- ions and the nitrosyl group as an NO^+ ion. On the other hand, the oxidation state of chromium is +3 if we choose to consider the nitrosyl group as an NO^- ion. In view of structural, spectroscopic or kinetic data, it may be more reasonable to choose one of these conventions rather than the other, but either *can* be used.

The *charge of an atom* in a molecule or polyatomic ion is a quantity (usually non-integral) which in principle can be calculated by various theoretical methods or can be measured by various techniques. Unfortunately atomic charges calculated or measured by various methods are seldom in agreement. The reason for this disagreement and other problems associated with the concept of atomic charge have been discussed in recent publications[44,54]. Inasmuch as core binding energies can be directly related by the potential model equation to atomic charges, the binding energies can serve as experimental data for testing methods for calculating atomic charges. Of course, binding energies can also be used to obtain qualitative information about atomic charges. For a set of similar compounds for which the V term of eqn. (2) would be expected to be constant or to change in a regular way, an increase in binding energy corresponds to an increase in the positive atomic charge on the ionizing atom.

The *formal charge* of an atom is defined as the charge which the atom would have if the bonding electrons in each bond were equally apportioned between the pair of bonded atoms. The term formal charge was applied to this quantity by Pauling[55] and Branch and Calvin[56], although the terms *residual atomic charge, electrovalence,* and *formal polar number* were used by Langmuir[57], Sidgwick[58] and Latimer[59], respectively, for the same quantity. Formal charges are commonly used by chemists when writing valence bond structures for molecules. Their usefulness guarantees their continued use for many years. Therefore, we should be careful not to confuse the formal charge of an atom either with its charge or with its oxidation state.

We can illustrate the concepts just discussed with a simple example. For the molecule carbon monoxide, most people would arbitrarily assign an oxidation state of −2 to the oxygen atom and hence assign an oxidation state of +2 to the carbon atom. Atomic charges have been calculated for this molecule by a variety of methods; the CNDO/2 method[60] yields +0.042 for the carbon, whereas the CHELEQ electronegativity equalization method[44] yields +0.172 for the carbon. The formal charge of the carbon atom is −1, as shown by the valence structure $^-{:}C{\equiv}O{:}^+$.

(b) Charge-oxidation state correlation

At present, there is no very reliable method for calculating atomic charges for transition metal compounds. Therefore, in general, one cannot attempt a quantitative correlation of

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* A set of rules for assigning oxidation numbers (oxidation states) and a definition of formal charge are given in ref. 1, p. 265.

TABLE 2

Some binding energies which increase with increasing oxidation state

Compound	Core level	E_B (eV)	Ref.
SnF_2	Sn(4*d*)	26.0	61
SnF_4	Sn(4*d*)	27.0	61
$(CH_3)_4NSnCl_3$	Sn(4*d*)	25.6	61
$(NH_4)_2SnCl_6$	Sn(4*d*)	26.1	61
$(C_6H_5)_3P$	P(2*p*)	131.2	61
$(C_6H_5)_3PO$	P(2*p*)	132.5	61
NiO	$Ni(2p_{3/2})$	854.0	62
Ni_2O_3	$Ni(2p_{3/2})$	855.9	62
$K_4Fe(CN)_6$	Fe(3*p*)	54.0	63
$K_3Fe(CN)_6$	Fe(3*p*)	55.0	63

binding energies with atomic charges for such compounds*. However, for a set of compounds in which the ligands are similar and in which the metal coordination number is constant, one expects and usually finds that binding energies for the metal show a correlation with oxidation state. Some illustrative data are given in Table 2. For each pair of compounds, the core binding energy increases with increasing oxidation state. However, it should be remembered that the chemical shifts are principally caused by changes in the atomic charge, and that atomic charge increases with oxidation state only for carefully chosen groups of compounds. It is quite possible, indeed common, for binding energy to decrease on going to a compound of higher oxidation state. Examples of this behavior are given in Table 3. These apparently anomalous results are a consequence of the partial covalent character of the metal—ligand bonds and of the differing electronegativities of the ligands. For example, in both MnF_2 and MnO_2 the manganese atoms have six-fold coordination, but the greater electronegativity of fluorine over that of oxygen causes the manganese atoms in MnF_2 to have a higher atomic charge than those in MnO_2. This explanation is essentially equivalent to assuming ionic lattices of Mn^{2+}, F^-, Mn^{4+}, and O^{2-} ions with much greater polarization of the O^{2-} ions in MnO_2 than of the F^- ions in MnF_2.

A striking demonstration of the effect of valence electron delocalization in a ligand is found in the nickel $2p_{3/2}$ binding energies for nickel dithiolate complexes[15]. Three different compounds, in which the $Ni[S_2C_2(C_6H_5)_2]_2$ complex has charges of O, −1, and −2, have binding energies of 852.9, 852.5, and 852.8 eV, respectively. Compounds con-

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* Recently the author has had some success in extending the CHELEQ atomic charge method[44] to transition metal compounds. The results will soon be published.

TABLE 3

Some binding energies which decrease with increasing oxidation state

Compound	Oxidation state	Core level	E_B (eV)	Ref.
$Fe_2(CO)_9$	0	Fe(3*p*)	54.6	63
FeS_2	2	Fe(3*p*)	53.0	63
$(CH_2CHCN)_2Ni$	0	Ni($2p_{3/2}$)	856.0	64
$Ni(PPh_2Et)_2Br_2$	2	Ni($2p_{3/2}$)	854.9	64
$K_2[Ni(CN)_4] . H_2O$	2	Ni($2p_{3/2}$)	856.6	65
$(B_{10}H_{10}CNH_3)_2Ni$	4	Ni($2p_{3/2}$)	856.5	65
$SnCl_2 . 2H_2O$	2	Sn(4*d*)	26.5	61
$SnCl_4[(C_4H_9)_3P]_2$	4	Sn(4*d*)	25.2	61
MnF_2	2	Mn($2p_{3/2}$)	642.8	66
MnO_2	4	Mn($2p_{3/2}$)	642.4	66

taining the cyano complexes, $Ni[S_2C_2(CN)_2]_2^{1-,2-}$ have identical nickel binding energies, 853.1 eV. Obviously oxidation or reduction of these complexes corresponds to the removal of electrons from, or the addition of electrons to, molecular orbitals which are centered on the ligand atoms (probably mainly on the sulfur atoms). Because the binding energies of these complexes are similar to that of nickel powder (852.8 eV) and less than those of most simple nickel(II) compounds, Grim et al.[15] assigned an oxidation state of zero to the nickel in the dithiolate complexes. It would probably be better to assign an *atomic charge* of approximately zero to the nickel atoms in these compounds and, recognizing the arbitrariness of oxidation states, to assign oxidation states in any convenient, consistent way. Thus, even an oxidation state of +4 for nickel in $Ni[S_2C_2(CN)_2]_2^{2-}$ is not per se inconsistent with an atomic charge of zero.

(c) Sensitivity of E_B to charge

Some investigators have claimed, on the basis of studies of certain compounds of rhodium[38], silver[13], and tin[61], that the core binding energies of these heavy elements are relatively insensitive to changes in atomic charge. These claims are probably somewhat exaggerated, and the apparent insensitivity to changes in atomic charge observed by these investigators may be partly a consequence of the types of compounds studied. Most of the compounds studied involved large, polarizable ligands which can spread out or delocalize changes in electron density due to changes in oxidation state. Of course it is true that the proportionality constant relating atomic charge to core binding energy (the k of eqn. (2)) is smaller for the heavier elements than for the lighter elements. Nevertheless the value of k never approaches zero. On the basis of a simple valence shell model[1] it can be shown that k should vary approximately as the inverse of the covalent radius.

Thus, the *k* values for tetracovalent compounds of carbon, silicon, germanium, and tin should be in the proportion 1 : 0.66 : 0.63 : 0.55. There is no question that the core binding energies of heavy elements are sensitive to changes in charge (and hence to changes in oxidation state for similar compounds). For example, the Eu($3d_{5/2}$) shift[40] between EuO and Eu_2O_3 is 9.6 eV, the Xe($3d_{5/2}$) shift[67] between Xe and XeF_6 is 7.9 eV, and the I($3d_{5/2}$) shift[40] between KI and KIO_4 is 6.1 eV. Some reports of very small chemical shifts between compounds which would be expected to have considerably different atomic charges may be in error because of surface contamination of one of the compounds. Thus, the reported[61] Sn(4*d*) chemical shift of 0.1 eV between SnO and SnO_2 may be due to a surface coating of SnO_2 on the sample of SnO. A similar explanation probably accounts for the incredibly low metal core binding energies which have been observed for $KMnO_4$ (ref. 66) and K_2FeO_4 (refs. 63, 68). The surfaces of these powerful oxidizing agents are probably contaminated with lower oxides such as MnO_2 and Fe_2O_3, respectively.

(iii) The identification of mixed and single oxidation states

Compounds containing two or more metal atoms with an average oxidation state which is either non-integral or uncommon for that metal have been the subject of considerable research. With regard to such compounds, a question to be answered is: What is the rate of electron exchange between the metal atoms? An equivalent question is: What is the lifetime of a given localized valence electronic state? If the sites occupied by the atoms are *structurally* equivalent, then the lifetime of a localized electronic configuration must be less than the time required for a bond vibration (i.e. less than about 10^{-13} sec), or else bond lengths would shift so as to trap the compound in a localized state. Now 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 in structurally equivalent sites if the lifetime of a given electronic configuration is greater than about 10^{-18} sec. One could refer to a compound of this type as a *mixed oxidation state compound with structurally equivalent sites.* A single binding energy peak should be obtained for atoms in structurally equivalent sites if the electronic configuration lifetime is less than about 10^{-18} sec. One could refer to a compound of the latter type as a *single or non-integral oxidation state compound.* Obviously separate binding energy peaks are possible for a compound with atoms in structurally nonequivalent sites. This is true whether the atoms are intrinsically nonequivalent (as in the case of different coordination numbers or different donor atoms) or intrinsically equivalent (sites which are exactly equivalent except for differences due to the different charge and size of the atoms). The possible number of peaks corresponding to various ranges for the electronic configuration lifetime and different structural types are indicated in the chart of Fig. 2.

The Fe(3*s*) photoelectron spectrum of $(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$ consists of a single symmetrical line, in agreement with X-ray diffraction data which show the iron

Types of Atomic Sites

		2 Structurally Equivalent Sites	2 Structurally Nonequivalent Sites	
			Intrinsically Equivalent	Intrinsically Nonequivalent
Lifetime of Valence Electronic Configuration (sec)	$t < 10^{-18}$	1 Peak	▨	2 Peaks
	$10^{-18} < t < 10^{-13}$	2 Peaks	▨	2 Peaks
	$10^{-13} < t$	▨	2 Peaks	2 Peaks

Fig. 2. Possible number of X-ray photoelectron peaks for mixed and single oxidation state compounds.

atoms to be structurally indistinguishable[69]. This means, if we assign the other elements to their usual oxidation states, that each iron atom has effectively the same oxidation state, +2.5. A fully delocalized molecular orbital description of the complex is appropriate. Similarly, the Fe($2p_{3/2}$) spectra of the ferredoxins from *Clostridium pasteurianum*, *Clostridium acidiurici*, and *Chromatium* have been interpreted as indicating the equivalence of the iron atoms in these compounds[70,71].

The compound biferrocenylene(II, III) picrate (having the structure shown in Fig. 3(a)) shows only a single peak in its Fe($2p_{3/2}$) spectrum[72]. This result again suggests equivalent iron atoms of +2.5 oxidation state. On the other hand, biferrocene(II, III) picrate (having the structure shown in Fig. 3(b)) shows two peaks in the Fe($2p_{3/2}$) spectrum (shown in Fig. 4); this spectrum has been interpreted in terms of nonequivalent +2 and +3 iron atoms[73]. The difference between these two cases is not understood. Perhaps one should question whether the latter spectrum really corresponds to two chemically-shifted peaks. The high binding energy peak is broad and looks suspiciously like the shake-up bands which frequently appear near the core photoelectron peaks of transition metal compounds. Indeed, the chemical shift of 3.4 eV between the two peaks seems rather large when compared with the data for other Fe^{II} and Fe^{III} compounds[63]. Similar remarks may be made regarding the Fe($2p_{3/2}$) spectrum of $KFe^{III}[Fe^{II}(CN)_6]$, Prussian blue[74, 75]. The reported spectrum consists of a relatively sharp peak and a broad peak at 4.4 eV higher binding energy. Admittedly the two iron environments in Prussian blue are different (the Fe^{III} atoms are coordinated to N atoms, and the Fe^{II} atoms are coordinated to C atoms), but it would not be unreasonable for the atomic charges to be very similar. Perhaps the lower binding energy peak is actually an unresolved doublet.

The Fe($2p_{3/2}$) spectrum of $K_{0.5}FeF_3$ is a barely-resolved doublet, the components having chemical shifts[11] corresponding to FeF_2 and FeF_3 (see Fig. 5). Thus, this compound seems to be a clean-cut example of mixed oxidation states.

Another example of mixed oxidation states is $[Pt^{II}(C_2H_5NH_2)_4]Cl_4 - \cdot [Pt^{IV}(C_2H_5NH_2)_4Cl_2] \cdot 4H_2O$, Wolfram's red salt[16]. The Pt($4f_{5/2}$ and $4f_{7/2}$) spectrum shows a splitting of peaks due to Pt^{II} and Pt^{IV}. On the other hand, the spectrum of the compound $K_2[Pt(CN)_4]Cl_{0.3} \cdot nH_2O$ shows no splitting, suggestive of a single fractional oxidation state for the platinum. However, the $4f_{5/2}$ and $4f_{7/2}$ binding energies are lower than those of both of the compounds $K_2[Pt(CN)_4] \cdot 3H_2O$ and $K_2[Pt(CN)_4Cl_2] \cdot 3H_2O$. This peculiarity does not seem to have been adequately explained.

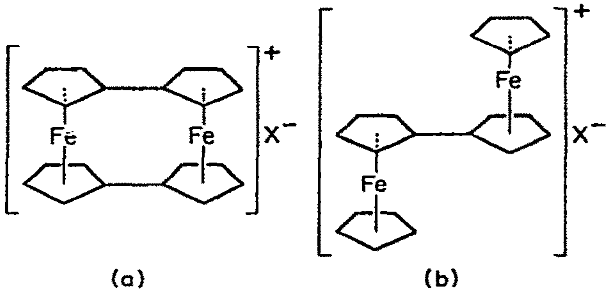


Fig. 3. Structures of the biferrocenylene(II, III) cation (a) and the biferrocene(II, III) cation (b).

The binuclear ruthenium complexes $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{4+,5+,6+}$ (pyr = pyrazine) have been recently studied by X-ray photoelectron spectroscopy[76]. The ruthenium core level spectrum of the +5 complex shows the presence of two kinds of ruthenium atoms (+2 and +3), whereas the spectra of the +4 and +6 complexes show peaks corresponding to only one kind of ruthenium atom. The electronic spectra of the complexes are also consistent with the formulation of the +5 complex as a mixed oxidation state compound[77]. Only the +5 complex shows a near-infrared band which can be assigned to the charge-transfer transition $[Ru^{II}, Ru^{III}] \rightarrow [Ru^{III}, Ru^{II}]^*$.

Certain limitations of the technique, when applied to the problem of mixed oxidation states, should be emphasized. In a mixed oxidation state compound in which the metal atoms have intrinsically different coordination sites (as in Prussian blue), it is conceivable that the metal atoms of different oxidation state might have practically the same atomic charge. In a mixed oxidation state compound in which the metal atoms have intrinsically identical coordination sites (as in the biferrocene(II, III) ion), the structural features of each coordination site will be slightly different because, for exam-

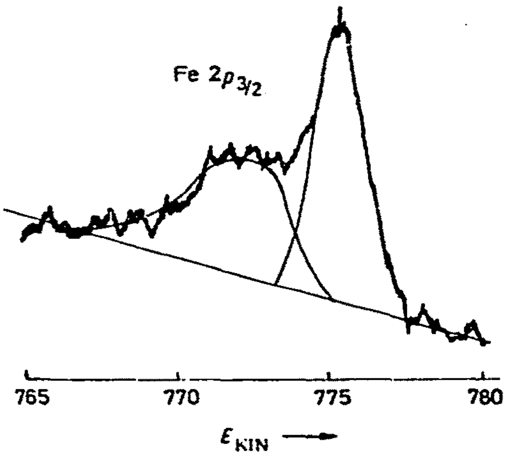


Fig. 4. Iron $2p_{3/2}$ photoelectron spectrum of biferrocene(II, III) picrate. (Reproduced with permission from ref. 73.)

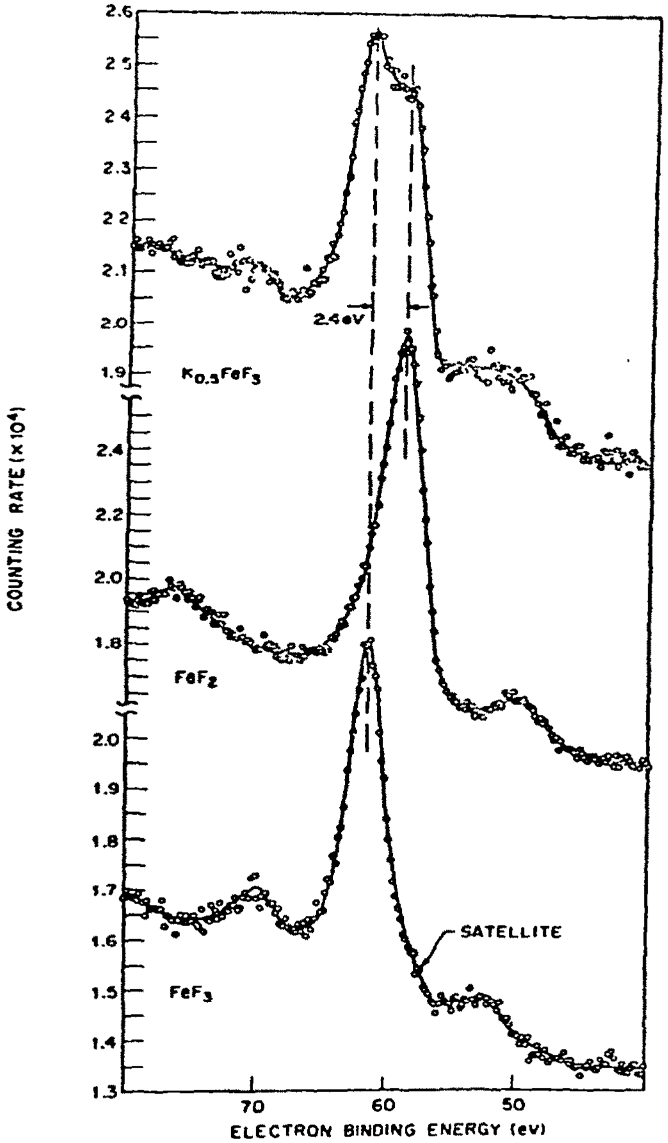


Fig. 5. Iron $2p_{3/2}$ photoelectron spectrum of $K_{0.5}FeF_3$, FeF_2 and FeF_3. (Reproduced with permission from ref. 11.)

ple, of the different polarization exerted by the differently charged metal atoms. The atom of higher oxidation state will have a higher positive charge, but the charge difference may be very slight if the valence electrons are largely delocalized onto the ligands in the immediate vicinity of each metal atom. Clearly the inability to observe more than one core binding energy peak for an element in a compound is not in itself proof of a single oxidation state.

(iv) Detection of metal→ligand π back bonding

(a) Nitrogen-containing ligands

Hendrickson et al.[34] determined the nitrogen 1s binding energies of NH_3, NO_2^-, and CN^- both in relatively "free" forms and as ligands coordinated to transition metal ions. Some of the data are given in Table 4. In the case of ammonia, the binding energies in the transition metal complexes are significantly greater than in the "free" ligand (solid NH_3), but not as high as found in an NH_4^+ salt. This result is quite reasonable, in view of the increase in the formal charge of the nitrogen atom upon coordination and the lower electronegativity of transition metals compared to hydrogen. In the case of nitrite ion, the binding energies in the complexes are essentially the same as that in the "free" ligand in $NaNO_2$. It is reasonable to conclude that metal-to-ligand π back-bonding has compensated for the increased formal charge on the coordinated nitrogen atom. Back-bonding causes a shift of electron density from a *d* orbital of the metal to the π antibonding molecular orbital of the nitrite ion. Inasmuch as the latter orbital is centered on both the nitrogen and oxygen atoms, back-bonding should increase the electron density of the nitrogen atom. In the case of cyanide ion, the binding energies in the complexes are significantly lower than in the "free" ligand in KCN. This result is reasonable, assuming the existence of π back-bonding. Simple σ coordination does not change the formal charge of the nitrogen atom, but the back-bonding causes the formal charge to drop to −1.

$^{-}\!:\!C{\equiv}N\!:$	$M^{-}{-}C{\equiv}N\!:$	$M{=}C{=}\underset{\cdot\cdot}{\ddot{N}}^{-}$
"free"	coordinated without back-bonding	coordinated with back-bonding

(b) Triphenylphosphine

The phosphorus 2*p* binding energies of triphenylphosphine and some of its derivatives are given in Table 5. Interpretation of the data is complicated by the fact that widely differing values for triphenylphosphine have been reported. (The discrepancies may reflect differing degrees of charging in the samples.) Nevertheless, it appears certain that formation of a phosphonium salt from triphenylphosphine, corresponding to an increase in the phosphorus formal charge from 0 to +1, causes the binding energy to increase. On the other hand, coordination to a transition metal atom causes very little change in binding energy. Back-bonding, which can effectively cancel the increase in formal charge of the phosphorus, is probably responsible for this result. A slight trend in the data for the nickel compounds suggests that back-bonding is favored when the metal is in a low oxidation state.

(c) Unsaturated hydrocarbons

The bonding of olefins to low-oxidation-state metal atoms is usually described as a synergistic combination of σ donor bonding and π back-bonding. Studies of metal core

TABLE 4

Nitrogen 1*s* binding energies of coordinated and uncoordinated nitrogen-containing ligands.

Compound	E_B (eV)
$\underline{N}H_4NO_3$	401.3
$[Rh(\underline{N}H_3)_6](NO_3)_3$	400.7
$[Ir(NH_3)_5Cl]Cl_2$	400.6
$Co(\underline{N}H_3)_3(NO_2)_3$	400.2
$[Co(NH_3)_6]_2(SO_4)_3$	400.0
$[Cr(NH_3)_6]Cl_3$	399.9
$NH_3(s)$	398.9
$[Rh(NH_3)_5\underline{N}O_2]Br_2$	404.4
$NaNO_2$	404.1
$Co(NH_3)_3(\underline{N}O_2)_3$	404.1
$K[Co(NH_3)_2(\underline{N}O_2)_4]$	404.0
trans-$[Co(en)_2(\underline{N}O_2)_2]NO_3$	403.8
KCN	399.0
$K_3[Cr(CN)_6]$	398.6
$K_3[Cr(C\underline{N})_5NO]$	398.4
$Na_2[Fe(C\underline{N})_5NO] \cdot 2H_2O$	399.2
$K_4[Fe(CN)_6] \cdot 3H_2O$	397.6

binding energies are in accord with this bonding description. Cook et al.[79] have shown that the Pt($4f_{7/2}$) binding energy in $(C_2H_4)Pt[P(C_6H_5)_3]_2$ is 0.6 eV higher than in $Pt(P(C_6H_5)_3]_4$. Assuming that the platinum atom in the latter compound has a zero charge (not an unreasonable assumption, in view of the above discussion), they concluded that in the ethylene complex more charge is transferred by metal-to-ligand π back-bonding than by ligand-to-metal σ donation. Holsboer et al.[21] studied both iridium core binding energies and ^{193}Ir Mössbauer shifts of the adducts of $[(C_6H_5)_3P]_2Ir(CO)Cl$ with acrylonitrile (ACN), fumaronitrile (FDN), and tetracyanoethelene (TCNE). The Ir($4f_{5/2,\,7/2}$) binding energy increases on going from the ACN adduct to the TCNE adduct, whereas the ^{193}Ir isomer shift is essentially constant in the series. One concludes that the overall atomic charge of iridium increases on going from the ANC adduct to the TCNE adduct, but that the *s* electron density at the iridium nucleus remains constant. This result was rationalized by assuming that, on going from the ACN adduct to the TCNE adduct, π back-bonding increases and σ donation decreases. (An increase in π back-bonding, involving a lowering of *d* electron density on the metal and a decrease in the nuclear shielding, would cause an *increase* in *s* electron density at the metal nucleus.)

TABLE 5

Some phosphorus 2*p* binding energies

Compound	E_B (eV)	Ref.
$P(C_6H_5)_3$	130.6	78
	130.9	64
	131.2	25
	131.9	26
	132.0	20
$[P(C_6H_5)_3CH_2C_6H_5]Cl$	132.5	78
$[P(C_6H_5)_3CH_3]Br$	133.2	25
$[P(C_6H_5)_4]Br$	133.7	25
$Mn(CO)_4ClP(C_6H_5)_3$	131.2	78
$Ni[P(C_6H_5)_3]_3$	131.3	64
$Ni(CO)_2[P(C_6H_5)_3]_2$	131.6	64
$NiCl_2[P(C_6H_5)_3]_2$	131.6	26
trans-$Rh(CO)Cl[P(C_6H_5)_3]_2$	131.6	78
$Ni(\pi\text{-}C_3H_5)BrP(C_6H_5)_3$	131.7	64
$Cu(SnCl_3)[P(C_6H_5)_3]_3$	131.7	20
$PtCl(SnCl_3)[P(C_6H_5)_3]_2$	132.5	20

Two different studies of the carbon 1*s* spectra of transition metal bis(cyclopentadienyl) complexes have given different results[80–82]. Both groups of investigators measured the C(1*s*) shifts of these compounds relative to benzene, which was used as a stand-in for the C_5H_5 radical. One group found a small positive shift for the complexes[80, 81]; the other group found a small negative shift for the same compounds[82]. Although further work should be done, it is clear that there is not a great deal of charge transfer in these complexes. Vapor phase studies would be very useful in resolving the discrepancy.

(d) Carbonyls

Studies of solid metal carbonyls[80, 81, 83, 84] have indicated that both the carbon 1*s* and oxygen 1*s* binding energies of the coordinated CO groups are lower than those of free CO. However, considerable uncertainty is associated with this comparison because of the difficulties of correcting for the use of solid phase data for the carbonyls and gas phase data for free carbon monoxide. In this respect the gas phase data of Perry et al.[85], given in Table 6, are more meaningful. However, even these data cannot be directly compared. Carbon monoxide is notorious for its poor fit in correlations of carbon and oxygen binding energies with ground-state properties of the molecule[42,44,86]. It is generally agreed that the reason for this atypical behavior lies in the extraordinarily low relaxation

TABLE 6

Core binding energies of gaseous carbonyls and carbon monoxide

Compound	E_B (eV)	
	C(1*s*)	O(1*s*)
$Cr(CO)_6$	293.11	539.96
$Mo(CO)_6$	293.06	539.91
$W(CO)_6$	292.98	539.87
CO	295.9	542.1

energies associated with the ejection of core electrons from carbon and oxygen atoms in this small molecule. It seems likely that the relaxation energies for CO are at least 1 eV lower than those for most other compounds of carbon and oxygen. Thus, the CO binding energies in Table 6 should be decreased by at least 1 eV before comparing them with the hexacarbonyl binding energies. After suitable correction, the hexacarbonyl binding energies would probably still be lower than the corresponding CO binding energies. Thus, the data are consistent with extensive back-bonding in these metal carbonyls.

(e) Trichlorostannate(II)

Conflicting results have been reported for the $SnCl_3^-$ ion. Parshall[88] found an increase in the $Sn(3d_{5/2})$ binding energy of about 1.5 eV upon coordination of $SnCl_3^-$ to platinum in several complexes, whereas Grutsch et al.[20] observed no significant change for a wide variety of complexes. Perhaps charging effects are responsible for the difference in the observations. The latter study involved gold sputtering; the former did not. Attempts to compare the two sets of results by using data which have been referenced to the carbon 1*s* line for the carbon-containing compounds may be inadequate. The observed C 1*s* line probably corresponds partly to a contaminating surface layer of hydrocarbon-like material rather than completely to the carbon atoms of the bulk compound.

(v) The study of ligand structure and orientation

(a) N_2 complexes

During the period immediately after the initial discovery of transition metal complexes of molecular nitrogen, there was some question as to the stereochemistry of the coordinated N_2. If N_2 behaves analogously to acetylenes, the two nitrogen atoms should be equidistant from the metal atom; if N_2 behaves analogously to CO and CN^-, only one nitrogen atom should be bound to the metal atom, and the other should be directed away from the metal atom. Structural studies, including X-ray photoelectron spectroscopy, have shown that the latter, end-on, stereochemistry does in fact prevail. Nitrogen 1*s* photoelectron spectra of such complexes consist of doublets, or broad bands indicative of unresolved doublets, as expected for the end-on stereochemistry[89,90]. The observed and estimated chemical shifts between the components of the doublets (1–2 eV) correspond to markedly different electron populations for the two nitrogen atoms. Presumably the directly coordinated nitrogen atom has the greater positive charge.

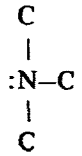
(b) Nitrosyls

Nitrosyl complexes fall into two categories: "linear" complexes, in which the metal–N–O bond angle is near 180°, and "bent" complexes, in which that bond angle in in the neighborhood of 125°. The linear complexes may be looked upon as complexes of the NO^+ ligand; the bent as complexes of the NO^- ligand. Nitrogen 1*s* binding energies of nitrosyl complexes[91] range from about 40–403 eV. Binding energies for the bent complexes invariably are, as expected, in the lower half of this range (400–401.5 eV). However, binding energies for the linear complexes cover the entire range. Those linear complexes of metals in very low oxidation states (a situation favoring back-bonding) generally have relatively low binding energies, e.g. $K_3[Cr(NO)(CN)_5]$, 400.7 eV; $Ir(NO)_2[P(C_6H_5)_3]_2^+$, 400.2 eV. Those linear complexes of metals in normal or high oxidation states (a situation not particularly conducive to back-bonding) have relatively high binding energies, e.g. $Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$, 403.3 eV. Thus, there is a correlation between the N(1*s*) binding energy of a nitrosyl group and the expected electron density on that group.

Brock et al.[24] have obtained evidence for conformational isomers of the complex $CoCl_2(NO)[P(CH_3)(C_6H_5)_2]_2$. One isomer has trigonal-bipyramidal geometry with a linear nitrosyl (NO^+), and the other isomer is believed to have square-pyramidal geometry with a bent nitrosyl (NO^-) at the apex. The investigators' proposal that the NO^- isomer is favored on the surface of the samples explains their observation that the relative intensities of the photoelectron peaks for the NO^- and NO^+ froms are the same for both ground and unground samples, whereas infrared spectra show a considerably increased concentration of the NO^- form in the ground samples.

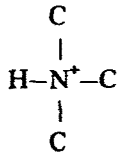
(c) Reactions of nitrogen-containing ligands

In ethylenediaminetetraacetic acid, H_4EDTA, and its disodium salt, Na_2H_2EDTA, it is believed that the two nitrogen atoms are protonated. The N(1*s*) spectra of these compounds are very similar; each consists of a single peak corresponding to a binding energy[18] of approximately 402.4 eV. In salts such as Na_4EDTA, Mg_2EDTA, $CaNa_2EDTA$, etc., the nitrogen atoms are unprotonated and the N(1*s*) spectra consist of a single peak with $E_B \simeq 400.2$ eV. The magnitude of this chemical shift is about that expected for the two structures



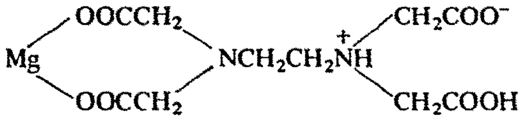
$$\begin{array}{c} C \\ | \\ :N-C \\ | \\ C \end{array}$$

and



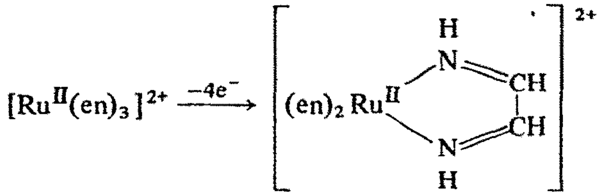
$$\begin{array}{c} C \\ | \\ H-N^+-C \\ | \\ C \end{array}$$

The N(1*s*) spectrum of MgH_2EDTA is unusual in that it consists of two equally strong peaks, of binding energies 399.8 and 402.2 eV. This spectrum has been explained[18] by assuming that one nitrogen atom is protonated and the other unprotonated, as shown in the structure



A similar study has been made of tetraphenylporphine and derived metalloporphyrins[17]. The N(1*s*) spectrum of tetraphenylporphine free base, H_2TPP, shows two peaks (at 399.1 and 397.2 eV), corresponding to protonated and unprotonated nitrogen atoms. This result is significant in view of considerable recent interest in the nature of the nitrogen atoms in porphine free bases. Obviously one must rule out any hydrogen-bonded structure with equivalent nitrogens. The tetraprotonated derivative, $(H_4TPP)Cl_2$, shows only one peak (at 399.2 eV), corresponding to protonated nitrogen atoms. Metalloporphyrins, such as ZnTPP, show one peak near 397.2 eV corresponding to unprotonated nitrogen atoms.

The product of the oxidation of $[Ru^{II}(en)_3]^{2+}$ or $[Ru^{III}(en)_3]^{3+}$ by air or I_2 was first characterized as $[Ru^{VI}(en_3-4H)]^{2+}$. The assignment of the oxidation state was based on the consumption of 4 equivalents of oxidant by $[Ru^{II}(en)_3]^{2+}$ and 3 equivalents of oxidant by $[Ru^{III}(en)_3]^{3+}$. Deprotonation of the coordinated ethylenediamine was suggested to account for the +2 charge found on the cation[92]. A completely different interpretation of the complex was made possible by ruthenium and nitrogen photoelectron spectroscopy, combined with magnetic susceptibility and NMR data[14]. From the Ru($3d_{5/2}$) binding energies in Table 7, it is clear that the complex in question has a ruthenium atomic charge between that found for typical Ru^{II} and Ru^{III} complexes; this fact and the observed diamagnetism of the complex strongly suggest that it is an Ru^{II} complex. Apparently oxidation of the ligand rather than the metal atom took place. The following reaction is proposed for the oxidation[14].



The N(1*s*) spectrum of the complex shows two overlapping peaks with an intensity ratio of 2 : 1. The stronger peak, of higher binding energy, has the same binding energy as that for $[Ru(en)_3]ZnCl_4$, and can be assigned to the four amine nitrogens, whereas the weaker peak can be assigned to the two imine nitrogens. This N(1*s*) spectrum is inconsistent with the Ru^{VI} formulation, for which the stronger peak should have a *lower* binding energy than the weaker peak, The NMR spectrum of the complex is consistent with the revised interpretation.

TABLE 7

Binding energies for ruthenium compounds

Compound	Oxidation state	E_B (eV) Ru($3d_{5/2}$)
Ru metal	0	279
$[Ru(NH_3)_6]I_2$	2	279.8
$[Ru(en)_3]ZnCl_4$	2	280.4
$[Ru(NH_3)_6](BF_4)_3$	3	282.2
$BaRuO_4$	6	284.4
$[Ru(en_3-4H)]I_2$	?	281.3

(d) Bridging and terminal chlorines

In mononuclear square-planar Pt^{II} and Pd^{II} chlorides such as $(R_3P)_2PtCl_2$, the Cl(2*p*) spectra appear as spin—orbit-split (ca. 1.8 eV) doublets. However, in chlorine-bridged complexes such as $(R_3P)_2Pt_2Cl_4$ the Cl(2*p*) spectra have been observed as broad unresolved peaks which can be deconvoluted to give four components[12], corresponding to the spin—orbit-split components for nonequivalent sets of chlorine atoms, chemically shifted by about 1.0 eV. Clark et al.[12], on the basis of NQR data for these compounds, assigned the lower binding energy peaks to the bridging chlorines and the higher binding energy peaks to the terminal chlorines. However, Moddeman et al.[39], in a study of $PtCl_2$ and K_2PtCl_4, concluded that bridging chlorines have a core binding energy 0.4 eV higher than that of terminal halogens. Although the latter result is qualitatively more reasonable in terms of the potential model, it is not immediately apparent why the latter workers observed a still higher chlorine binding energy for the relatively ionic KCl. Leigh and Bremser[9] studied a series of heavy metal complexes of the types K_2MCl_6, $MCl_4(PR_3)_2$ and $MCl_3(PR_3)_3$, and concluded that the chlorine binding energies are relatively insensitive to changes in the complexes. Clearly further work, with interpretations which include consideration of the Madelung potentials, will be necessary before halogen binding energy shifts can be reliably interpreted in terms of structural differences.

(vi) Detection of ligand→central atom $p\pi \rightarrow d\pi$ *bonding*

There is no question that *d* orbitals of principal quantum number one less than that of the outer valence electrons of an atom can be involved in chemical bonding — transition metal chemistry is largely the chemistry of penultimate shell *d* electrons. On the other hand, there is considerable argument as to whether or not *d* orbitals of the same principal quantum number as the valence electrons are ever significantly involved in chemical bonding. For example, in silicon tetrafluoride, we do not know the extent to which the silicon 3*d* orbitals can accept electron density from the fluorine $2p\pi$ orbitals. Such $p\pi \rightarrow d\pi$ bonding corresponds to contribution from resonance structures such as

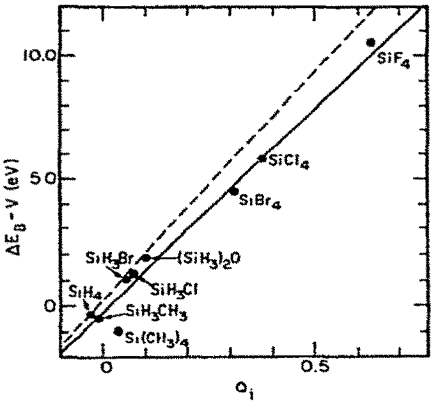
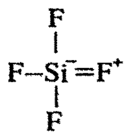


Fig. 6. A plot of $E_B - V$ vs. Q_i for various silicon compounds. The solid line corresponds to a least-squares fit. The dashed line is a theoretical line for compounds with no *d* orbital bonding. (E_B for SiH_4 taken as zero.)



$$F-\overset{\displaystyle F}{\underset{\displaystyle F}{\overset{|}{\underset{|}{Si^{-}}}}}=F^{+}$$

in which the silicon atom acquires a negative formal charge. One would expect that if the 3*d* orbitals of silicon were significantly occupied in one of its compounds, the charge on the silicon atom would be lower (more negative) than predicted on the basis of the non-participation of these orbitals. Thus, X-ray photoelectron spectroscopy, in combination with techniques for predicting atomic charges, would seem to be a logical tool to use to study this question.

Figure 6 is a plot of ($E_B - V$) vs. Q_i for various silicon compounds, in which the binding energies are silicon $2p_{3/2}$ energies and the atomic charges were calculated by the CHELEQ electronegativity equalization procedure*. The charge calculation procedure takes no account of possible *d* orbital participation. The solid line corresponds to a least-squares fit to the data, with a standard deviation of ±0.56 eV. Thus, the plot gives a fairly good linear correlation, in agreement with eqn. (2), and may be taken as evidence that *d* orbitals play a negligible role in the bonding of these compounds. Nevertheless, if one has a mind to, one can use the data of Fig. 6 to argue for the opposite view. Only one point in the plot corresponds to a compound in which $p\pi \rightarrow d\pi$ bonding is definitely negligible – i.e. the point for SiH_4. One can argue that a straight line corresponding to compounds without $p\pi \rightarrow d\pi$ bonding should pass through that point with a slope which can be determined theoretically by comparison with the slope obtained from a plot for the analogous compounds of carbon. The dashed line in Fig. 6 is such a line[93]. Negative deviations of

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* The binding energies are from ref. 93, and the calculations were recently made by Perry and Jolly using the method of ref. 44.

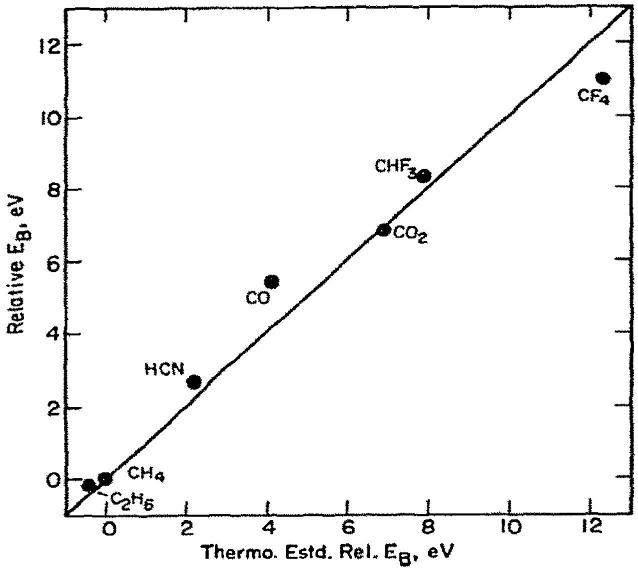

Fig. 7. Plot of carbon 1*s* binding energies vs. thermodynamically estimated energies. (Reproduced with permission from ref. 95.)

($E_B - V$) from the dashed line may be ascribed to extraordinary negative charges on the silicon atoms due to $p\pi \rightarrow d\pi$ bonding. It will be noted that the greatest negative deviations correspond to compounds in which the silicon is bound principally to atoms other than hydrogen, i.e. to the silicon tetrahalides and tetramethylsilane. Participation of *d* orbitals can be easily rationalized for the tetrahalides; however, for $Si(CH_3)_4$ hyperconjugation must be invoked. On the other hand, the pronounced negative deviation of $Si(CH_3)_4$ and the fact that the deviation of $SiBr_4$ is about the same as that of SiF_4 suggest that the deviations are actually due to increased relaxation energies for these relatively polarizable molecules (see Section C(*i*)(*b*)). All in all, the data offer little support for the use of *d* orbitals in the bonding of silicon compounds[94]. The same conclusion can be drawn from analogous data for germanium compounds[93].

(vii) The concept of equivalent cores

One can write chemical equations which correspond to chemical shifts in core binding energies. For example, the difference between the carbon 1*s* energies of gaseous methane and gaseous carbon dioxide is the energy of the reaction

$$CH_4 + CO_2^{+*} \rightarrow CH_4^{+*} + CO_2 \qquad \Delta E = \Delta E_B \qquad (3)$$

(The asterisks indicate 1*s* holes.) To transform this equation into one involving conventional chemical species, we apply the approximation of *the equivalence of equally charged* *cores*[48, 95]. That is, we assume that the exchange of the +5 cores between the species CH_4^{+*} and NO_2^+ involves no energy.

$$CH_4^{+*} + NO_2^+ \rightarrow NH_4^+ + CO_2^{+*} \qquad \Delta E = 0 \tag{4}$$

Addition of eqns. (3) and (4) yields eqn. (5).

$$CH_4 + NO_2^+ \rightarrow NH_4^+ + CO_2 \qquad \Delta E = \Delta E_B \tag{5}$$

Thus, we express the binding energy shift as the energy (or heat) of a straightforward chemical reaction. The experimental binding energy shift is 6.8 eV; this compares favorably with the energy of reaction (5) as calculated from available thermodynamic data[3], 6.9 eV. Similar comparisons for other carbon compounds are shown graphically in Fig. 7, where experimental binding energy shifts are plotted against the corresponding thermodynamically estimated energies.

By this same general technique, good agreement has been obtained in the prediction of binding energies for compounds of boron[41], nitrogen[96], xenon[3,95] and iodine[48]. When the necessary thermodynamic data have been lacking, empirical and theoretical methods for calculating these data have yielded good results[95, 97–100]. Application of the method to the estimation of chemical shifts for solid compounds is more complicated and less accurate than that for gases, and the method is readily applied only to atoms in molecular solids and in the anions of salts[48,95]. However, it is hoped that further study will yield a relatively simple method for treating all solids.

(viii) Other calculational methods

Various quantum mechanical methods, with wide ranges of rigor, sophistication and accuracy, have been used for calculating binding energies and binding energy shifts. These methods have been reviewed by Shirley[4]; in general they are relatively time-consuming, complicated, or demanding of much computer time. Hence, they are not useful to the inorganic or organic chemist who wants a simple but reliable method for predicting or correlating binding energies.

D. SHAKEUP

The X-ray photoelectron spectra of some compounds show, on the high binding energy side of the core photolines, satellites which are not due to Auger electrons, chemical decomposition, or multiplet splitting. These satellites have been assigned to two-electron, "shakeup", processes in which valence-shell excitations take place in parallel with core electron ejection. Examples of shakeup satellites are shown in the lanthanum 3*d* spectrum of LaF_3 (Fig. 8) and the copper 2*p* spectrum of Cu_2O (Fig. 9). The LaF_3 satellites have been attributed to excitation from the valence band to empty 4*f* levels[101], and the Cu_2O

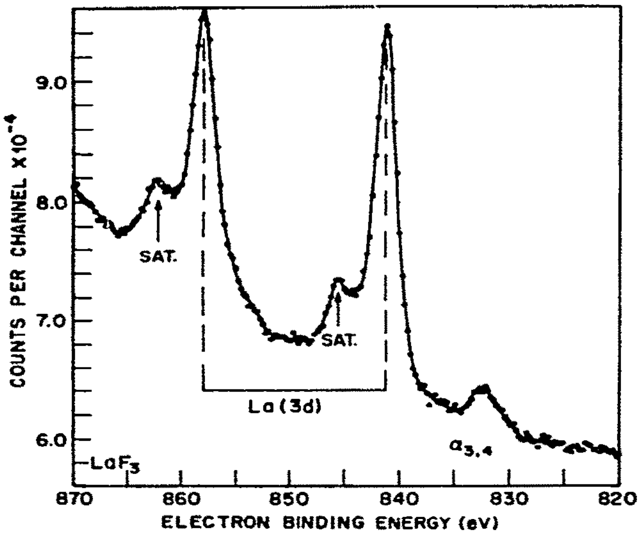

Fig. 8. Shakeup satellites of the 3*d* photoelectron peaks of LaF_3. (Reproduced with permission from ref. 101.)

satellites have been attributed to excitation from the valence band to the conduction band[102]. The Cu_2O system is rather peculiar in that the satellites disappear after gentle heating in vacuum. It has been suggested that adsorbed oxygen (or water) is responsible for relaxation of the selection rules which forbid the transition in the stoichiometric phase.

The nickel 2*p* spectra of paramagnetic nickel complexes have features which are absent in the spectra of diamagnetic nickel salts. Shakeup satellites are observed about 6 eV from the primary lines; these lines have been assigned to $3d \rightarrow 4s$ transitions[103]. In addition, the primary lines either show a shoulder on the high binding energy side or are perceptibly wider than the corresponding lines for diamagnetic complexes; these features have been assigned to $d \rightarrow d$ transitions[104]. Thus, it is possible to differentiate between pairs of nickel complex isomers when one is diamagnetic (square-planar coordination) and the other is paramagnetic (tetrahedral or octahedral coordination) on the basis of the appearance or lack of shakeup satellites in the X-ray photoelectron spectra[105, 106].

E. MULTIPLET SPLITTING

Ejection of a core electron from a compound with a closed shell electronic configuration normally results in only one final state. However, if there are unpaired valence electrons in the compound, more than one final state can occur because the magnitude of the exchange interaction of the unpaired valence electrons with the unpaired electron in the core shell depends on whether or not the latter has its spin up or down[66, 107; 108]. If a core

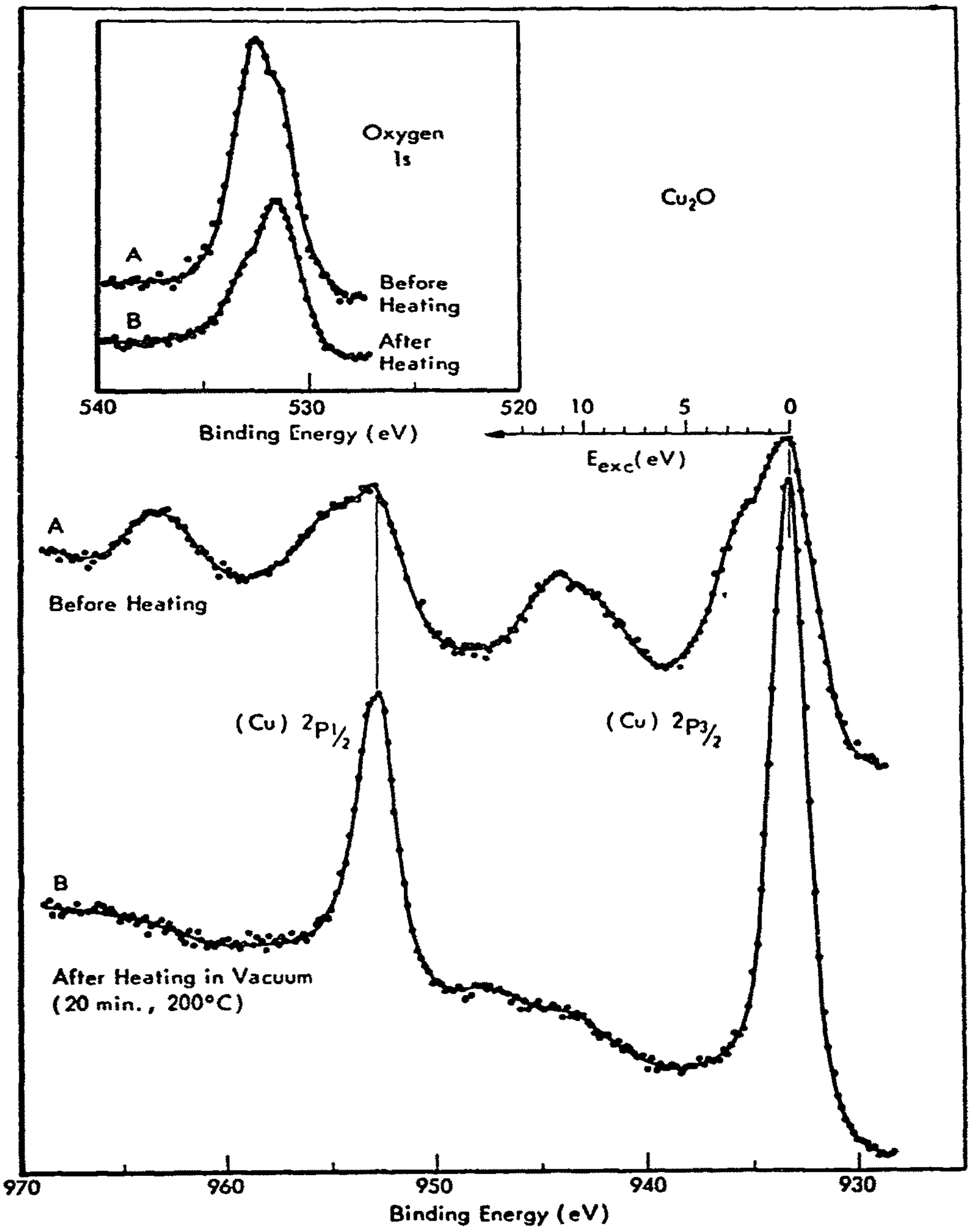

Fig. 9. The copper 2*p* and oxygen 1*s* photoelectron spectra of Cu_2O. (Reproduced with permission from ref. 102.) The spectra marked "A" are for Cu_2O "from the shelf". The spectra marked "B" are for the sample heated in situ for about 20 min.

s electron is ejected, two final states are formed, and a doublet spectrum is expected. If an electron is ejected from a core orbital of higher angular momentum, the number of final states is much larger, and a relatively complex multiplet is expected. According to simple multiplet theory, the relative intensities of the lines should be the statistical weights of the final states. For example, in the ejection of a core *s* electron from an Mn^{2+} ion (which has five unpaired *d* electrons) the final-state spin (J) can be $\frac{5}{2} \pm \frac{1}{2}$, and the intensities of the two lines are expected to be in the ratio of the $(2J + 1)$ values, 7 : 5. The manganese 3*s* spectrum[109] of MnF_2 is shown in Fig. 10. Two anomalous features of the spectrum indicate the naïvety of the preceding discussion. First, satellite peaks appear on the high binding energy side of the spectrum. Second, the intensity ratio of the main doublet is 2.3 : 1 instead of 1.4 : 1. Both of these features were actually predicted by Sasaki and Bagus, who included configuration interaction in their calculations[110].

The magnitude of the splittings for free transition-metal ions can be calculated using a relatively simple spin-unrestricted Hartree–Fock code. The calculated splittings for free ions are always larger than the splittings observed for compounds[66]. This reduction in splitting is in part due to configuration interaction and in part due to the involvement of the valence *d* orbitals of the metal in chemical bonding, which causes delocalization of the unpaired electrons, and consequently poorer overlap between the core and valence *d* orbitals. Of course, in some cases a strong ligand field causes complete pairing of the *d* electrons and elimination of any splitting.

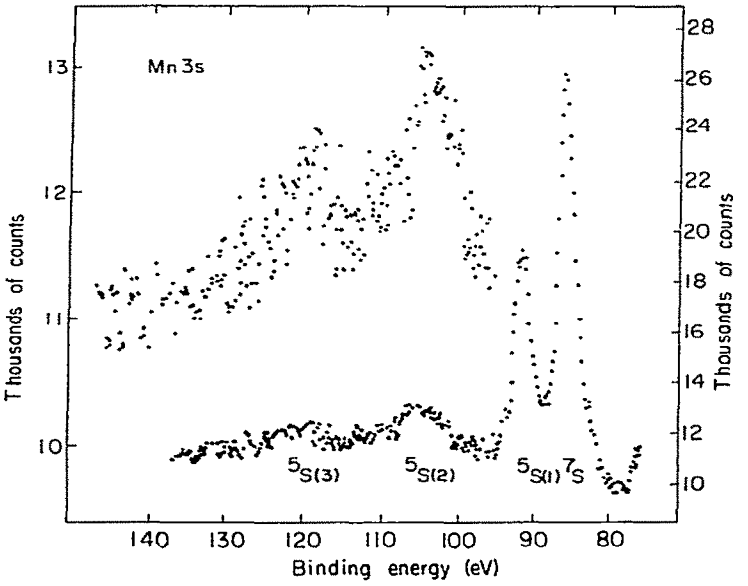

Fig. 10. Manganese 3*s* photoelectron spectrum of MnF_2. (Reproduced with permission from ref. 109). The right ordinate refers to the complete spectrum, and the left ordinate refers to the expanded portion of the spectrum.

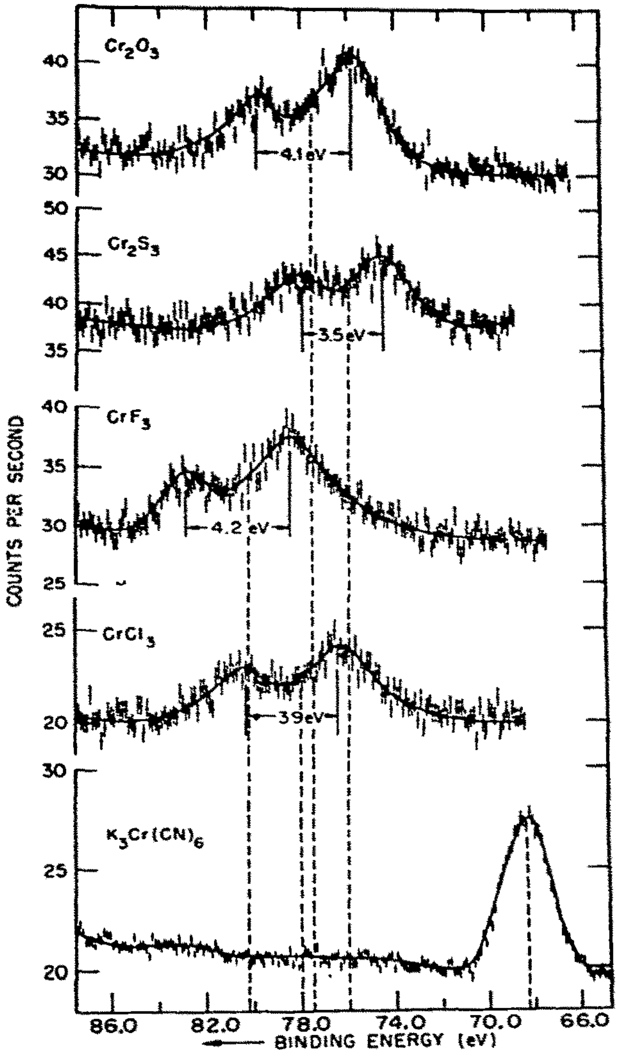

Fig. 11. Chromium 3*s* photoelectron spectra of Cr_2O_3, Cr_2S_3, CrF_3, $CrCl_3$, and $K_2Cr(CN)_6$. In each spectrum, except that for $K_3Cr(CN)_6$, the multiplet splitting is indicated. (Reproduced with permission from ref. 108.)

Figure 11 illustrates the reduction in the magnitude of the splitting on going from Cr_2O_3 to Cr_2S_3 and from CrF_3 to $CrCl_3$, and the disappearance of splitting in $K_3Cr(CN)_6$ (refs. 66, 108). These changes have been rationalized in terms of a small amount of metal – ligand π-bonding in the sulfide and the chloride, and a large amount of such π-bonding in the hexacyano complex.

Shirley[4] has issued a warning that, although multiplet splitting studies appear to be a powerful diagnostic tool for elucidating spin distributions, caution must be exercised be-

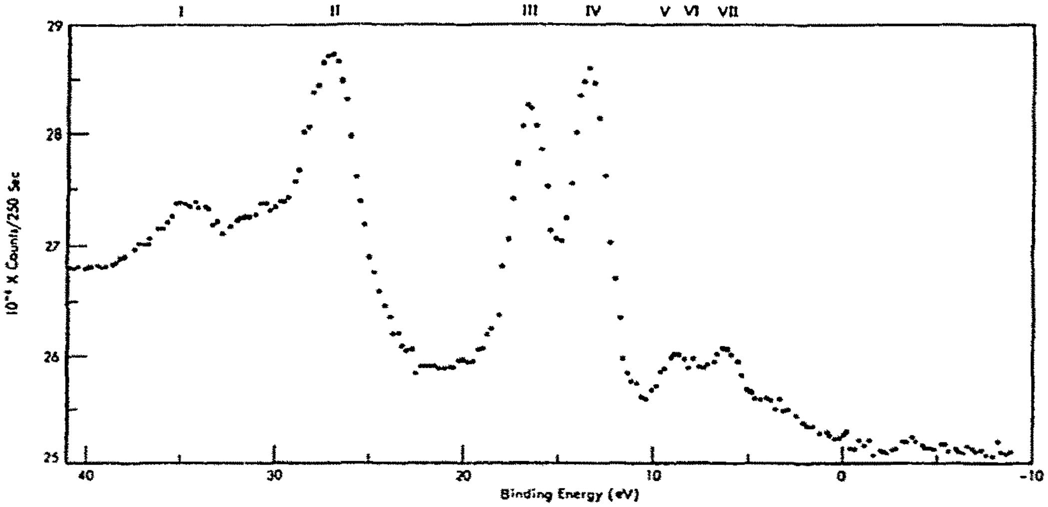

Fig. 12. X-ray photoelectron spectrum of the valence region of $LiClO_4$. (Reproduced with permission from ref. 114.)

cause of the difficulty of distinguishing multiplet splitting from other effects that can give rise to extra peaks — e.g. Auger peaks, shakeup peaks, mixed oxidation states, chemical shifts due to surface impurities, etc.

F. VALENCE ORBITAL SPECTRA

In ultraviolet photoelectron spectroscopy, the exciting photon is usually the 21.2 eV He I resonance line or the 40.8 eV He II resonance line. Most valence shell electrons in molecules and atoms have binding energies less than 40.8 eV, and therefore UV photoelectron spectroscopy is useful for studying the occupancy and energies of molecular orbitals[111, 112]. The technique is generally employed with gaseous molecules, and relatively sharp spectra are obtained. X-Ray photoelectron spectra of molecular levels in gaseous systems are relatively weak, and the lines are much broader than those obtained by UV photoelectron spectroscopy. Nevertheless, the X-ray method has at least two advantages which can sometimes be exploited. First, electrons with binding energies greater than 40 eV can be easily studied, and, second, the atomic orbital parentages of the molecular orbitals can be obtained from a relatively simple analysis of the line intensities[113].

When UV photoelectron spectroscopy is applied to solids, the average escape depth of the photoelectron is exceedingly short, and hence the study is restricted almost entirely to the surface of the samples. Because of the great difficulties involved in avoiding surface contamination, the technique is seldom applied to solid compounds. However, in X-ray photoelectron spectroscopy the surface contamination problem is not quite as serious because of the somewhat greater average escape depth for the photoelectrons. Consequently,

TABLE 8

Observed and calculated binding energies for valence electrons in ClO_4^-

Molecular orbital	E_B(eV)	
	Exp.[a]	Calc.[b]
$1t_1$	6.3	3.0
$1e, 5t_2$	9.0	6.8, 4.8
$4t_2$	13.4	11.9
$5a_1$	16.5	16.5
$3t_2$	27.0	29.0
$4a_1$	34.4	35.8

[a] Ref. 114.
[b] Ref. 115.

X-ray photoelectron spectroscopy has been used to study the molecular orbitals of anions in a variety of salts, including $LiClO_4$ (refs. 114, 115), Li_2SO_4 (refs. 114, 115), $LiClO_3$ (ref. 115), Li_2CO_3 (ref. 115), Li_3PO_4 (ref. 115), Li_2CrO_4 (refs. 116, 117), $LiMnO_4$ (refs. 116, 117), KNO_3 (ref. 118), NaCN (ref. 118), $Li_2Cr_2O_7$ (ref. 117), Li_3VO_4 (ref. 117), K_2FeO_4 (ref. 117), LiN_3 (ref. 119), $LiNO_2$ (ref. 119) and $LiNO_3$ (ref. 119).

The X-ray photoelectron spectrum of the valence region of $LiClO_4$ is shown in Fig. 12.

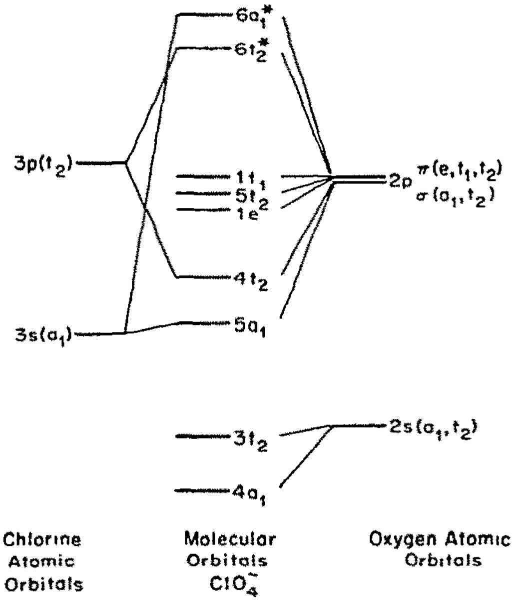

Fig. 13. Molecular orbital energy level diagram for ClO_4^-.

The six peaks, which are easily distinguished, have been assigned by Prins and Novakov[114] to seven molecular orbitals as indicated in Table 8. The corresponding energy level diagram is shown in Fig. 13. The valence shell consists of four main groups of orbitals, of which the lower three groups are occupied. The lowest group consists of two levels, $4a_1$ and $3t_2$, which are essentially nonbonding oxygen $2s$ orbitals. The corresponding photoelectron peaks have an intensity ratio approximately equal to the ratio of the orbital degeneracies, and their intensities are high, in agreement with the fact that the cross section for electron emission from s orbitals is greater than that from p orbitals. The next group consists of two strongly bonding levels, $5a_1$ and $4t_2$, derived from chlorine $3s$ and $3p$ orbitals and oxygen $2s$ and $2p_\sigma$ orbitals. The fact that the corresponding photolines have about the same intensity in spite of the different degeneracies is a consequence of the relative proportions of chlorine $3s$ and $3p$ character in these orbitals. Strong support for the assignment is found in the fact that, in the spectrum of Cl, the $3s$ and $3p$ photolines have about the same intensity. The next group of orbitals (the highest occupied orbitals) consists of three levels, $1s$, $5t_2$ and $1t_1$, which are essentially nonbonding $2p\pi$ orbitals on the oxygen atoms. As expected, the intensities of the corresponding photolines are low. These data admirably illustrate the power of intensity ratio arguments in making spectral assignments.

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