PHOTOELECTRON SPECTROSCOPY OF TRANSITION METAL COMPLEXES

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Abstract - The use of ab initio molecular orbital calculations in the understanding of the low energy photoelectron spectra of transition metal complexes is discussed. The role of orbital relaxation and correlation effects are illustrated by considering carbonyl and arene complexes, and complexes having chromium and molybdenum multiple bonds, respectively.

INTRODUCTION

During the past decade molecular photoelectron (p.e.) spectroscopy has been the most successful experimental technique for studying molecular electronic structure. With this tool, the whole manifold of molecular ionization potentials (i.p.) arising from both the core and valence electrons can be measured. For closed-shell molecules such measurements may be directly correlated with the orbital energies obtained from self-consistent field molecular orbital (SCF-MO) calculations, via the much-used Koopmans' theorem. For open shell molecules the situation is rather more complicated but here too Koopmans' theorem is applicable in certain instances. Thus, it is possible, at least in principle, to obtain directly from experiment an orbital energy diagram for the molecule in question.

In this lecture I shall first discuss the general interpretation of p.e. spectra by means of ab-initio methods followed by the application of these methods to some specific examples of transition metal complexes.

THEORETICAL BACKGROUND

By the use of the orbital approximation the closed-shell ground state wavefunction Ψ of a 2n-electron molecule may be written in terms of n doubly occupied spin orbitals ϕ

$$\Psi = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2 - - - -\phi_n\bar{\phi}_n|$$

where ϕ are eigenfunctions of the Hartree-Fock operator $\underline{F}$

$$\underline{F}\phi = \epsilon\phi$$

ϵ being the corresponding eigenvalues (orbital energies)

Within this approximation the energy $E(\Psi_j^+)$ of the corresponding ion (Ψ_j^+) corresponding to the removal of an electron from ϕ_j is given as

$$E(\Psi_j^+) = E(\Psi) -\epsilon_j$$

yielding the ionization energy (measured experimentally in p.e. spectroscopy) as the negative of the corresponding orbital energy, this result being generally referred to as Koopmans' theorem. In the linear combination of atomic orbitals (LCAO) method the one-electron orbitals (ϕ) are expanded in terms of basis functions $\underline{\chi}$ which for large molecular systems are usually taken to be Gaussian type functions (GTF). This is the ab-initio type of calculation I shall be describing where all electrons are treated explicitly and there are no adjustable parameters or experimental data used in the calculations. The only input to the calculation is the molecular geometry, and the basis functions $\underline{\chi}$. The best single determinantal function Ψ, the Hartree-Fock limit, still yields a molecular energy greater than the experimental value, due to the use of the orbital approximation, the energy difference being the correlation error.

The approximations in the use of Koopmans' theorem to interpret i.p.s are
thus twofold

i)   It is assumed that the orbitals, ϕ, of the molecule are appropriate for
     the various states of the ion, and

ii) Differences in correlation error between the molecule and ion are
     neglected.

The first approximation, the neglect of orbital relaxation upon ionization
leads to an overestimation of the i.p., whilst the neglect of correlation
energy (ii), which is generally larger in the unionized than in the ionized
molecule will usually lead to an underestimation of the i.p. Thus, the
effect of these two approximations being in opposite directions accounts for
the frequent success of Koopmans' theorem. However, when i.p.s are quite
close together, Koopmans' theorem may give an incorrect ordering of the
i.p.s, the well-known case being N_2 where this approximation predicts the
ground ionic state to be $^2\Pi_u$ whilst the inclusion of correlation effects is
necessary to predict the correct ionic ground state, $^2\Sigma_g^+$ (1).

As illustration of these features we show in Table 1, calculations of

TABLE 1.   Theoretical and experimental vertical (calculated for
           the ground state H_2O geometry) ionization potentials, in eV.

Orbital Ejected	State of H_2O^+	Koopmans' Theorem	Direct Hole State SCF	Direct Hole State CI	Experiment
$1a_1$	$^2A_1$	559.5	539.1	539.6	539.7
$2a_1$	$^2A_1$	36.77	34.22	32.25	32.19
$1b_2$	$^2B_2$	19.50	17.59	18.73	18.55
$3a_1$	$^2A_1$	15.87	13.32	14.54	14.73
$1b_1$	$^2B_1$	13.86	11.10	12.34	12.61

the i.p.s of H_2O (2). It can be seen that whereas the relaxation energies
associated with the valence electron ionization are near 2eV, much larger
relaxation energies are associated with core electron ionization. Such
relaxation energies are an order of magnitude larger than the chemical
shifts that are commonly observed in ESCA spectra, so that they must be
carefully considered when such chemical shifts are theoretically interpreted.

So far we have discussed p.e. spectra in terms of the independent particle
picture. That is to say, each peak in the p.e. spectrum corresponds to an
orbital occupied in the molecular ground state. However, there are numerous
ionic states which may be described in terms of an orbital model in which
orbitals that are unoccupied in the unionized molecule, are occupied in the
ion. To investigate whether such "shake-up" or satellite states can be
observed experimentally we must look at the expression for the intensity (I)
of photoelectron peaks.

$$I \propto \left| \langle \Psi(2n) | \Sigma e \underline{r}_i | \Psi(2n-1)\psi(1) \rangle \right|^2$$

Here $\Psi(2n)$ and $\Psi(2n-1)$ are the 2n and (2n-1) wavefunctions for the unionized
and ionized molecule respectively, and Ψ is that of the outgoing electron.
Briefly, it follows that if Koopmans' theorem is used, then for I to be
non-zero $\Psi(2n-1)$ can differ from $\Psi(2n)$ by only one spin-orbital; ie. there
is a one-to-one correspondence between the p.e. peaks and the orbitals
occupied in the ground state. However, if relaxation effects are considered
(ie. $\Psi(2n)$ and $\Psi(2n-1)$ are constructed from different one-electron orbitals),
or if correlation effects are included so that $\Psi(2n)$ and/or $\Psi(2n-1)$ are
multi-determinantal functions, then the transition to shake-up states may
have observable intensities. Such shake-up peaks have been observed in a
variety of small molecules (e.g. H_2O, CO, N_2) (3) mainly associated with
core-electron ionization, due to the larger relaxation energies arising from
core than from valence electron ionization. To interpret such satellite
spectra, accurate treatments of both relaxation and correlation effects are

necessary, but using configuration interaction (CI) techniques, this is now possible, the results of such a calculation on CO being shown in Table 2 (4).

TABLE 2.   The C_{1s} hole state and associated satellites in carbon monoxide from the extended root set CI calculation

State No	Total energy (a.u.)	Transition energies (eV)	
		Calculated	Experimental
1	-101.9899^a	0.0	0.0
2	-101.6759	8.54	8.3
3	-101.4125	15.71	14.9
4	-101.3230	18.15	
			17.8
5	-101.3189	18.26	
6			19.1

[a]Carbon 1s hole state. SCF energy = -101.7246 a.u.

Very intense satellite peaks are observed in the carbon and oxygen 1s p.e. spectra of transition metal carbonyls (Fig. 1) (5), which have no
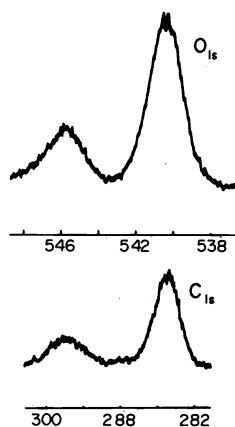

Figure 1. Photoelectron spectrum of $Cr(CO)_6$ (5). The horizontal scale gives the binding energy in eV.

counterpart in the spectra of free CO. Such shake-up peaks clearly thus involve both the metal and ligand orbitals, and can again be interpreted by means of CI calculations (6). However, in this lecture I shall confine myself to a more detailed discussion of the interpretation of valence p.e. spectra of transition metal complexes, although high energy p.e. spectroscopy (ESCA) has also been valuable in investigating the bonding in transition metal complexes.

VALENCE PHOTO-ELECTRON SPECTRA OF TRANSITION METAL COMPLEXES

There are, of course, many instances where the transition metal complexes themselves are too large to be treated by accurate ab-initio methods. However, in these cases a study of the electronic structure of the ligand itself, and simple "complexes" of it, not involving a transition metal, is often useful in understanding the p.e. spectrum of the complex. To illustrate such a situation I shall discuss the p.e. spectra of PF_3, PF_3O and the transition metal complexes $Ni(PF_3)_4$ and $Pt(PF_3)_4$.

For many smaller transition metal complexes ab-initio calculations are possible but here it is frequently found that Koopmans' theorem leads

to an incorrect assignment of the p.e. spectrum. To illustrate this feature I shall describe calculations on transition metal carbonyls and ferrocene. The final part of my discussion of valence p.e. spectra will be concerned with the very topical area of understanding multiple metal-to-metal bonds.

The bonding and photo-electron spectra of $Ni(PF_3)_4$ and $Pt(PF_3)_4$

The ligand properties of phosphines are generally discussed in terms of σ-donation from the highest filled m.o. of the ligand, of predominant phosphorous lone pair character and π-back bonding into the first ligand virtual orbital of mainly phosphorous 3d character. Such a bonding scheme may be investigated by consideration of the p.e. spectra of PF_3 and PF_3O coupled with ab-initio calculations on these molecules (7). In Table 3 we show the measured i.p.s of these molecules, together with their assignments, which are substantiated by the results of ab-initio calculations (Table 4).

TABLE 3. Experimental vertical ionization potentials (eV) for PF_3 and PF_3O

Symmetry	IP		
	PF_3	PF_3O	ΔIP
e	...	13.5	
a_1	12.3	15.7	
a_2	15.8	17.1	1.3
e	16.3	17.7	1.4
e	17.5	18.8	1.3
a_1	18.6	19.5	0.9
e	19.4	20.8	1.4

TABLE 4.   Calculated electronic structure of PF_3 and PF_3O

Atomic populations		PF_3	PF_3O
Phosphorous	3s	1.51	0.81
	3p	1.88	1.82
	3d	0.66	1.32
Atomic charge		+1.02	+1.11
Fluorine	2s	1.91	1.91
	2p	5.43	5.41
Atomic charge		-0.34	-0.32
Oxygen	2s	...	1.88
	2p	...	4.27
Atomic charge		...	-0.15

Valence molecular orbital energies (eV)

PF_3		PF_3O		ΔE
Symmetry	Energy	Symmetry	Energy	
		7e	-14.0	
$8a_1$	-12.6	$10a_1$	-16.3	
$1a_2$	-17.8	$1a_2$	-19.1	-1.3
6e	-18.2	6e	-19.7	-1.5
5e	-19.6	5e	-21.0	-1.4
$7a_1$	-21.0	$9a_1$	-21.9	-0.9
4e	-21.4	4e	-22.8	-1.4
$6a_1$	-24.6	$8a_1$	-25.1	

The first i.p. of PF_3 at 12.3 eV, arising from the phosphorous lone pair
m.o. correlates with the second i.p. of PF_3O at 15.7 eV, which is the P-O
σ-bonding orbital. The first i.p. of PF_3O corresponds to ionization from an
e m.o. which has substantial phosphorous d character and is unfilled in the
free ligand. The $1a_2$-$9a_1$ m.o.s of PF_3O and their counterparts in PF_3
($1a_2$-$7a_1$) are predominantly fluorine 2p character and are shifted to
1-1.5 eV higher i.p. on formation of the P-O bond. Thus, σ-donation results
in a stabilization of the highest σ m.o. in PF_3 on complex formation, there
being a net decrease in electron density on the fluorine atoms resulting
in an increase in the F 2p i.p.s. The delocalization of the lone pair
electrons is also evident in the decrease in P-F bond length from 1.57 to
1.52 Å on complex formation owing to the P-F antibonding character of the
$8a_1$ (phosphorous lone pair) orbital of PF_3.

These considerations allow an interpretation of the p.e. spectra of $Ni(PF_3)_4$
and $Pt(PF_3)_4$ shown in Fig. 2 (8). The first two i.p.s of the complexes
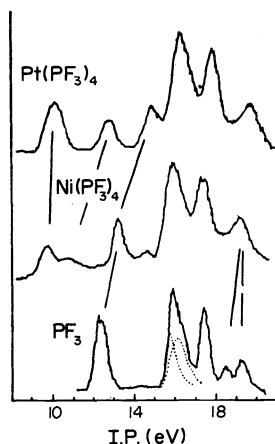
Figure 2. Photoelectron spectrum of PF_3 and its Ni and Pt complexes (8).

correspond to ionization from the orbitals of mainly metal d-character of t_2 and e symmetry. The remaining i.p.s have counterparts in the free ligands, that at 13.2 eV in the nickel and at 14.5 eV in the platinum complex correspond to ionization from orbitals that correlate with the phosphorous lone pair orbital (at 15.7 eV in PF_3O). The lowering of the orbital energy is thus substantially greater in the platinum than in the nickel complex indicating a greater degree of σ-donation in the former. This is in accord with the increased t_2-e splitting in the platinum complex, for the t_2 metal orbital has a σ-antibonding component involving the phosphorous lone pair orbitals, which will be greater the larger the σ-donation. This greater σ-donation in $Pt(PF_3)_4$ than in $Ni(PF_3)_4$ also correlates with the P-F bond lengths, that in the platinum complex (1.546 Å) being less than the value in the nickel complex (1.561 Å). The spectra show very little difference between the i.p.s of the fluorine 2p electrons (at 16-19 eV) on complex formation, suggesting, that unlike the situation in PF_3O, the degree of σ-donation in both molecules is compensated by π-back bonding. This conclusion, coupled with the larger lone pair i.p. in the platinum complex suggests the extent of the delocalization by both mechanisms to be greater in the platinum than in the nickel complex.

Orbital relaxation effects in the interpretation of the P.E. spectra of

transition metal complexes

Deviations from Koopmans' theorem, which occur for large numbers of transition metal complexes can be illustrated by first considering the spectra of simple transition metal carbonys (9). The valence p.e. spectrum of $Ni(CO)_4$ (Fig. 3) shows two low energy peaks at 8.9 and 9.8 eV which can be assigned

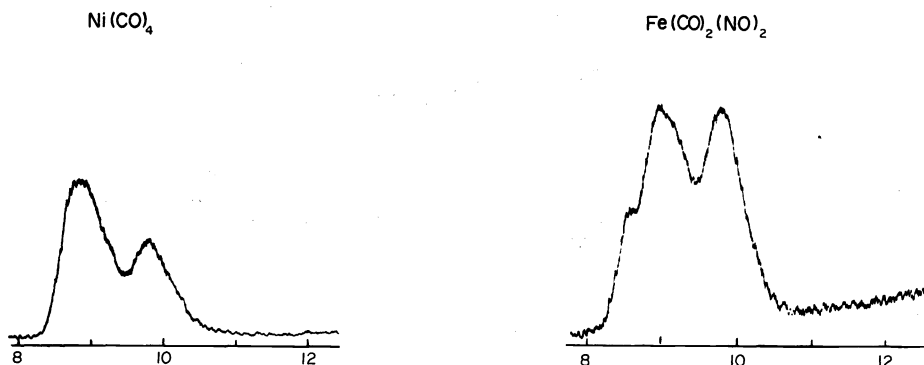**Figure 3.** Photoelectron spectrum of $Ni(CO)_4$ and $Fe(CO)_2(NO)_2$ (15). The horizontal scale gives the ionization energy in eV.

on intensity grounds to the triply degenerate $^2T_2$ and doubly degenerate ^2E

states of Ni(CO)$_4^+$ respectively arising from ionization of the $9t_2$ and 2e orbitals of mainly nickel 3d character. As for most transition metal complexes the large number of electrons (particularly valence electrons) precludes an ab-initio SCF-MO calculation near the Hartree-Fock limit. However, it is possible to perform a calculation with a basis of near minimal or double zeta quality for the valence orbitals yielding i.p.s for the $9t_2$ and 2e orbitals (using Koopmans' theorem) of 10.8 and 12.8 (10), and 11.7 and 13.5 eV (9) respectively depending upon the basis used. Thus, although the absolute values of the i.p.s differ by about 1 eV on change of basis, the calculated t_2-e splitting is close to 2 eV in both calculations, twice the experimental splitting. Direct SCF calculations (9) of the $^2T_2$ and ^2E ionic states (ΔSCF method), thus allowing for orbital relaxation upon ionization yields i.p.s of 7.0 and 7.8 eV for the $9t_2$ and 2e m.o.s, a splitting in essentially exact agreement with the experimental value (0.87 eV). The energy associated with such orbital relaxation is thus large, 4.7 eV for the $9t_2$ m.o and 5.7 eV for the 2e, these orbitals having 74% and 90% metal character respectively. Turning now to the substituted carbonyl, Fe(CO)$_2$(NO)$_2$, the low energy region of the valence p.e. spectrum (Fig. 3) shows three peaks with approximate intensity ratios 1:2:2 covering an energy range of less than 1 eV. In contrast, the first five orbital energies span a range of 7 eV (Table 5). Thus, on the basis of Koopmans' approximation

TABLE 5.   Ab-initio eigenvalues for the ground state of Fe(CO)$_2$(NO)$_2$, computed and experimental ionization potentials (eV)

MO	Energy	Cation State	ΔSCF	Experimental i.p.
6b$_1$(NO)	-8.7	$^2B_1$	7.9	8.97
10a$_1$(NO)	-9.1	$^2A_1$	8.1	
6b$_2$(3d)	-12.6	$^2B_2$	7.5	8.56
9a$_1$(3d)	-15.1	$^2A_1$	9.4	9.74
3a$_2$(3d)	-16.0	$^2A_2$	9.6	

there is no satisfactory interpretation of the p.e. spectrum. However, as in the case of Ni(CO)$_4$ there is a large orbital relaxation associated with ionization from the predominantly metal orbitals, 6b$_2$, 9a$_1$, 3a$_2$, whilst the relaxation energy associated with the primarily ligand orbitals 6b$_1$, 10a$_1$, 5b$_2$ is much smaller (Table 5). This leads to the energy spread of these five ionic states being calculated to be only 2 eV, much less than the Koopmans' theorem value of 7 eV and close to the experimental value of 0.8 eV. The assignment of this first group of bands given by the ΔSCF calculations is as follows. The low energy shoulder at 8.56 eV to the 6b$_2$ m.o. (mainly metal), the peak at 8.97 eV to the 6b$_1$ and 10a$_1$ m.o.s both of mainly ligand (NO) character, and the peak at 9.74 eV to the other two metal orbitals 9a$_1$ and 3a$_2$. In this molecule, there is a thus a change in the ordering of the ionic states from that given by Koopmans' theorem.

A more dramatic failure of Koopmans' theorem arises in the case of ferrocene, where the first four i.p.s. are assigned to e$_{2g}$(3d), a$_{1g}$(3d), e$_{1u}$(π-Cp) and e$_{1g}$(π-Cp) respectively (11) (Fig. 4). Thus on the basis of
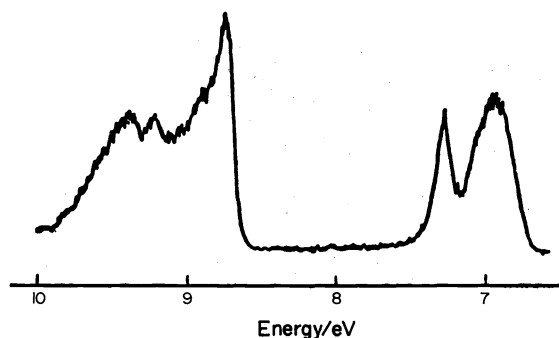
Figure 4. The He(I)UPS of ferrocene (11)

Koopmans' theorem, the experimental p.e. spectrum would lead to an ordering of the m.o.s. of

$$e_{1g}(\pi-Cp) <e_{1u}(\pi-Cp) <a_{1g}(3d) <e_{2g}(3d).$$

However, both small and large basis calculations give the highest occupied m.o. to be the e_{1u} and e_{1g} m.o.s. of predominantly cyclopentadienyl π-character, the metal a_{1g} and e_{2g} m.o.s. being more tightly bound by 3-4 eV (Table 6). This discrepancy arises from the result which has already emerged from our discussion of the spectra of $Ni(CO)_4$ and $Fe(CO)_2(NO)_2$

TABLE 6. Ab-initio eigenvalues for the ground state of ferrocene, computed and experimental ionization potentials

MO	Energy	Cation State	ΔSCF (12)	Experimental i.p. (11)
$e_{2g}(3d)$	14.42	$^2E_{2g}$	5.7	6.9
$a_{1g}(3d)$	16.57	$^2A_{1g}$	7.5	7.2
$e_{1u}(\pi-Cp)$	11.67	$^2E_{1u}$	8.9	8.7
$e_{1g}(\pi-Cp)$	11.89	$^2E_{1g}$	8.8	9.4

namely, that there is considerably more orbital relaxation associated with ionization from the localized metal orbitals than from the delocalized ligand orbitals. When such orbital relaxation is included by means of ΔSCF calculations the ground state of the ferrocenium ion is correctly predicted to be $^2E_{2g}$, with its first excited state to be $^2A_{1g}$, both states arising from ionization of the predominantly metal orbitals (12,13). The third and fourth states of $Fe(Cp)_2^+$ are predicted to arise from ionization from the e_{1u} and e_{1g} π-orbitals of the ligand, in agreement with the experimental assignment of the p.e. spectrum. There is thus some 6-7 eV relaxation energy arising from ionization of the metal m.o.s. compared with only ~0.5 eV from ligand orbital ionization. It is this differential relaxation that causes the inversion of the metal and ligand levels from that given by Koopmans' theorem. In the case of ferrocene, calculations using both a near-minimal (13) and an extended basis (12) yield essentially the same values for the relaxation energy showing that the striking differential relaxation effects that we have discussed are not artefacts of the basis set used in the molecular calculation. It may be noted here that the widely used MS-Xα method, using "muffin tin" potentials incorrectly predicts the first i.p. of ferrocene to be from the $a_{1g}(3d)$ m.o. (14), whilst both minimal and extended basis ab-initio calculations correctly predict the first ionization to arise from the e_{2g} m.o.

The large relaxation energies associated with metal orbital ionization in these transition metal complexes are found to be molecular in origin, for the calculated relaxation energies for 3d ionization from Ni and Fe atoms are 3.4 and 2.5 eV, considerably less than the molecular values (9). In contrast the molecular ligand relaxation energies are the values expected

from the corresponding atom values. Such large values for the relaxation energy associated with metal orbital ionization arise from the ligand to metal change transfer which occurs upon metal orbital ionization. This leads to essentially the same iron atom charge in neutral ferrocene and all its valence ionic states (12). Such charge transfer is shown pictorially by means of density difference maps for ionization from $Co(CO)_3NO$ (9).

The differential orbital relaxation that we have described frequently means that orbital energy diagrams cannot be obtained directly from p.e. spectra of transition metal complexes. Such an effect has been noted by us for a variety of complexes (e.g. $Co(CO)_3NO$ (9), $Cr(C_6H_6)_2$, $Cr(CO)_3$ (C_6H_6) (15), $Fe(CO)_3$ (C_4H_6) (16), and by other groups, particularly Veillard and co-workers ($Ni(C_3H_5)_2$ (17), $CuCl_4^{2-}$ (18)). It would thus appear that for many transition metal complexes an interpretation of their p.e. spectra is possible within the Hartree-Fock approximation as long as orbital relaxation effects are considered explicitly, correlation effects being apparently relatively unimportant, at least as far as the relative energies of ionic states are concerned.

I shall now consider an interesting situation that we have been studying recently where correlation, rather than relaxation effects prevent a straightforward interpretation of p.e. spectra in terms of Koopmans' theorem.

The photo-electron spectra of dimolybdenum and dichromium complexes

We will discuss complexes containing the metal-metal bonded entities Cr_2^{4+} and Mo_2^{4+}, particularly the dimolybdenum(II) and dichromium(II) tetra-μ-carboxylates. In these molecules simple molecular orbital considerations lead to a description of the metal-metal interaction in terms of $\sigma^2\pi^4\sigma^2$ quadruple bond configuration (19), and it is anticipated that p.e. spectroscopy will provide data on the energies of these metal-metal bonding orbitals.

In the case of the dimolybdenum complex $Mo_2(O_2CH)_4$ an ab-initio Hartree-Fock calculation (Table 7) leads to a straightforward interpretation of the p.e.

TABLE 7.   Valence molecular orbitals of $Mo_2(O_2CH)_4$

| Orbital | Energy (a.u.) | Population Analysis (%) | | | | | | | |
| | | Mo | | | O | | C | | H |
		s	p	d	s	p	s	p	s
$2b_{2g}$	-0.3459			84				16	
$5a_{1g}$	-0.4233	13	1	76		8			1
$6e_u$	-0.4247			86	1	11	1		
$1a_{1u}$	-0.4487					100			
$4e_g$	-0.4661					100			
$5e_u$	-0.5043		1	7		69		8	15
$3e_g$	-0.5094			1	1	98			
$3b_{2u}$	-0.5212			2	4	93		1	
$3a_{2u}$	-0.5254	2		3	3	92			
$1b_{1u}$	-0.5305			17		83			
$4b_{1g}$	-0.5746			17	2	58	1	7	14
$4a_{1g}$	-0.5788	5		15	2	56	2	6	14
$1a_{2g}$	-0.6377					60		40	
$4e_u$	-0.6569					60		40	
$2e_g$	-0.6695			2	11	68		19	
$1b_{2g}$	-0.6927			10		58		33	
$2b_{2u}$	-0.7155			13	6	62		18	
$2a_{2u}$	-0.7198	6		5	6	65		18	
$3b_{1g}$	-0.7326			1	16	52	1	27	5
$3e_u$	-0.7400			6	18	53	1	20	3
$3a_{1g}$	-0.7412	2		1	14	51		27	5
$2e_u$	-0.8727				12	18	28	22	19
$2b_{1g}$	-0.8897			5	11	22	28	17	16
$2a_{1g}$	-0.8958	1		2	11	24	29	17	16
$1e_g$	-1.3422		1		78	2		19	
$1b_{2u}$	-1.3500			2	78	2		18	
$1a_{2u}$	-1.3536	1		1	78	2		18	
$1e_u$	-1.4714		1		61	8	25	5	1
$1b_{1g}$	-1.4773			1	62	8	24	4	1
$1a_{1g}$	-1.4815	-1			62	8	24	5	1

spectrum of this molecule shown in Fig. 5.   Thus band A is assigned to the
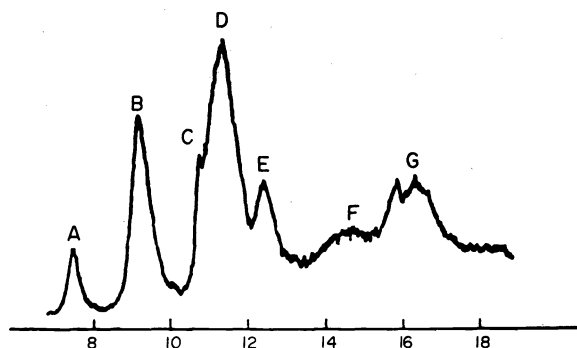
Figure 5. Photoelectron spectrum of $Mo_2(O_2CH)_4$ (22).

metal-metal bonding δ-orbital, band B to the accidentally degenerate π and σ metal bonding orbitals, band E to the Mo-O bonding orbitals and the remaining peaks to ligand orbitals (20). As was also noted in the case of ferrocene, such an interpretation given by ab-initio calculations is at variance with that given by a MS-Xα calculation which predicts the metal-metal σ-orbital to give rise to band E (21). In Fig. 6 we show the p.e. spectrum of $Cr_2(O_2CMe)_4$ and $Mo_2(O_2CMe)_4$ (22), together with that of the acetate anion for comparison with that of the complexed ligand. Here we see that the major difference between the spectra of the two complexes is
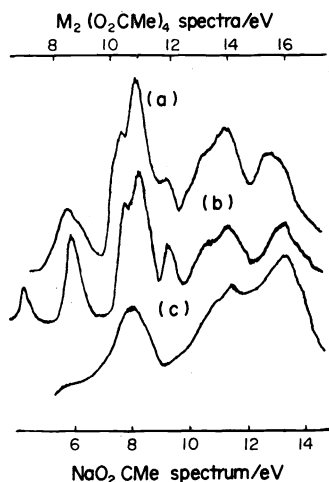

Figure 6. Photoelectron spectrum of (a) $Cr_2(O_2CMe)_4$, (b) $Mo_2(O_2CMe)_4$ (22), and (c) NaO_2CMe

that in the case of the chromium complex a broad band occurs in the region of the metal ionizations compared with the two distinct bands in the case of the molybdenum complex. Theoretically, the interpretation of the metal ionizations in the chromium complex is not as straightforward as for those of the molybdenum complex (23,24). At the single determinantal level, where correlation effects are ignored, the ground state of the molecule is predicted to be the no-bond $\sigma^2\sigma^{*2}\sigma^2\sigma^{*2}$ configuration. However, when correlation effects are allowed for in the quadruple bond configuration, by allowing to mix with it, configurations generated from it, by excitations of the type $\sigma^2\rightarrow\sigma^{*2}$, $\pi^2\rightarrow\pi^{*2}$ and $\delta^2\rightarrow\delta^{*2}$ (as well as other configurations), then the ground state is predicted to be such a multideterminantal wavefunction. However, the quadruple bond configuration contributes only 16% to such a wavefunction so that it is quite inappropriate to use Koopmans' theorem to interpret the observed p.e. spectrum (Table 8). When the intra-pair correlation effects

TABLE 8.   Summary of APSG calculations on $Mo_2(O_2CH)_4$ and $Cr_2(O_2CH)_4$

Dominant Configurations in APSG Wave functions

Configuration	Coefficient and percentage in Wave functions	
	$Mo_2(O_2CH)_4$	$Cr_2(O_2CH)_4$
$\sigma^2\pi^4\delta^2$	0.817 (67%)	0.398 (16%)
$\sigma^{*2}\pi^4\delta^2$	-0.185 (3%)	-0.223 (5%)
$\sigma^2\pi^2\pi^{*2}\delta^2$	-0.235 (6%)	-0.318 (10%)
$\sigma^2\pi^4\delta^{*2}$	-0.382 (15%)	-0.354 (13%)
$\sigma^{*2}\pi^{*2}\pi^2\delta^2$	0.053	0.178 (3%)
$\sigma^{*2}\pi^4\delta^{*2}$	0.087 (1%)	0.199 (4%)
$\sigma^2\pi^{*4}\delta^2$	0.067	0.253 (6%)
$\sigma^2\pi^2\pi^{*2}\delta^{*2}$	0.110 (1%)	0.283 (8%)
$\sigma^{*2}\pi^{*2}\pi^2\delta^{*2}$	-0.025	-0.159 (3%)
$\sigma^2\pi^{*4}\delta^{*2}$	-0.032	-0.226 (5%)
$\sigma^{*2}\pi^{*4}\delta^2$	-0.015	-0.142 (2%)
$\sigma^{*2}\pi^{*4}\delta^{*4}$	0.007	0.127 (2%)

Pair Correlation Energies (a.u.)

	σ_g	π_u	δ_g
$Mo_2(O_2CH)_4$	0.030	0.040	0.059
$Cr_2(O_2CH)_4$	0.147	0.226	0.261

are included by means of the anti-symmetric product of strongly orthogonal geminals (APSG) method, the i.p.s given by Koopmans' theorem may be corrected by means of estimated pair correlation energies leading to the prediction that the three i.p.s due to the δ, π and σ metal-metal bonding orbitals are close together and lie under the first broad band in the p.e. spectrum (25). Such a prediction is in line with considerations of the shape of this band which lead to the conclusion that it contains at least three ionizations (22). As in the case of $Mo_2(O_2CH)_4$ this assignment is at variance with the MS-Xα calculations which assign only the δ and π ionizations to this band and place the σ ionization to higher energy (26). This latter assignment is also given by the application of Koopmans' theorem to the quadruple bond configuration. However, such an interpretation is erroneous due to neglect of correlation effects.

Correlation effects are expected to be especially important in the dichromium complexes, which in general have rather longer metal-metal bonds than the dimolybdenum complexes (the metal-metal bond length in $Cr_2(O_2CMe)_4$ is 2.29 Å compared to 2.09 Å in $Mo_2(O_2CMe)_4$) due to the inability of the single determinantal molecular orbital method to correctly describe dissociation. This drawback is severe for multiply bonded situations such as the metal-metal quadruple bond, especially at longer bond lengths.

In this brief review we have seen that the interpretation of the valence p.e. spectra of transition metal complexes is rather more complicated than is usually the case for molecules containing only first and second row atoms. There are thus situations where relaxation and correlation effects are of crucial importance. However, these effects can be rigorously, and as I hope I have shown, successfully treated within the framework of all electron ab-initio calculations.

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