The Helium-(I) Photoelectron Spectrum of Tris(hexafluoroacetylacetonato)iron(III)

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Summary An alternative explanation is suggested for the weak low-ionisation-energy band in the He(I) photoelectron spectrum of $Fe(hfa)_3$.

IN a recent communication[1] Lloyd has reported briefly on the helium-(I) photoelectron spectra of the transition-metal complexes $M(hfa)_3$ and $M(tfa)_3$, where M = Fe, Co, and Cr and where hfa and tfa are the enolate anions derived from hexafluoro- and trifluoro-acetylacetone, respectively. We have also studied the vapour-phase P.E. spectra of molecules of this type but in certain crucial respects reach different conclusions from Lloyd.

We content ourselves here with two observations, the first an experimental one concerning the P.E. spectrum of $Fe(hfa)_3$. The spectrum obtained by Lloyd,[1] with its first strong band (A) at 10·14 ev, shows a very weak low-ionisation-energy (I.E.) band (B) around 8·28 ev: the relative intensities of these P.E. bands are approximately 100 : 1. For comparison the helium-(I) 21.21 ev P.E. spectrum measured on a spectrometer† recently constructed in this laboratory[2] is reproduced in Figure 1. An exceedingly weak P.E. band is indeed detectable at low I.E. (between 8·2 and 8·5 ev), its integrated intensity being about one-hundredth of that observed at higher I.E. (10·13 ev). However, we do not agree with Lloyd[1] that this weak band relates to the 21·21 ev ionisation of the e_g electrons of $Fe(hfa)_3$. We believe the band to be merely a 'shadow,' excited by an additional line at 23·09 ev‡ in the helium source,§ of the prominent P.E. band A. This 23·09 ev radiation would be expected to produce a spurious band some 1·88 ev to the low-I.E. side of band A—where, within experimental error, band B is in fact observed. Thus we contend that the vertical ionisation potential of $Fe(hfa)_3$ is 10·13 ± 0·03 ev, which compares reasonably well with the value 10·34 ± 0·01 ev determined by electron-impact spectroscopy.[6]

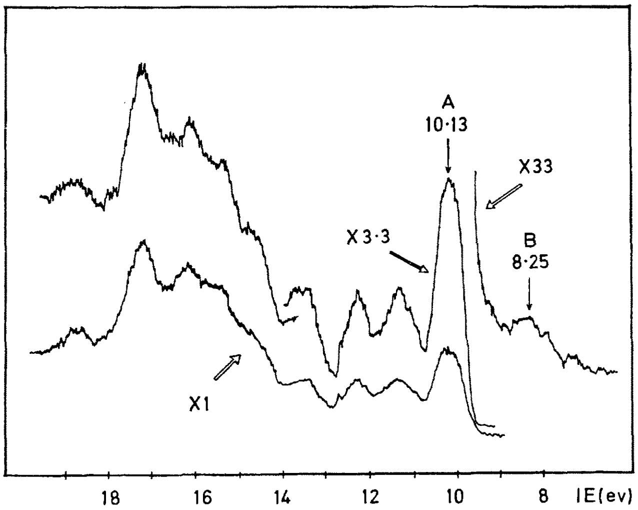

FIGURE 1. *The* He(I) *photoelectron spectrum of* $Fe(hfa)_3$.

To reinforce our conclusions we show in Figure 2 the P.E. spectrum of xenon excited by the same source. The production of secondary P.E. bands, B′ and B″, 1·88 ev to lower I.E. than the 21·21 ev bands, A′ and A″, is clearly discernible. The proportion of 23·09 ev radiation in our helium source, as estimated from xenon P.E. spectra, depends on the actual operating conditions: we have found between 0·7% and 1·1% at different times.

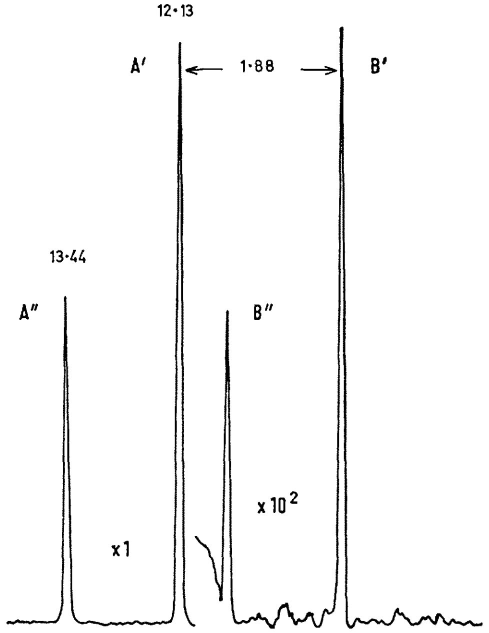

FIGURE 2. *The* He(I) *photoelectron spectrum of xenon showing the production of additional low-I.E. bands due to the* 23·09 ev *line.*

Our second comment concerns the arguments used by Lloyd in the interpretation of his P.E. spectra. It is incorrect to suppose that the difference in I.E. for the t_{2g} and e_g electrons can be identified with the spectroscopically determined ligand-field parameter, Δ. The latter quantity

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† This instrument (ref. 2) is rather similar as regards general design principles to that described by Branton *et al.* (ref. 3), except that a 127° sector electrostatic analyser is employed. The method of scanning (refs. 3, 4) leads to essentially constant resolution and sensitivity over the I.E. range 0—20 ev.

‡ The presence of this 23·09 ev radiation, to an extent of some 2%, has been reported in a He(I) microwave discharge source (ref. 3). It arises from the He(I) emission $1s3p\,^1P \rightarrow 1s^2\,^1S$, the predominant He(I) line at 21·21 ev being due to the corresponding $2p$ emission process (ref. 5).

§ Both our machine and the Perkin-Elmer spectrometer used by Lloyd employ helium discharge lamps powered by a high-voltage D.C. supply.

relates to the energy difference between t_{2g} and e_g electrons in a molecular field from which the interelectronic repulsions within and between the t_{2g} and e_g subshells are omitted: on the other hand, the t_{2g} and e_g ionisation energies depend critically upon the precise nature of these interelectronic terms. In a rigorous open-shell SCF–MO theory it is even possible that the $e_g - t_{2g}$ orbital energy difference may be of opposite sign to the observed $t_{2g} - e_g$ I.E. separation. Equally, it is in principle conceivable that the ionisation of essentially ligand electrons may occur at lower I.E. than the metal *d*-electrons, without this necessarily violating one's intuitive notion of the sequence of *average of configuration*[7] orbital energies.

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