Photoelectron Spectra of Transition-metal Hexafluoroacetylacetonates and the Supposed Breakdown of Koopmans' Theorem in these Compounds

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Summary The initial parts of the photoelectron spectra of the trishexafluoroacetylacetone complexes of chromium, iron, and cobalt are presented; from the spectra there is no evidence for any inversion of orbital sequence upon ionization, but the chromium and iron complexes show an effect which may be ascribed to their open-shell nature.

THE theorem which is due to Koopmans[1] equates the calculated binding energy of an occupied SCF molecular orbital with the negative of the corresponding vertical ionization potential (I.P) of the molecule. For valence orbitals the terms ignored by the theorem are fairly small, and cancel to some extent,[2] therefore, in interpreting the results of photoelectron spectroscopy it is usual to assume that the sequence of orbital energies is the same as the sequence of I.P. In one case, the ionization of molecular nitrogen, it has been demonstrated[2] that there is an inversion of the highest lying $3\sigma_g, 1\pi_u$ levels upon ionization, *i.e.* a breakdown of Koopmans' Theorem. This communication examines another case in which breakdown has been claimed:[3,4] the ionization of the transition-metal complexes of the type $M(aca)_3$, $M(tfa)_3$, and $M(hfa)_3$ [(aca), (tfa), and (hfa) represent the enolate anions of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone]. The basis of this claim is that I.P. for the complexes as determined on a mass spectrometer do not show the variations expected from magnetic and spectral data, but that the increase in the I.P. of the free enol ligands and of the aluminium complexes upon fluorination is paralleled by an increase in I.P. of the corresponding transition-metal complexes. It was suggested in this work[3,4] that upon ionization the metal *d*-orbital energies fall below the ligand levels.

It has been shown elsewhere[5] that the basis of this claim is incorrect since the electron-impact measurements fail to detect the first I.P., at least for the transition-metal complexes of (tfa) and (hfa). Figure 1 shows the low I.P. region of the spectra of Cr(hfa)$_3$, Fe(hfa)$_3$, and Co(hfa)$_3$,† where it is clear that the first I.P. does depend on the metal. The *d*-type orbital configurations of these complexes[3] are Cr,t_{2g}^3; Fe,$t_{2g}^3e_g^2$; Co,t_{2g}^6, and in agreement with this the iron complex has the lowest I.P., therefore it is considered that the first ionizations are from the *d*-type orbitals. As predicted, the intensity of the first ionization in Co(hfa)$_3$ is approximately twice that in Cr(hfa)$_3$, referred to the intensity of the remainder of the spectrum. For some reason not presently clear the Fe(hfa)$_3$ complex has a very low intensity for this *d*-type ionization, and the same low intensity is observed in the spectrum of Fe(tfa)$_3$. Figure 1 shows that there is evidence for the start of a second ionization in Fe(hfa)$_3$, also of low intensity, before the first high-intensity band. This feature occurs at about 1·5 ev to higher I.P. than the first ionization. Since the spectroscopic difference Δ of the e_g and t_{2g} orbital energies in the complex is 1·7 ev, this second I.P. is assigned to the t_{2g} orbitals.‡ The vertical I.P. measured from the bands shown on Figure 1 are Cr(hfa)$_3$, 9·54, 10·12 ev; Fe(hfa)$_3$, 8·28, 10·14 ev Co(hfa)$_3$ 9·56, 9·95, 10·62 ev, with standard deviations of 0·03 ev or better.

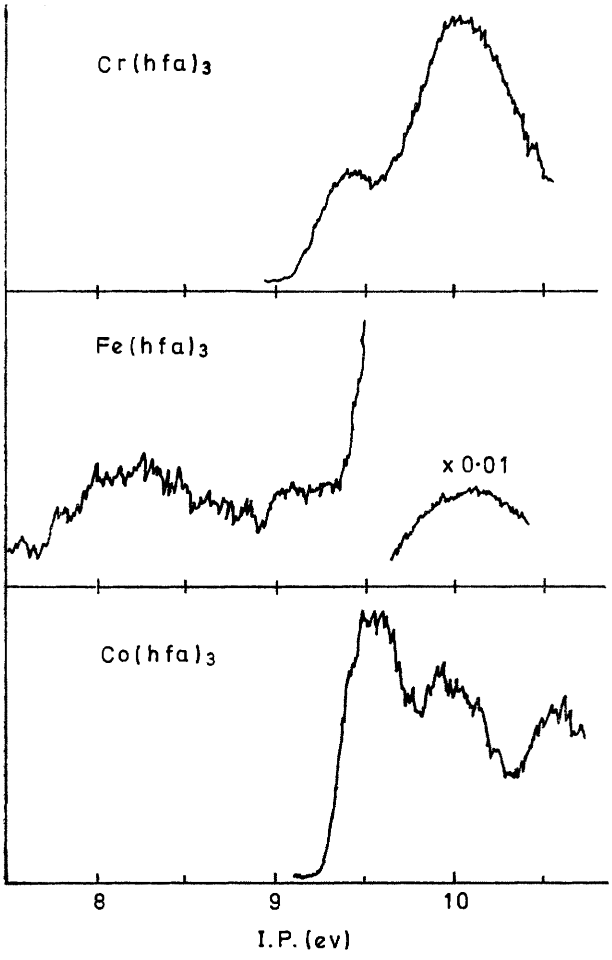

FIGURE 1. *The first bands in the photoelectron spectra of the trishexafluoroacetylacetone complexes of chromium*(III), *iron*(III), *and cobalt*(III). *The spectrum of* Fe(hfa)$_3$ *is shown on two different count rate scales.*

The energy levels measured for the three complexes are shown in Figure 2, where the positions of the e_g orbitals for the Cr and Co complexes have been calculated from the t_{2g} I.P. and the spectroscopic Δ values, while the t_{2g} I.P. for the Fe complex is calculated from Δ and the e_g I.P. The orbital lying below these levels is almost certainly mainly localised on the ligands. The second I.P. of the Cr and Co complexes, and the third I.P. of the Fe complex, are almost the same as the first I.P. of the Al complex, 10·21 ev, and this I.P. probably corresponds to the triply degenerate π_3 set of orbitals. In the Co complex these π_3 orbitals appear

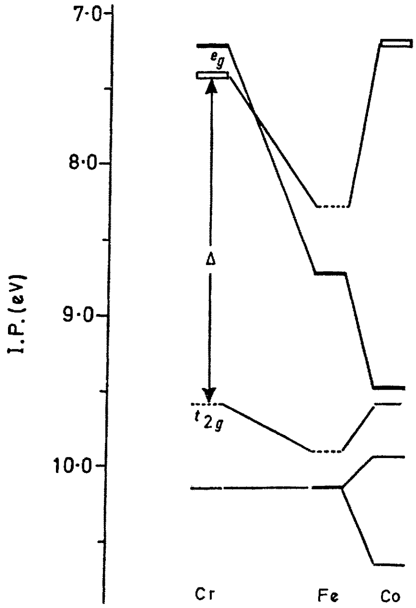

FIGURE 2. *Energy levels in the trishexafluoroacetylacetone complexes of chromium*(III), *iron*(III), *and cobalt*(III) *as deduced from ionization potentials and spectra. Open boxes* (☐) *represent empty* d*-type orbitals, dotted lines* (----) *are partially filled orbitals, and lines* (——) *are completely filled orbitals. The heavy lines are VOIP for configuration* $d^{n-1}s$.

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† SAFETY NOTE: Co(hfa)$_3$ was prepared by the method of Veening *et al.* (ref. 6) and on one occasion a violent explosion occurred in this reaction.

‡ Values of Δ are taken from the aquo-complexes, *cf.* refs. 7—9. The *d*-type orbitals are described in O_h notation, since there is no evidence of trigonal splitting in these bands; from the optical spectra this splitting is expected (ref. 8) to be about 0·1 ev, much less than the ionization band half-widths.

to split giving two ionization bands; this may be partly because of the smaller Co–O distance[10] and the consequently increased ligand–ligand interaction, compared to the Fe and Cr complexes. However, no splitting is observed in the Al complex and not all the details of the higher I.P. region are yet understood.

Also shown on Figure 2 are averaged I.P. (VOIP)[11] for the free metal atom *d*-orbitals in the configuration of $d^{n-1}s$, which give an indication of the *d*-orbital energy of the metal. From chromium to iron both t_{2g} and e_g orbitals fall in energy, though slightly less rapidly than the free *d*-orbitals, but there is an abrupt reversal between iron and cobalt. However, Koopmans' Theorem is not rigorously applicable to open-shell molecules,[2] and since the Co complex has only closed shells while the other two have open shells, I suggest that this discontinuity indicates the extent of departure from the Theorem by the open-shell molecules. From extrapolation of the open-shell energies on Figure 2 to the cobalt compound, it appears that the *d*-orbital energies indicated by the I.P. for the iron and chromium compounds are about 1 ev more negative than the true energies. If this is so, then these *d*-orbital energies in the open-shell molecules are well removed from the π_3 orbital energies, in agreement with the lack of π_3–d charge-transfer spectra.[12]

From this discussion it seems probable that in these three complexes there is no inversion of sequence of orbitals upon ionization. However, Koopmans' Theorem does not apply to the open-shell molecules, in that the energies of the partially-filled orbitals are not correctly represented by the ionization potentials.

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