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ADVANCES IN THE KNOWLEDGE OF THE ELECTRONIC STRUCTURE OF COORDINATION COMPOUNDS FROM PHOTOELECTRON SPECTROSCOPIC TECHNIQUES

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In this conference, which has been devoted to the progress and future perspectives of coordination chemistry, the impact of new investigation techniques on our knowledge of the structure of coordination compounds has played one of the most important, even if not, in the author's opinion, essential roles. In fact, the most significant advancements in this field are due mainly to the introduction of new concepts and models such as the ligand field model, or the correlation of optical and magnetic spectroscopic data with electronic structure, and of reaction mechanisms with the nature of coordination bonds, rather than to new experimental investigation techniques. The latter have proved, however, extremely valuable in supplying proofs and validity tests for theoretical models, in monitoring new developments both in the theory and synthesis of coordination compounds, and in suggesting and clarifying links to other branches of the physical, chemical, and biological sciences.

In this respect, the impact of photoelectron spectroscopy has been, in the author's opinion, the most important and most spectacular one in the last ten years, and is probably the most promising for the next ten years. This technique (Fig. 1) owes its success to the inherent simplicity of the investigated physical phenomenon (the collision of a photon of energy $h\nu$ larger than the ionization threshold with a system M containing bound electrons) and to its deep and intimate relationship to the electronic structure of the target M

$$\mathrm{M} + h\nu \rightarrow \mathrm{M}_i^+ + e^-$$

$$h\nu = \mathrm{I.E.}_i + \mathrm{E}_{\mathrm{kin},e^-}$$

In the gas-phase version of the technique (UPS), where hard UV photons are normally used (e.g., He $2p \rightarrow 1s$ at 21.22 eV), ionizations consist of elimination of one electron from filled molecular orbitals of the valence shell (~ -10 to -20 eV), and the measured ionization energy is related to the orbital energy of the latter, thus giving perhaps the most direct evidence for

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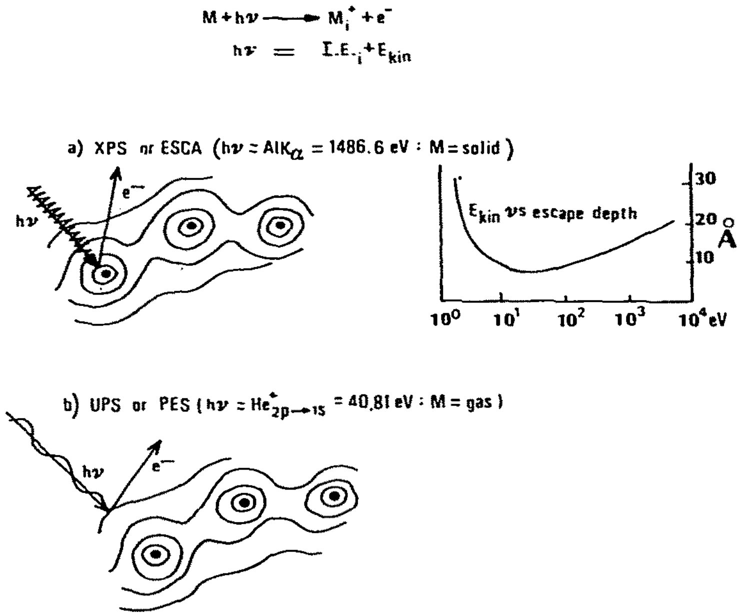
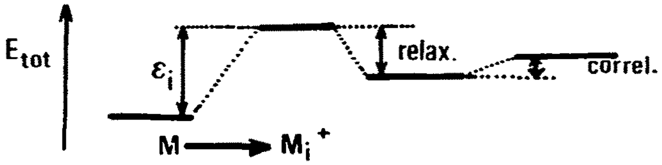


Fig. 1. Basic features of photoelectron spectroscopic techniques. (a) XPS measures (b.e.)$_i$ of inner core pseudoatomic orbitals ψ_i, and chemical shifts due to inter- and intramolecular potentials, and hence determines atomic charge distributions (note limited escape depth of photoelectrons, hence surface technique). (b) UPS or PES measures b.e. of filled molecular orbitals (valence shell), and determines relative energies of molecular ions M_i^+ (exactly), or orbital energies of M in the valence shell (approximately).

the experimental characterization of molecular orbitals. In the XPS version, where soft X-ray photons (e.g., Al *Kα* at 1487 eV) are used on solid samples, ionization consists of ejection of one electron from inner-shell orbitals (~ -50 to -1200 eV). These are pseudoatomic in character and their energy depends on a small but measurable chemical shift due to the atomic charges localized both on the ionized and on the neighbouring atoms (in other words on the electric potential felt by the photoelectron before ejection, and generated by both intra- and interatomic charges), and is therefore related to the net atomic charges. This again represents an almost unique chance for the direct experimental evaluation of the latter quantities. More generally, the electric potential of the chemical surrounding affecting the measured XPS ionization energies (or binding energies, as they are currently called) depends on the nature of the chemical surrounding itself, including solid-state effects.

Thus the possibility of getting close to a direct experimental characterization of such important quantities as the energy of molecular orbital levels and atomic charge distributions within the coordination sphere, with obvious implications of significant validity tests and systematic concrete applications



Koopmans' theorem I.E.$_i = -\epsilon_{SCF.i}$ for closed shells (-relaxation and correlation effects)

UPS data

Investigation of molecular ions: ΔI.E.$_{i,j}$ equal exactly total energy differences of $M_{i,j}^+$ (at frozen nuclei); M_i^+ differ from g.st.M in normal vibration frequencies ($\bar{\nu}_1(H_2O) = 3610$ cm^{-1}; $(H_2O^+) = 2850$ cm^{-1}), or in equilibrium geometry (NH_3^+ planar; CH_4^+ J.T. distorted.)

(UPS,XPS) of coordination compounds

→ electronic structure of coordination compounds from valence-shell ϵ_i(UPS) and atomic charges (XPS)

→
- fundamental and chemical aspects of particle/matter collisions
- production of molecular ions; direct observation of properties of m.i.s.
- coordination chemistry and solid state chemistry: coordination compounds as molecular solids
- surface properties of coordination compounds: surface coordination chemistry, heterogeneous catalysis.

Fig. 2. Chemical information from photoelectron spectroscopy data.

of bond theories (Fig. 2), is available. It is, however, to be pointed out that the quantities experimentally measured in XPS or UPS spectra (particularly ionization energies) are not simply or at least only approximately related to properties of the molecule, M, to be ionized. In fact, the underlying physical phenomenon, $M + h\nu \rightarrow M_i^+ + e^-$, is a process involving four particles, so any physical observable measured for such a process depends in principle on all four particles and not only on the ground-state properties of M alone. The ionization energy involved in the process can be shown to be exactly equal in absolute value to the energy of the ionized orbital of M only in the limiting situation where all remaining filled orbitals remain completely unchanged in M_i^+ ("frozen orbitals" or Koopmans' approximation) [1]. This opens two perspectives: on the one hand, if our interest is in the ground-state properties of the non-ionized system M, it can be done in an approximate way by use of Koopmans' theorem, I.E.$_i = -\epsilon_{SCF}$ [1]. Actually, most of the current structural studies based on XPS or UPS use this approximation, even if deviations from Koopmans' behaviour are larger and more frequent for open-shell systems and for *d*-orbital ionization, as is the case particularly for coordination compounds [2]. A more accurate evaluation of ground-state quantities is possible, both in principle and in practice, by use of more extended and powerful theoretical models, e.g. the ΔSCF procedure [3]. Viewed from a wider angle, the rigorous approach shows that besides approximate information on ground-state properties, we can extract from XPS or UPS measurements exact information on the +1 molecular ions produced, and further data can be extracted from XPS or UPS on electronic and geometric structure of the molecular ions M_i^+, particularly on the difference from the neutral species M. Furthermore, much significant chemical information is associated with the observation of mass spectra of fragmentation products of M_i^+ (PIMS = photo-ion mass spectrometry). Therefore, what at first sight appears as a limitation to the availability of direct information on the ground-state properties of coordination compounds M, turns to be a unique chance for investigation of such interesting species as molecular radical cations. The use of photoelectron spectroscopic techniques is not only an additional means to confirm and extend the knowledge of the electronic structure of ground-state species of coordination compounds, as already secured by other techniques such as optical absorption or radiofrequency spectroscopy, but opens also an effective link between the chemical chapter of coordination compounds and three other main fields. These are the physics of photon collisions, the chemistry of the solid state, and the physics and chemistry of excited molecular ions. In this connection, mention has also to be made of the peculiar character of surface investigation technique revealed by solid-state XPS. While in fact the soft X-rays used in exciting core photoemission from solids do penetrate a depth of one or more thousand Ångström below the solid surface, photoelectrons have a much shorter mean free path in solids (due to electron–electron scattering, and depending mainly on the kinetic energy of photoelectrons), so that an XPS experiment usually sees electrons coming from an "escape depth" of the order of only 10–50 Å below the sample surface. XPS is therefore a technique particularly, or even uniquely, suitable for the investigation of phenomena occurring at the surface or near the surface of solids, hence also of the role of coordination compounds in surface phenomena, with an obvious correlation to the understanding of the mechanisms of heterogeneous catalysis.

In the present review, the more rigorous approach and the consequent treatment of molecular ions is neglected and instead attention is concentrated in the approximate investigation of ground-state properties and structure by UP and XP spectroscopy, emphasizing on the one side complementarity with previous, more conventional techniques, and confirmation of already proposed structural interpretations, and on the other side opening of perspectives of new links to neighbouring or related fields. Also, no attempt has been made to present a complete, or even a completely systematic, coverage of all applications of photoelectron spectroscopic techniques (UPS and XPS) to coordination chemistry; although relatively new (definitely not more than ten years until now) these lines of research have produced such a vast amount of literature and of research results that a complete review would lie beyond the scope and the extension of the present intervention [4,5]. Rather, I confine myself to the illustration of some selected examples, chosen to represent categories or problems of general significance.

To start with (Fig. 3), the dependence of chemical shifts of binding energies of inner core orbitals in XPS of solids on atomic charges represents perhaps the most immediate, although approximate, structural correlation in photoelectron spectroscopy. In a widely used approximation [6–8]

$$(\text{b.e.})_i = (\text{b.e.})_{0i} + k_i q_i + \sum_{j=i} \frac{q_j}{R_{ij}}$$

where i denotes the atom being ionized, and j runs over the atoms of the coordination environment around i; the measured chemical shift $(\text{b.e.})_i - (\text{b.e.})_{0i}$ depends therefore both on the actual charge on i (roughly related to the oxidation number of i and to the electronegativity of its neighbours), and on the charges of the neighbouring atoms. Table 1 collects selected literature data [9–11] pertaining to the $4f$ signals of rhenium in various coordination compounds; the effect of Re oxidation state is evident, e.g. in the series

$$\Delta(\text{b.e.})_i = f(\text{V}_i, \Sigma_j \text{V}_j)$$

$$(\text{b.e.})_i = (\text{b.e.})_{0,i} + k_i q_i + \sum_{j \neq i} \frac{q_j}{R_{ij}}$$

Intra-atomic potential V_i → operative definition of q_i

$|k_i| \sim I_1(Z) - I_2(Z+1)$

Interatomic potential V_j ("Madelung potential") → check of stereochemical arrangements

Consistent atomic charge distributions from:

$$\begin{cases} (\text{b.e.})_1 = (\text{b.e.})_{0.1} + k_1 q_1 + \Sigma_{j \neq 1} q_j / R_{1j} \\ (\text{b.e.})_2 = (\text{b.e.})_{0.2} + k_2 q_2 + \Sigma_{j \neq 2} q_j / R_{2j} \\ \cdots\cdots\cdots \\ \cdots\cdots\cdots \end{cases}$$

provided k_i, R_{ij}, $(\text{b.e.})_{0,i}$ known, and all i, j atoms give at least one observable XPS signal (neglecting differential relaxation effects)

Fig. 3. Atomic charge distributions from XPS data.

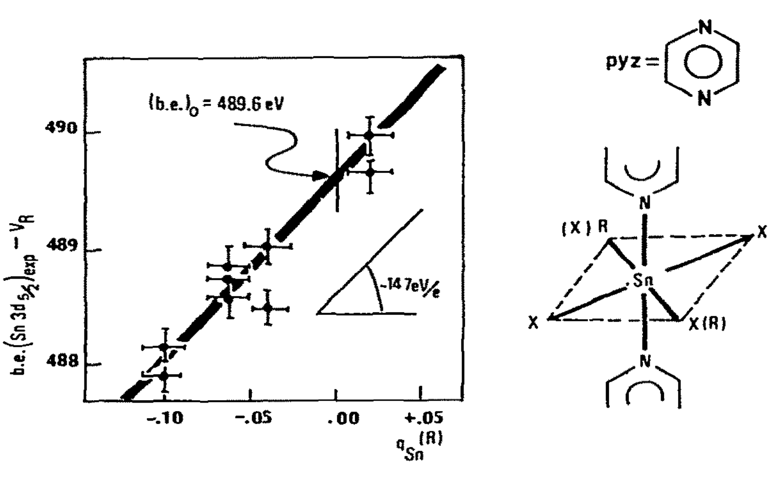
TABLE I

Re 4f b.e. in some complexes of rhenium (from refs. 9, 10 and 11).

Complex	Formal oxidation No.	Re 4f7/2 b.e.	Av. (eV)
$ReCl_2N(PR_3)_2$	V	42.9	43.2
$ReCl_3(NC_6H_5)(PR_3)_2$	V	43.5	
$ReCl_4(PR_3)_2$	IV	43.8	43.7
$ReCl_4(NO)(PR_3)_2$	IV	43.8	
K_2ReCl_6	IV	43.5	
$ReCl_3(PR_3)_3$	III	42.0	42.6
$ReCl_3(NO)(PR_3)_2$	III	43.3	
$[ReCl(CO)(PR_3)_4][FeCl_4]$	II	42.1	41.2
$ReCl_2(PR_3)_4$	II	40.7	
$[ReCl(CO)(P\frown P)_2][FeCl_4]$	II	40.9	
$ReCl(CO)(P\frown P)_2$	I	40.4	40.6
$ReCl(N_2)py(PR_3)_3$	I	41.1	
$ReCl(N_2)(PR_3)_4$	I	40.5	

$ReCl_n(PR_3)_{6-n}$ ($4f_{7/2}$ at 43.8 eV for $n = 4$, 42.0 eV for $n = 3$, and 40.7 eV for $n = 2$). Other structural effects include the strong π-acceptor ability of the dinitrogen ligand (π^* N–N orbitals) leading to higher b.e.s in the N_2-containing complexes if compared to other complexes of Re in the same oxidation state and similar ligand environment (e.g. 42.4 eV in $[Re^{II}Cl(N_2)(PR_3)_4]^+$ $[FeCl_4]^-$ [11] against 40.7 eV in Re^{II} $Cl_2(PR_3)_4$ [11]).

Since several structural effects contribute to the chemical shift on the ith atomic orbital, the single effects cannot be sorted out from the $(b.e.)_i$ data of i alone; however, if several atoms in the same chromophore are measured, the number of experimental chemical shift data may overcome the number of unknown atomic charges $q_{i,j}$ and thus make the system (over)determined. This is important because it opens the way to an operative definition of atomic charges $q_{i,j}$ (otherwise a somewhat undefined theoretical quantity) directly related to an experimental observable. In practice, the applicability of such a procedure is as yet still seriously impaired by the fact that k_i coefficients are not strictly constant and depend to some extent on the occurrence of intra- and intermolecular relaxation effects; the uncertainty in the knowledge of the reference values $(b.e.)_{0i}$ which do not correspond to a direct observable, can be overcome both in principle and in practice by increasing the number of measured j chemical shifts. Therefore, the current application is rather to test values of atomic charges computed by some



Compound	Sn $3d_{5/2}$ exp (eV)	Sn $3d_{5/2}$ $-V_R$	Q_RSn	δ (mm s^{-1})
$SnCl_4 \cdot$pyz	488.0	489.6	+0.016	0.52
$SnBr_4 \cdot$pyz	487.6	488.4	−0.039	0.83
$SnI_4 \cdot$pyz	487.8	487.9	−0.103	1.29
$SnCl_4 \cdot (pyz)_2$	488.3	490.1	+0.016	0.50
$MeSnCl_3 \cdot$pyz	487.7	488.6	−0.066	0.99
$Bu^nSnCl_3 \cdot$pyz	487.8	488.9	−0.065	1.13
$Oct^nSnCl_3 \cdot$pyz	487.8	488.9	−0.065	1.13
$PhSnCl_3 \cdot$pyz	488.1	489.1	−0.045	0.91
$Ph_2SnCl_2 \cdot$pyz	487.8	488.1	−0.101	1.36

Fig. 4. Charge/b.e. correlation in organometallic Sn complexes (from ref. 12).

theoretical method, from the simplest to the most sophisticated, and see whether the observed trend is consistent with computed data. Nevertheless, the importance of the method in principle remains unaffected and some cases where, with the aid of particularly favourable circumstances, chemical shift data can be actually worked out to give fully experimental evaluation of atomic charges can be seen.

An example of correlation between b.e. data and computed atomic charges is given in Fig. 4 for some series of tin–organic coordination compounds [12]. The theoretical model employed is relatively crude, i.e. that of equilibrated electronegativities or CHELEQ [13], but gives, anyway, a reasonable picture of charge distribution, which corresponds closely to the experimental observations. The agreement consists of good linearity between experimental b.e. values (corrected in a self-consistent way for interatomic

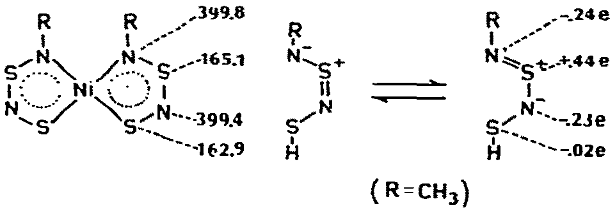
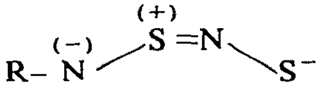


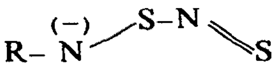
Fig. 5. XPS b.e. in unequivalent atoms: N1s and S2p_{3v} in Ni(II) diazadithiachelates (from ref. 14).

potential contributions) and calculated charges, with a plausible slope k around 14 eV/unit of charge (the value of k being related to atomic interelectronic repulsion integrals), and a reasonable (b.e.)$_0$ intercept around 490 eV, close to the free atom value [6,8].

Another typical application of X-ray photoelectron spectroscopy as applied to the determination of binding energies of inner core levels is a quantitative characterization of the differences in atomic charges between inequivalent atoms of the same element. One of the most conceptually simple examples is found among the complexes of diazadithiane $H_2N_2S_2$ [14] (Fig. 5). Although there is controversy in the literature as to the actual assignment [14], it is clear that the two nitrogen and two sulfur atoms in the chelate ring are inequivalent, both because of ligand asymmetry and donor effects on the terminal ligand atoms. A CNDO/2 calculation on the free ligand [14] suggests the charge distribution reported in Fig. 5; in the complexes, charge on $S_{(2)}$ and $N_{(1)}$ should be somewhat more positive because of σ donation, and the whole situation is consistent with the ligand anion behaving essentially as

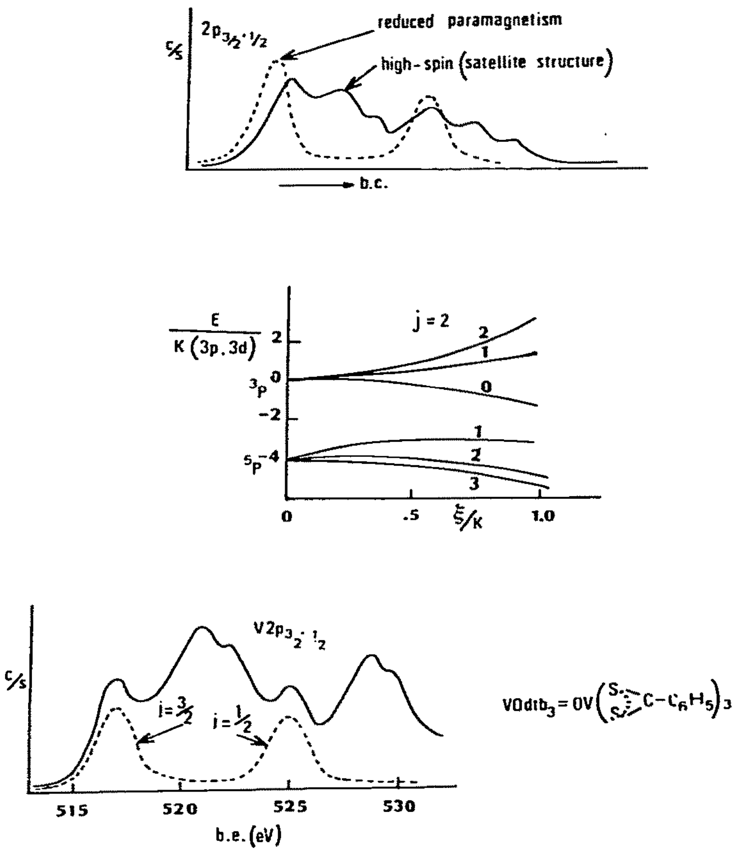


rather than as



An additional source of structural information from core XPS spectra lies in the satellite structure (Fig. 6) that sometimes accompanies main ionization peaks (e.g. $2p_j$ or $2s$ or $3s$ in first-row transition metal complexes). Such structures arise from several possible mechanisms, such as multiplet coupling between photohole and previously existing partly filled shells, or electronic coexcitations, or time-of-flight coupling of the photoelectron with partly filled valence shells. Energy and intensity of satellite transitions reflect, therefore, either interelectronic coupling parameters or valence-shell energy levels involved in coexcitations. They are, therefore, potential sources of additional information on the electronic structure, particularly in the case of coexcitations, since the energy levels involved cover a larger energy region than usually explored by conventional electronic absorption spectroscopy, and the operating selection rules are different, monopole- rather than dipole-allowed transitions being expected.

The actual assignment is still very difficult and controversial, but it is, anyway, certain that (i) satellite structures occur typically if not exclusively



Satellite peaks

higher energy required for elastic emission:

coexcitations ↗ specific (shake up, shake off)
↘ collective (e.g. plasmons)

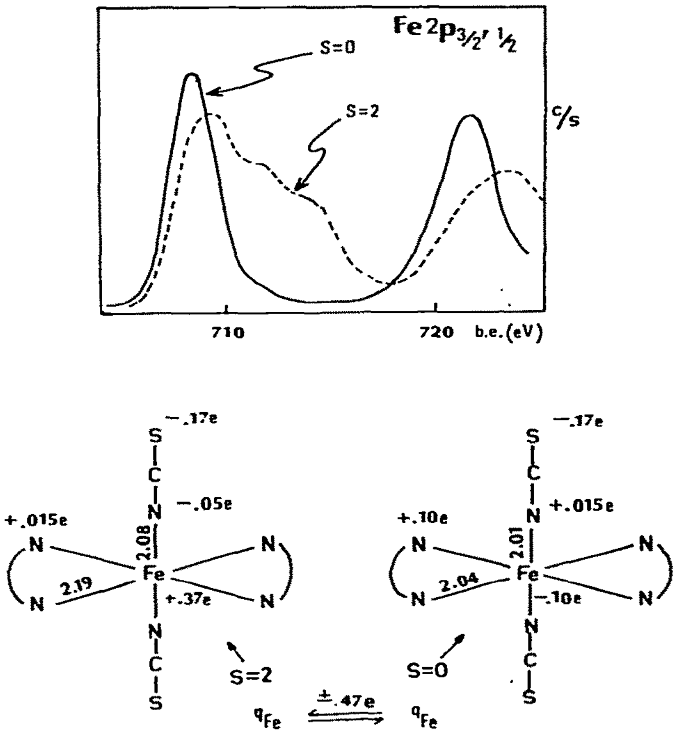
Mechanisms of shakeup processes in metal complexes

(1) *Multiplet splitting*: photohole (e.g. $M2p_j^{-1}$) couples with ^{2s+1}L terms to give $^{2s+1\mp1}(L, L \mp 1)$(e.g. $t_2^3(T_d) \approx {}^4S$ couples to $3p^{-1}$ to give $^{5,3}P$

(2) *Shakeup monopole transitions*: charge transfers L → M of $\gamma_i \to \gamma_i$ type (typically $e_x(\sigma_L) \to e_g^*(d)$ in octahedral complexes.)

(3) *Time-of-flight coupling* of photoelectron to p.f. valence shell. Direct relation to paramagnetism; limiting intensity ratio: $(4S^2-1)/2(4S^2+1)$.

Fig. 6. Possible origin of XPS satellite peaks in coordination compounds.

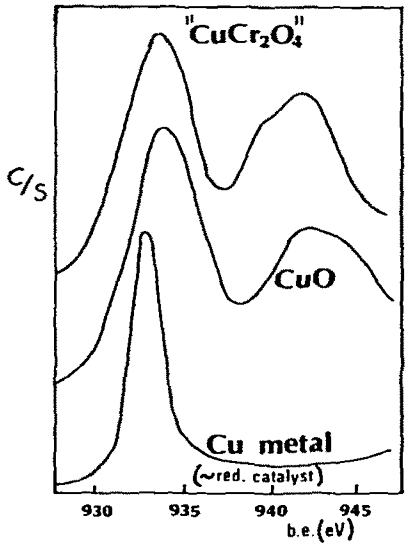


Spin isomers of $Fe^{II}(NCS)_2(ophen)_2$
($S=0\rightleftharpoons2$ at 174 K)

S	$Fe2p_{3/2}$ (ΔE)	$Fe2p_{1/2}$	$\Delta 2p$Fe	N1s(NCS)	N1s(ophen)
0	708.3	721.3	13.0	399.5	398.0
2	709.2(2.5–5.0–7.5)	722.6	13.4	399.0	397.9

Fig. 7. Spin isomers of $Fe^{II}(ophen)_2$ $(NCS)_2$ ($S=0\rightleftharpoons2$ at 174 K) (from ref. 15); note that eight equations of type $(\text{b.e.})_i=(\text{b.e.})_{0,i}+k_iq_i+\Sigma_{j\neq i}q_j/R_{ij}$ can be set up for $i=\text{Fe}2p$, $\text{S}2p$, N1s(NCS) and N1s (ophen) for each spin isomer, plus two electroneutrality conditions, making the system fully determined in the eight unknown atomic charges (depicted in the lower part of the diagram), and in two $(\text{b.e.})_{0,i}$ values.

with spin-unpaired complexes, and their intensity is roughly proportional to the magnitude of the uncompensated moment; (ii) even if the identification of the actual transition involved in the satellite excitation is uncertain, the shape of satellite structures depends critically on coordination environment and can serve as fingerprint characterization of the latter. Coming to an actual example (Fig. 7), a typical application of satellite investigation is in cases of spin isomerism. The author and co-workers investigated recently [15] Fe^{II}(NCS)$_2$(ophen)$_2$, a *trans*-octahedral complex exhibiting reversible $S=0 \rightleftharpoons 2$ transition at 174 K. The transition is nearly isostructural, apart from a small increase in bond distances in the paramagnetic form, and the XPS signals of Fe2p_j ionization are well differentiated in the two spin forms (Fig. 7). As is common in such cases the paramagnetic form has a well developed and intense satellite structure, whereas the diamagnetic form has only the main 2p_j peaks, devoid of satellites. This spin system is also



Solid	Cu 2$p_{3/2}$	Cu2p sat. (ΔE, %int)	Cr 2$p_{3/2}$	Species present (surface)
CuO	934.6	8.6–31	–	Cu(II)
CuCr$_2$O$_4$	934.8	7.3–50	577.3	Cu(II) + Cr(III)
Catalyst as received	935.0	7.5–45	576.9 579.8	Cu(II) + {Cr(III) Cr(VI)}
After pretreatment *	932.5	–	577.3	Cu(0) + Cr(III)
Used catalyst (active)	932.8	–	577.5	Cu(0) + Cr(III)
Reoxidized catalyst	933.2	10.2–20 (8.5)	577.4	Cu(0) Cu(I) + Cr(III) Cu(II)

* H$_2$ 1 atm at 270°C (20')

Cu LMM Auger: Cu(0) 918.3 eV
Cu(I) 916.0 eV
Cu(II)917.3 eV

Fig. 8. Catalysts: surface characteristics of "copper chromite", (from ref. 18a).

interesting because it allows a complete analysis of atomic charges in both isomers, since the eight chemical shifts of Fe2*p*, S2*p*, and N1*s* in NCS^- and in ophen in both spin forms, together with two electroneutrality conditions, forms a fully determined (actually overdetermined) system for the atomic charges on all relevant atoms in the chromophore, or a slightly undetermined system if we include $(\mathrm{b.e.})_0$ values into the set of the unknowns. The most serious limitation to the validity of such a treatment is the large difference in relaxation effects on the N1*s* b.e. for the NCS^- and the ophen nitrogens, but nevertheless a reasonable, even if numerically not very accurate, scheme of atomic charge distribution for the couple of spin isomers (Fig. 7), which represents an attempt at a fairly direct experimental determination of quantitative covalency changes accompanying the spin transition, can be arrived at.

Satellite structures (Fig. 8) play an important role also in surface studies of coordination compounds. The author and co-workers are reinvestigating [16–18] in their laboratory the surface structure of the so-called "copper chromite" catalysts which are actually non-stoichiometric mixtures of approximate composition CuO: $CuCr_2O_4$, ca. 1 : 1. The investigation aims at clarifying the mechanism by which the catalytic activity depends on the oxidation state, coordination environment, and domain segregation of the copper species on the surface, depending also on history, activating pretreatments, and use or aging of the catalysts. Since XPS investigates only the uppermost layers of a solid, including a probing depth of ca. 10–20 Å for Cu2*p* ionization and Al *Kα* excitation, and since in heterogeneous catalysts significant variations are expected between surface and bulk of the investigated material (differently from most molecular solids), the surface coordination chemistry of copper is being investigated here. Here, satellite structures on copper $2p_j$ ionization are expected for Cu(II) but not for Cu(I) or Cu(0) species; the catalytically active component, e.g. in selective hydrogenation of conjugated double bonds, is a Cu(0) species, possibly in a highly dispersed form, behaving differently from massive copper; isomerization of double bonds is instead assisted by higher oxidation states of Cu, which are also present among the surface species (Cu(I) or Cu(II)), the latter being also important both as a precursor and as the reoxidation product of the active species. Now, the possible chemical environments around Cu(II) in this system are at least of three types, and all three can be distinguished by XPS, even if present in the surface layers in subanalytical quantities: Cu(II) oxide, either massive or dispersed on the substrate, characterized by b.e. 934.6 eV and satellites at 8.6 eV ΔE and intensity ratio 0.31 to the main $2p$ peaks; the pseudospinel compound $CuCr_2O_4$, with higher b.e. at 934.8 eV and satellites at 7.3 ΔeV with intensity ratio ~0.50; in other cases, b.e. of Cu(II) in metallates or mixed oxides is shifted to even higher values from simple

Cu(II) oxide (e.g. by 1.0 eV in $CuAl_2O_4$ with respect to CuO according to Ertl et al. [18b]). $Cu(OH)_2$ and hydrated oxide forms have b.e. around 935.4 eV and satellite intensity ratio intermediate between the former cases. Data indicate that the actual surface species is $CuCr_2O_4$ rather than CuO (possibly segregated and contaminated with hydrated species). A similar species is also easily formed by partial air reoxidation of the active catalyst; however, partial presence of surface reoxidation products does not substantially reduce the activity of the catalyst in hydrogenation reactions, that is, they are particularly reactive and easily reduced; reduction to Cu(0) is accompanied by apparent decrease in Cu signal intensity, which indicates possible conglomeration of particles, and the size of metal particles is determining for the catalytic activity. Obviously, the author's results refer to a system containing copper in excess of possible mixed oxide formation, whereas other common catalysts contain more dilute dispersions of copper species and may behave quite differently. The relevant point of general significance here is the possibility offered by XP spectrometry to extend identification and characterization of coordination structures to thin surface layers, which are important, e.g. for catalytic applications, and at the same time not accessible, or not easily accessible, to other conventional techniques. Thus a link

TABLE 2

A comparison between electronic absorption spectroscopy and ultraviolet photoelectron spectroscopy.

Electronic absorption spectroscopy	Ultraviolet photoelectron spectroscopy
Orbital energy differences	Absolute values of orbital energies (Koopmans' approximation)
Transition energies between filled ϕ_f and empty ϕ_e energy levels	Energies of filled levels only
Dipole selection rules $(\Gamma_f \cdot \Gamma_u \cdot \Gamma_e) \sim \Gamma_1$ highly selective	Dipole selection rules between ionized orbital and outgoing free photoelectron wave allows ionization from every filled level
Only *d*-levels (l.f. transitions) and highest filled ligand orbitals (LMCT) are observable	All valence levels (d, σ- and π-ligand) are observed down to $-20 \sim -30$ eV
Measured transition energies require correction for interelectronic repulsion terms to give m.o. energy values	Measured ionization energies require correction for relaxation and correlation effects in M_i^+
Δ, B, C values refer to M(g.st.)	Δ, B, C, values refer to M^+ in frozen (vertical) nuclear configuration

between coordination chemistry and surface sciences is achieved.

In contrast with solid-state XPS where one gets mainly indications on atomic charges, and only indirectly differences of energy levels of valence orbitals (from satellite structures, whenever resolved), the gas-phase UPS version of photoelectron spectroscopy allows almost direct determination of the energy levels of all valence orbitals (energy region ~ −5 to −30 eV), apart from the limitations deriving from Koopmans' approximation and provided the observed levels are sufficiently resolved in energy. The data supplied by UP spectra in the gas phase of volatile coordination compounds is therefore of the same nature as that supplied by electronic absorption spectroscopy with the following differences: (i) energy measurements in UPS are "absolute", or at least referred to the vacuum level, whereas they are relative to one another in EAS; (ii) there are no selection rules forbidding any orbital ionization in UPS, in contrast to the stringent dipole selection rules operating in EAS; (iii) all filled orbital levels (*d* levels, σ or π bonding levels, ligands own and lone pair levels, irrespective of whether high or low in energy) give rise to UPS signals, whereas only *d*-type orbitals of the partly filled shells, and possibly just the highest filled π orbitals of the ligands (in

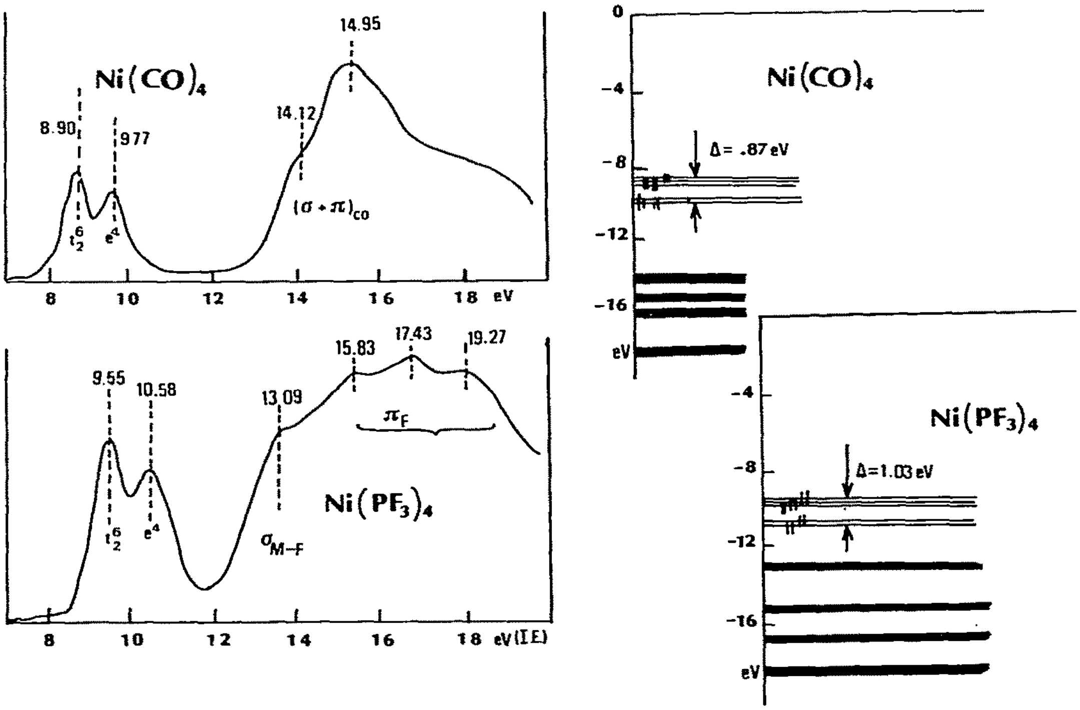


Fig. 9. UV photoelectron spectra (gas-phase) and approximate orbital energy levels of tetrahedral Ni(0) complexes.

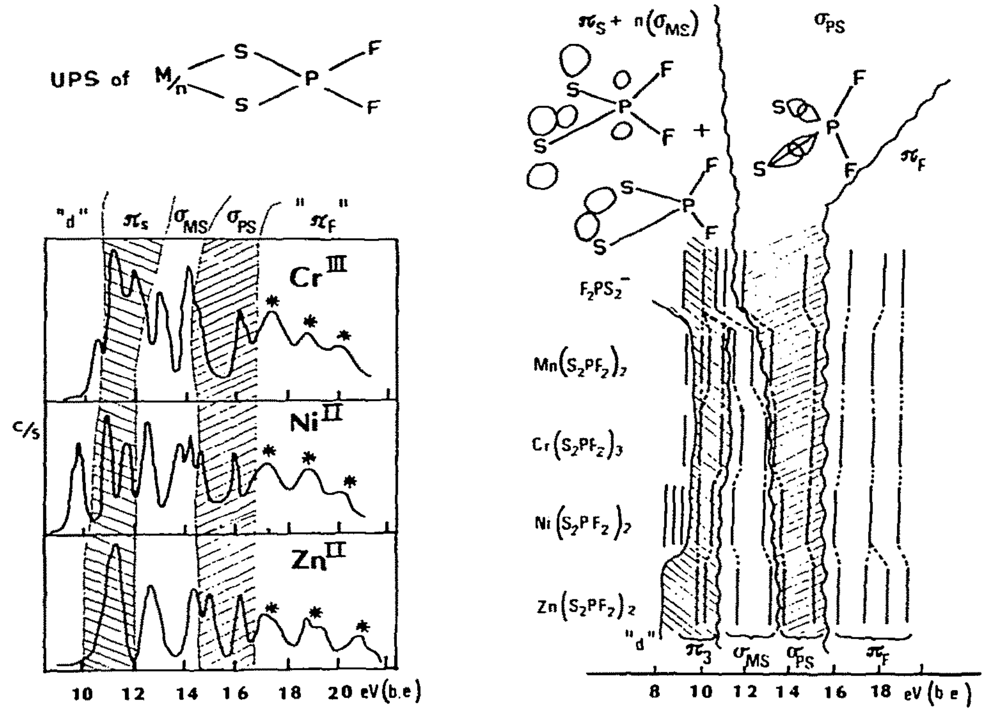
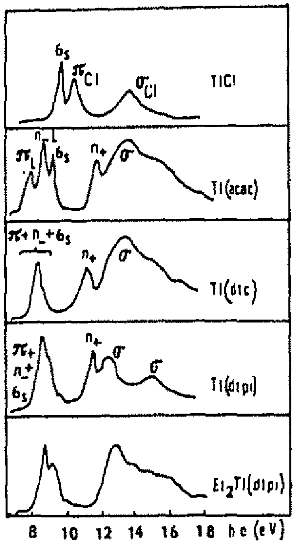


Fig. 10. UV photoelectron spectra and approximate orbital energy levels for volatile transition-metal difluorodithiophosphates $M(S_2PF_2)_n$.

CT bands) are observed in EAS; (iv) UPS sees only filled orbitals, whereas EAS can see energy differences between filled and partly filled or empty (virtual) orbitals; (v) energy data from UP spectroscopy have to be corrected for relaxation and correlation effects, and EA spectroscopic data have to be corrected for interelectronic repulsion terms in order to give molecular energy levels. As a result of all the above limitations, complementarity between the two techniques is seldom realized in practice, at least at the present stage of imperfect theoretical interpretation. The interesting new possibility opened by UP spectroscopy is the observation of the whole spectrum of energy levels of the valence shell; typical is the observation of the energy levels of closed shells of *d* orbitals (e.g. in $Ni(CO)_4$ and $Ni(PF_3)_4$ [19,20]; see Fig. 9), where *d*–*d* EA transitions cannot occur.

Before we consider the interpretation of UP spectra of actual systems, I note two points of general relevance: (i) relaxation effects are often different, and usually larger, for *d* orbitals than for ligand-based (of $2p$ or $3p$ atomic character) orbital ionizations; (ii) even after allowing for the previous effects, it turns out clearly that *d* shell orbitals are generally not the highest



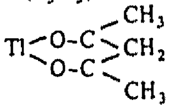
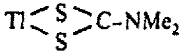
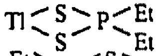
Compound	6s(a1)	L	5d	
			$^2D5/2$	$^2D3/2$
TlCl	9.92	$10.38(\pi_u)-13.89(\sigma_u)$	20.97/21.24/21.41	23.30/23.42
$TlNO_3$	9.9			
$Tl(C_5H_5)$	10.12	....	19.46	21.57
	9.30	8.00/8.81/11.42 π_1 n_- n_+	19.88	22.17
	$\underbrace{8.11/8.24/8.66}_{\pi_1+\pi_2+6s+n_-}$	11.68 n_+	19.32	21.51
	8.30/8.70	11.21	19.65	21.77
	8.39/8.89		19.22	21.52

Fig. 11. UV photoelectron spectra of Tl(I) and related compounds.

occupied, but are often lower in energy than ligand-based σ or π orbitals, or intermixed with them.

Of the many possible examples of UPS characterization of valence shells of coordination compounds, besides the carbonyl-type compounds mentioned before, some relatively simple chelates of sulfur-containing anions are considered first. Thus, dithiophosphates such as $F_2PS_2^-$ [21] (see Fig. 10) are among the simplest chelating agents and form tetrahedral or quadratic 1:2 as well as octahedral 1:3 complexes with transition metals. The UP spectra of such inner complexes in gas phase exhibit bands due to d ionizations, reflecting the ligand field splitting patterns (see the single $^4A_{2g}(t_{2g})^3$ level of Cr(III), the threefold splitting of the d^8 levels of quadratic Ni(II), and so on). Besides, the ionization of ligand-based orbitals corresponds to energy levels derived mainly from sulfur $3p$ orbitals, six in number for each chelate ring and having, as predominant bond character, in order of increasing energy, σ_{P-S} character (twice, with large energy splitting between the symmetric and antisymmetric combination; typical energy values are 13.47 and 14.76 eV in $Ni(S_2PF_2)_2$ [21]), σ_{M-S} character (two sulfur lone pairs in the free ligands, shifted to lower energy and split because of σ bonding to the metals, typically at 11.70 and 13.40 eV in $Zn(S_2PF_2)_2$ [21]), and π character for the two highest sulfur-based orbitals (10.12 and 10.34 eV in $Zn(S_2PF_2)_2$ [21]). A full description of the whole system of energy levels within the valence shell of the system investigated is thus obtained, including the varying position of the d levels with respect to the ligand-based σ and π levels. This exemplifies a general tendency, that of decreasing d orbital energy with increasing atomic number along a transition period, which supports the suggestion of d orbital levels lying higher than any other filled m.o. in complexes of early transition metals (say, up to Cr), but lower or mixed with them for late transition metals, typically Cu or Zn.

The electronic structure of sulfur-containing complexes is exemplified in a simple and representative fashion by Tl(I) chelates such as Tl(dtc) ($dtc^- = (C_2H_5)_2N{-}CSS^-$) or Tl(dtp) ($dtp^- = (C_2H_5O)_2PSS^-$) [22,23] (see Fig. 11). There is in fact, in these monomeric gas-phase species, only one chelate ring, so only one set of two π and two σ(Tl–S) orbitals, besides two σ(S–P)/(S–C) orbitals (now quite close in energy and often not distinguishable: e.g. two band groups at 8.30 and 11.21 eV in $Tl(S_2PEt_2)_2$ [23]). Besides, ionization of a totally symmetric orbital, practically the atomic Tl $6s$ orbital, is observed at relatively low, i.e. 8.66 eV in $Tl(S_2C{-}NEt_2)$ [23] which becomes split into ionization of two levels in the corresponding dialkylthallium species where the s (lone pair) p^2 bond system becomes sp^3 (at 8.44 and 8.74 eV in $Et_2Tl(S_2C{-}NMe_2)$ [23]); last, pseudovalence $5d$ orbitals are ionized at ca. 19.5 and 21.5 eV ($j = 5/2$, $3/2$), and reflect no direct covalent bond effect, but just the trend of atomic charges on thallium.

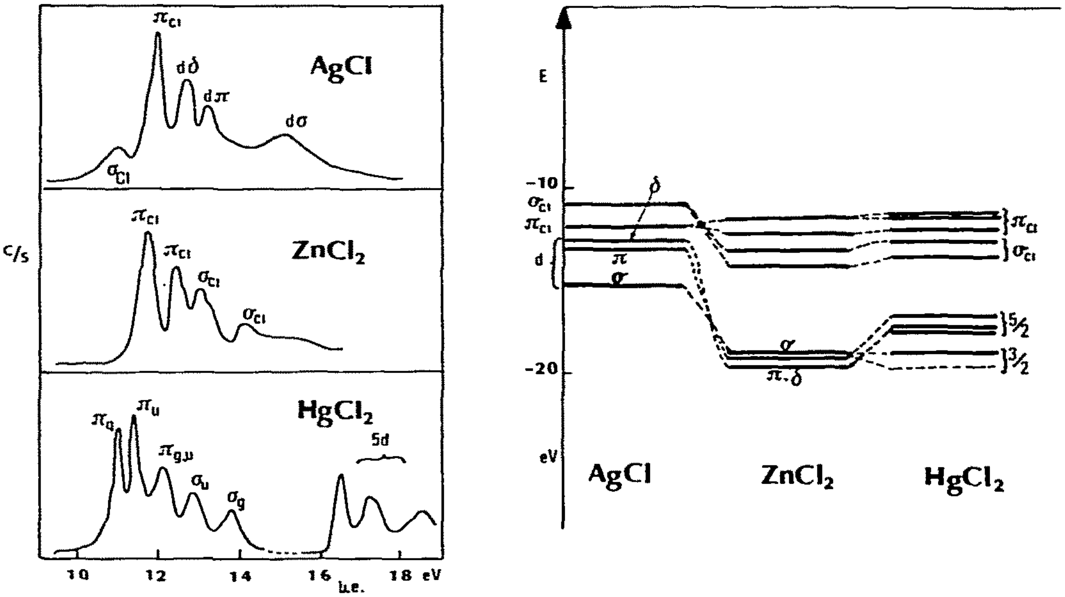


Fig. 12. UV photoelectron spectra of gaseous d^{10} halides, with approximate orbital energy levels (from refs. 24, 25 and 26).

Covalency effects on pseudovalence metal orbitals are more evident, e.g. in silver halides [24], where d orbitals (d^{10}) are fairly low in energy, and exhibit a 2:2:1 splitting (total splitting for the effect of the linear ligand-field ca. 3 eV), i.e. an orbital energy sequence $\delta > \pi > \sigma$, which is the antiligand field sequence, expected for bonding rather than antibonding d orbitals. By contrast, ligand field effects are much smaller in linear MX_2 [25] ($M = Zn$, Cd, Hg) where d levels are much lower in energy, and interact to a smaller extent with halogen np; thus, the overall splitting is only ca. 0.5 eV, with a strong contribution from spin–orbit splitting, and a sequence $d\sigma > (d\pi_{3/2} + d\delta_{5/2}) > (d\pi_{1/2} + d\delta_{3/2})$, or $\sigma > \pi \sim \delta$ as far as ligand field effects alone are concerned. The sequence is now as if the dominant l.f. effect were of electrostatic nature, and not of covalent bonding type.

UP spectroscopy is also widely used in the characterization of the electronic structure of metallocenes and related compounds. Typical investigated molecular structures include, e.g. sandwich-like bis-cyclopentadienyl metal derivatives with two parallel pentatomic rings such as in $Fe(C_5H_5)_2$ [27] or $Mn(C_5Me_5)_2$ [28], or C_{2v} dihalobis-cyclopentadienides such as $Ti(C_5H_5)_2X_2$ [29]; the magnetic behaviour varies from spin-paired such as in ferrocene, to high-spin such as in $Mn(C_5H_5)_2$ at high temperature. Ionizations are observed from metal-centred d-type high-lying orbitals, and pseudo-π orbitals of the cyclopentadienyl rings (and possibly X orbitals of σ and π type); use

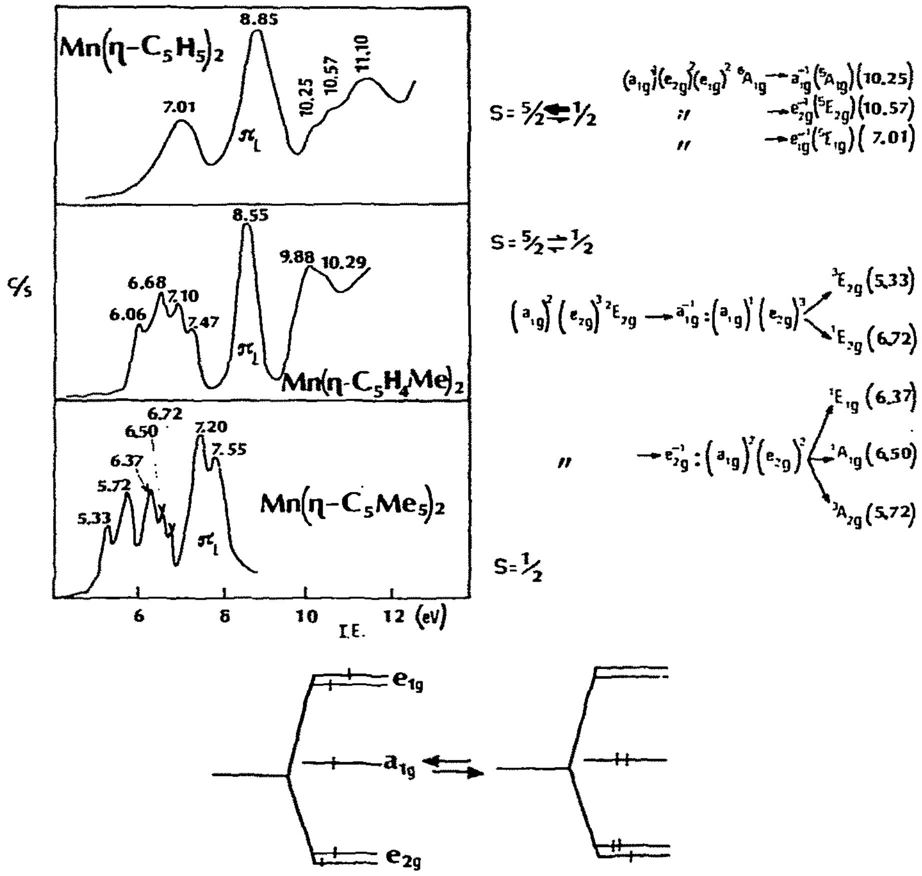


Fig. 13. *d*-Ionization patterns and energy sequence of molecular ions from substituted manganocenes with different spin ground states (from ref. 28).

of alternative sources HeI/HeII is often instrumental in band assignment, thanks to the considerable increase in intensity of *d* ionizations under HeII; this, e.g. confirms the energy level sequence $^2E_{2g}(d) > {}^2A_{1g}(d) > {}^3E_{1u}(\pi) > {}^2E_{1g}(\pi)$ for ferrocene, as first proposed by Orchard et al. [27]. Whilst ferrocene is a typical and relatively simple case of electronic structure determination from UPS for a closed shell system, open shell systems are considerably more complicated. As an example [28] (see Fig. 13), $Mn(\eta\text{-}C_5H_5)_2$ and $Mn(\eta\text{-}C_5H_4Me)_2$ which exhibit spin isomerism in gas phase, whereas $Mn(\eta\text{-}C_5Me_5)_2$ is definitely low-spin both in solution and in gas phase. Accordingly, the experimental p.e. spectra look quite different; Fig. 13 shows how the system of energy levels of excited ions depend on the high- or low-spin configuration of Mn d^5. A ligand field treatment (Fig. 14) can be performed to extract Δ_2, *B* and *C* from the UPS data for the Mn^{III} species;

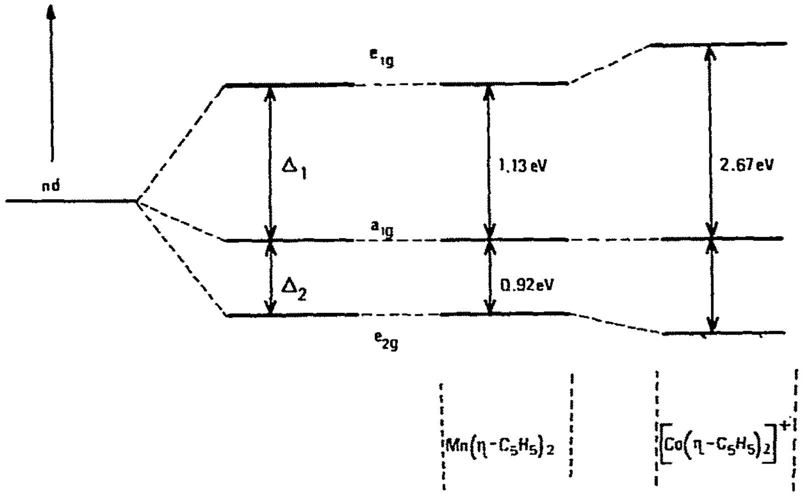


Fig. 14. Crystal field energy levels for metallocenes from UPS data (from ref. 28).

the data collected in Figs. 13 and 14 and taken from ref. 28 show how UPS data can in some case give even quantitatively the same kind of information as usually given by electronic absorption spectroscopic data. The detail and quality of data on the electronic structure is not always so clear-cut and exhaustive as in the case of metallocenes; often only a limited number of data is available, their assignment is not always unequivocal, and, furthermore, uncertainties due to failure of Koopmans' behaviour have to be taken into account. There are however no limitations in principle to availability of data for a full characterization of the electronic structure of either solid or gas phase species from p.e. data, either XPS or UPS. For the present, improvement of instrumental resolution and better understanding of theoretical interpretation can be expected as normal developments of progress in research. Photoelectron spectroscopic techniques are going to play, even more than now, a fundamental role, to open new frontiers in the future investigation of the electronic structures of coordination compounds.

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