Photoelectron Spectroscopy of f-Element Coordination Compounds.
2. He-II Spectra of β-Diketonate Complexes of Uranium(IV), Thorium(IV), Zirconium(IV) and Dioxouranium(VI)

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Fig. 1. He-II excited PE spectra of a) $Zr(acac)_4$, b) $Th(acac)_4$ and c) $U(acac)_4$.

This study presentes the He-II excited photoelectron spectra (PE) of a series of transition-metal and actinide complexes with an identical ligand array $M(acac)_4$ (M = Zr, Th, U) and the closely related $UO_2(acac)_2$**. This paper is complementary to a previous paper where the He-I spectra were presented [1]. The motivation for this further investigation is that it is becoming [2, 3] apparent that even though 5f covalency may be important in bonding, the metal 6d orbitals may play an equal or even more important role, thus promoting a chemistry of actinide elements not unlike that of the early transition elements. Within this context, only can a comparison of the He-I and He-II spectra provide unambiguous evidence about the involvement of specific metal electrons in bonding on varying relevant aspects of the metal electronic configuration from Zr(IV) (d^0) to Th(IV) ($5f^0$) and U(IV) ($5f^2$).

Previous studies have, in fact, shown how spectral intensities of ionizations associated with various atomic orbitals (or molecular orbitals composed thereof) depend on photon energy. When C_{2p} or O_{2p} are taken as references, cross-sections on going from He-I to He-II radiation of metal d electrons become greater. The enhancement has a maximum with the 4d subshells and falls-off with increasing atomic number [3, 4]. Compared to C_{2p}, the metal 5f subshells display a very remarkable increase at higher photon energies [3]. In reality, as far as the actinide complexes of the β-diketonate anion ligand

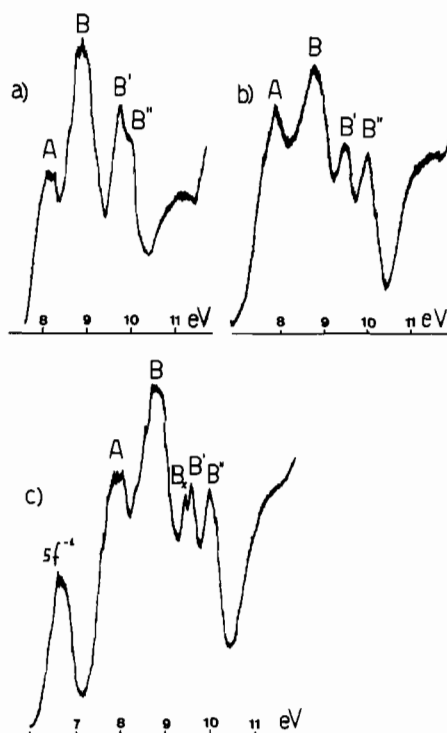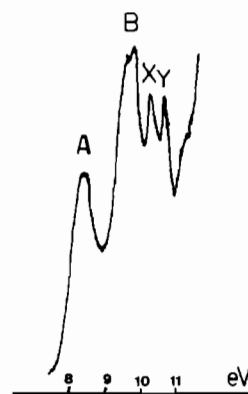Fig. 2. He-II excited PE spectrum of $UO_2(acac)_2$.

are concerned, variations relative to O_{2p} are of major importance, most of the relevant ligand valence orbitals being O_{2p} based. Suitable experimental data have not been reported so far. However, the evident increase of the relative intensity of the onset band ($5f^2$ ionization [1]) in the spectrum of $U(acac)_4$ (Fig. 1, Table I) is evidence of such behaviour. The spectra are presented in Figs. 1, 2, while relevant spectral data are collected in Table I. Sample prepara-

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**acac = acetylacetonate anion.

TABLE I. Ionization Energies (eV) and Relative Band Intensities (in Brackets[a]) of tetrakis(β-diketonate) Complexes and UO_2-$(acac)_2$.

Band System	$Zr(acac)_4$	$Th(acac)_4$	$U(acac)_4$	Assignment[c]	Band System	$UO_2(acac)_2$	Assignment[c]
			6.65 (1; 6)	metal $5f^{-1}$			
A	7.95 (1; 1)	7.85 (1; 1.2)	7.75 (12; 12)	$b_1 + b_3$ (π_3)	A	8.40 (1; 1.2)	$b_{1u} + b_{3g}$ (π_3)
B	8.95 (1.3; 2)	8.75 (1.7; 1.4)	8.70 (19; 17) ⎱ $a + b_2$ (π_3),	B	9.65 (2.3; 2)	$b_{1g} + b_{3u}$ (n_),
B_x		9.40[b] ⎱	9.25 ⎱ (12; 11) ⎰ $a + b_1$ (n_)				$b_{2g} + b_{3g}$ (π_g)
B'	9.75 ⎱ (1; 1.5)	9.60 ⎰ (1; 1.1)	9.45 ⎰		X	10.30 (1; 1.6)	b_{1u} (σ_u)
B''	10.10 ⎰	10.05 (0.9; 1)	10.05 (11; 11) ⎰ $b_2 + b_3$ (n_)		Y	10.80 (1.2; 1.6)	$b_{2u} + b_{3u}$ (π_u)

[a]First and second numbers refer respectively to He-I and He-II spectra. Intensity ratio values refer to peak heights. The almost constant values of band half-widths on passing from He-I to He-II spectra render these parameters reliable.   [b]This band is not resolved in the He-II spectrum.   [c]See ref. 1.

tion and purification methods, as well as details of the experimental equipment used to run the He-II spectra, are described elsewhere [1].

Tetrakis Complexes

Table I presents the assignments which have been proposed already [1] for PE bands appearing in the low ionization energy (IE) region (<11.0 eV) (Fig. 1). The notation adopted in this paper for uppermost ligand based MOs follows that proposed by Evans [5]. In particular n_+, n_- and π_3 indicate respectively the in- and out-of-phase combinations of oxygen lone pairs located in the ligand plane and the top-most out-of-plane orbital. The major implications of the proposed assignments are i) the IE splitting of symmetry combinations of π_3 orbitals, mainly because of interligand repulsion (bands A and B in the figure), and ii) specific metal-ligand interaction which results in the energy differentiation (depending upon the particular metal atom in each complex) of n_- combinations (bands B, B_x, B', B'').

In the spectrum of $Zr(acac)_4$ the bands B, B' and B'' increase in intensity* with respect to band A (Table I), thus indicating some 4d admixture into the corresponding MOs. This observation lends support to the proposed involvement [1] of metal $4d_{xz}$ and $4d_{yz}$ into the n_- combinations b_2 and b_3 (in D_2 symmetry) responsible for bands B' and B''. By contrast, there remain doubts as to the origin of the intensity change in band B since it included ionizations of both n_- and π_3 combinations (Table I).

Although some admixture of appropriate 4d orbitals with π_3 combinations cannot be excluded,

simple overlap arguments suggest that the interactions between metal 4d orbitals of a and b_1 symmetry with the corresponding n_- combinations are the most plausible origin of the observed intensity trend.

Turning to the spectra of actinide complexes, a different pattern of intensity changes is observed. The band B decreases relative to A*, the effect being more pronounced in the case of $Th(acac)_4$ (Table I) while the bands B' (B' + B_x in the case of $U(acac)_4$) and B'' do not show remarkable variations. We have already pointed out that upon increasing the energy of ionizing photons, orbitals having metal 6d contribution will give rise to less intense PE bands whereas those having 5f admixture will be related to stronger PE bands. Therefore the trend of intensities observed for band B in the actinide complexes can be explained within a bonding model similar to that adopted for the analogous d transition element complex $Zr(acac)_4$. This means the admixture of metal 6d orbitals into n_- combinations a and b_1. As far as the remaining n_- combinations b_2 and b_3 are concerned, there are indications of some additional involvement of metal 5f electrons beside that of 6d. The observation that the bands B' and B'', in contrast to $Zr(acac)_4$, do not change their intensity (Table I) on passing to He-II spectra becomes understandable if both 6d and 5f orbitals, whose effects upon He-II intensities tend to cancel each other, are admixed into the n_- combinations b_2 and b_3. Obviously, the possible alternative of no involvement of metal electrons** into these MOs

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*The band A represents a convenient reference since it is related to non-bonding orbitals and, hence, not admixed with metal orbitals (see Ref. 1).

**If any admixture with metal orbitals is excluded, the orbitals which are symmetry combinations either of π_3 or of n_- ligand orbitals will give PE bands having comparable intensities both in He-I and He-II spectra. Such conclusions can be arrived at by comparing He-I/He-II spectra of alkaline metal acetylacetonates (I. Fragalà, unpublished results).

must be dismissed on the grounds of the dependence of spectral patterns [1] upon changing the central metal atom (Table I).

UO$_2$(acac)$_2$

Table I presents the assignments which we have proposed [1] on the grounds of the He-I data. The more relevant conclusion was the energy ordering of upper filled orbitals localized on the UO$_2^{++}$ group: $\pi_g > \sigma_u > \pi_u > \sigma_g$ (D$_{\infty h}$ symmetry).

This is at variance with the ordering which was postulated on the basis of the electronic spectra [6]: $\sigma_u > \pi_u > \sigma_g > \pi_g$. In reality. the intensity changes observed on passing to He-II spectra indicate unambiguously that an orbital of g symmetry lies at higher energy. In fact the band B (Fig. 2), which within our assignment includes the π_g ionization (Table I), decreases in intensity and, because of symmetry restrictions, this observation can be explained only by assuming the admixture of metal 6d subshells into UO$_2^{++}$ orbitals of g symmetry. Moreover, the following bands X and Y increase considerably on He-II excitation (Table I). This trend strongly supports the proposed assignment of these bands to σ_u and π_u orbitals since they are expected to possess higher He-II cross section because of the uranium 5f contribution.

Conclusions

This study reinforces our earlier contention that a comparison of the He-I and He-II PE spectra of a series of transition metal and actinide complexes with an identical ligand array is the most valuable tool for investigating the bonding of actinide compounds on a purely experimental basis. The most striking result of the present investigation is the close similarity of bonding characteristics within the present series of d and f transition element classical coordination compounds. Similar results have been found for some series of organometallic complexes [3].

Acknowledgements

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