Photoelectron Spectra of Metal Tetrahydroborates

By **Anthony J. Downs, Russell G. Egdell, Anthony F. Orchard,** * and **Patrick D. P. Thomas,** Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR

Helium-(I) and -(II) excited photoelectron spectra of the metal tetrakis(tetrahydroborates) $M(BH_4)_4$ (M = Zr, Hf, or U) and the He(I) spectrum of $Al(BH_4)_3$ are reported. A simple molecular-orbital model is developed to account for features in the spectra associated with ligand ionizations. Final-state structure and cross-section variations for the outermost metal f subshells in $U(BH_4)_4$ and $Hf(BH_4)_4$ are discussed in relation to the expected atomic behaviour.

THE volatile metal tetrahydroborates form an intriguing class of electron-deficient compounds. The interest they have aroused is reflected in two recent review articles.[1,2] Vibrational spectroscopy of the metal tetrakis(tetrahydroborates)[3] indicates that, despite the large number of atoms present in $M(BH_4)_4$ (M = Zr, Hf, or U) molecules, the vapour-phase species belong to the tetrahedral point group T_d, a view confirmed by an electron-diffraction study of $Zr(BH_4)_4$.[4] The latter investigation indicates also that each tetrahydroborate unit is linked symmetrically to the central metal atom *via* three bridging hydrogen atoms. In contrast, the tris complex $Al(BH_4)_3$ has doubly bridged BH_4 ligands and possesses D_{3h} or possibly D_3 symmetry, the metal atom being surrounded by a trigonal prism of hydrogen atoms.[5-9]

Despite the extensive exploration of the stereochemical properties of metal tetrahydroborates little attention has been devoted to their electronic structures. Recent elegant studies of the electronic-absorption spectra of $U(BH_4)_4$[10] and the compound $Er(BH_4)_3\cdot3thf$ (thf = tetrahydrofuran)[11] furnish detailed information about the excited f^n ligand-field states, but can give little insight into even the gross features of the metal–ligand bonding in these and related tetrahydroborates. We were prompted therefore to study the electronic structure of metal tetrahydroborates by the technique of photoelectron (p.e.) spectroscopy.

The $M(BH_4)_4$ species were of considerable interest to us also because they are isoelectronic with the corresponding fluorides MF_4: the halides of Group 4 A have been the subject of an earlier investigation in this laboratory.[12] An additional motivation for the present study was the presence in both $Hf(BH_4)_4$ and $U(BH_4)_4$ of an occupied f-subshell ionizable by vacuum-ultraviolet (v.u.v.) radiation. Little is known about f-subshell ionization cross-sections in molecular systems, and a study of the metal tetrahydroborates by p.e. spectroscopy held the promise of shedding some light on these properties.

EXPERIMENTAL AND RESULTS

The compounds $Al(BH_4)_3$,[13] $Zr(BH_4)_4$,[14] and $Hf(BH_4)_4$[14] were prepared by metathetical reactions between $Li[BH_4]$ and the corresponding metal chloride; $U(BH_4)_4$[15] was obtained from the reaction of UF_4 with $Al(BH_4)_3$. The volatile tetrahydroborates were purified by trap-to-trap sublimation or distillation *in vacuo*.

Photoelectron spectra were recorded on a Perkin-Elmer PS-16/18 spectrometer, modified for He(II) measurements by inclusion of a hollow-cathode discharge lamp and high-current power supply (Helectros Developments, Beaconsfield). Spectra were calibrated by reference to He(Iα) excited signals of Xe and Ar, and He(IIα) and He(IIβ) excited helium self-ionization peaks.

Both $U(BH_4)_4$ and $Al(BH_4)_3$ produced a reversible increase in the threshold of the electron multiplier and spectra had to be accumulated in rapid scans. A further problem arose from the ' backstreaming ' of vapours into the lamp

[1] B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.*, 1970, **11**, 99.
[2] T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.
[3] N. Davies, M. G. H. Wallbridge, B. E. Smith, and B. D. James, *J.C.S. Dalton*, 1973, 162.
[4] V. Plato and K. Hedberg, *Inorg. Chem.*, 1971, **10**, 590.
[5] S. H. Bauer, *J. Amer. Chem. Soc.*, 1950, **72**, 622.
[6] A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, 1968, **22**, 328.
[7] W. C. Price, *J. Chem. Phys.*, 1949, **17**, 1044.
[8] A. R. Emery and R. C. Taylor, *Spectrochim. Acta*, 1960, **16**, 1455.

[9] D. A. Coe and J. W. Nibler, *Spectrochim. Acta*, 1973, **A29**, 1789.
[10] E. R. Bernstein and T. A. Keiderling, *J. Chem. Phys.*, 1973, **59**, 2105.
[11] E. R. Bernstein and K. M. Chen, *Chem. Phys.*, 1975, **10**, 215.
[12] R. G. Egdell and A. F. Orchard, *J.C.S. Faraday II*, 1978, 485.
[13] H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *J. Amer. Chem. Soc.*, 1953, **75**, 209.
[14] W. E. Reid, jun., J. M. Bish, and A. Brenner, *J. Electrochem. Soc.*, 1957, **104**, 21.
[15] H. I. Schlesinger and H. C. Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 219.

discharge; ready decomposition of the tetrahydroborate molecules in the discharge plasma occasionally led to extinction of the lamp. The problem could be overcome by operating the lamp at high helium pressures; but this led in turn to strong helium self-ionization peaks in the He(II) spectra.

The p.e. spectra are shown in Figures 1—4. Ionization-energy data and corrected [12] relative band areas are given in Table 1.

TABLE 1

Ionization energies (eV) and relative band intensities from the p.e. spectra of $Zr(BH_4)_4$, $Hf(BH_4)_4$, $U(BH_4)_4$, and $Al(BH_4)_3$

Band	Ionization energy [a]	Relative intensity [b] He(I)	Relative intensity [b] He(II)	Assignment [c]
(i) $Zr(BH_4)_4$				
(a)	11.6 ± 0.1	3.3	2.9	$2a_1 + 3t_2$ (l.a.t.b.)
(b)	12.7 ± 0.1	8.7	9.1	$1t_1 + 2t_2 + 1e$
	13.2 ± 0.1			(bridging)
(c)	18.18 ± 0.05		2.6	$1t_2(B\ 2s)$
(d)	19.32 ± 0.05		1.1	$1a_1(B\ 2s)$
(ii) $Hf(BH_4)_4$				
(a)	11.6 ± 0.1	3.2	3.1	$2a_1 + 3t_2$ (l.a.t.b.)
(b)	12.6 ± 0.1	8.8	8.9	$1t_1 + 2t_2 + 1e$
	13.5 ± 0.1			(bridging)
(c)	18.35 ± 0.05		2.4	$1t_2(B\ 2s)$
(d)	19.70 ± 0.05		1.2	$1a_1(B\ 2s)$
(y)	26.11 ± 0.05		0.1	$4f_{\frac{5}{2}}(Hf)$
(iii) $U(BH_4)_4$				
(y)	9.58 ± 0.10	0.2	4.6	$5f_{\frac{5}{2}}(U)$
(a)	11.9 ± 0.1			$2a_1 + 3t_2$ (l.a.t.b.)
		12.0	12.0	$1t_1 + 2t_2 + 1e$ (bridging)
(b)	13.0 ± 0.1 (s)			
(c)	17.78 ± 0.10			$1t_2(B\ 2s)$
	18.29 ± 0.10		3.8	
(d)	19.04 ± 0.10			$1a_1(B\ 2s)$
(iv) $Al(BH_4)_3$				
(a)	12.9 (vbr)			$a_1' + e'$ (l.a.t.b.) $+ a_2' + e'$ (terminal)
(b)	14.4			$e'' + a_2''$
	15.0			(bridging)
(c)	19.0			$e'(B\ 2s)$

[a] Bands (a) and (b) are generally rather broad and it is meaningful to quote ionization energies only to the nearest 0.1 eV. [b] Intensities are normalized such that the areas of bands (a) and (b) together equal 12.0. [c] Given in terms of the symmetry species for the ionized orbital. Localization properties in the m.o. scheme are given in parentheses.

DISCUSSION

A Molecular-orbital Model for Metal Tetrahydroborates.—A qualitative description of the electronic structure of metal tetrahydroborates is easily developed using individual bond orbitals as the basis for construction of molecular orbitals (m.o.s). The former are of two distinct types, namely *terminal* (two-centre) B–H bonds and *bridging* (three-centre) $\overline{M(\mu\text{-}H)B}$ bonds. Moreover, it is useful to consider combinations of $\overline{M(\mu\text{-}H)B}$ bond orbitals within a given tetrahydroborate unit which (*i*) are totally symmetric with respect to the local M–B axis, or (*ii*) contain the M–B axis in a nodal plane.

These two types of combination are conveniently labelled as σ-bridging and π-bridging respectively. Designating the three bridging bond orbitals for a triply bridged tetrahydroborate group as τ_1, τ_2, and τ_3, the σ- and π-type combinations are the familiar trigonal combinations (1)—(3). Similarly, for a doubly bridged

$$\sigma \quad 3^{-\frac{1}{2}}(\tau_1 + \tau_2 + \tau_3) \qquad (1)$$

$$\pi \begin{cases} 2^{-\frac{1}{2}}(\tau_2 - \tau_3) & (2) \\ 6^{-\frac{1}{2}}(2\tau_1 - \tau_2 - \tau_3) & (3) \end{cases}$$

tetrahydroborate unit with bond orbitals δ_1 and δ_2 we have (4) and (5). The bond orbitals together span the

$$\sigma \quad 2^{-\frac{1}{2}}(\delta_1 + \delta_2) \qquad (4)$$

$$\pi \quad 2^{-\frac{1}{2}}(\delta_1 - \delta_2) \qquad (5)$$

following irreducible representations in the two relevant point groups: *

	T_d (tridentate BH_4)	D_{3h} (bidentate BH_4)
Terminal	$a_1 + t_2$	$a_1' + e' + a_2' + e'$
σ-Bridging	$a_1 + t_2$	$a_1' + e'$
π-Bridging	$t_1 + t_2 + e$	$a_2'' + e''$

Since certain irreducible representations are spanned only by π-bridging basis functions (t_1 and e in tetrahedral symmetry), it follows that some molecular orbitals are essentially restricted to the M–B bridging region. However, other irreducible representations are covered by both terminal and bridging bond orbitals: the two types of basis function may then of course become mixed in the molecular orbitals of the metal complexes.

In both tetrahedral and trigonal-prismatic systems we expect purely ligand interactions involving the π-basis functions to be less important than those between terminal and σ-bridging orbitals: the former interactions are mediated by overlap between atomic orbitals on different tetrahydroborate units, whereas the latter occur by virtue of overlap within a given tetrahydroborate unit. Hence π-bridging group orbitals are in all probability close to true symmetry-adapted molecular orbitals of the $M(BH_4)_n$ species. Moreover, in $Al(BH_4)_3$, one of the terminal e' orbitals (that formed from locally out-of-phase combinations of B–H bonds) is, for similar reasons, the most likely to be close to a true m.o. of the system.

The mixed terminal–bridging BH_4 group orbitals which are in phase at the boron centres must have very substantial boron $2s$ atomic character, and one can loosely term them the ' boron $2s$ ' molecular orbitals. The remaining locally antisymmetric terminal–bridging orbitals will be referred to as l.a.t.b. orbitals.

* It is worth recalling at this stage the transformation properties for the valence orbitals of the metal atom:

	T_d	D_{3h}
s	a_1	a_1'
p	t_2	$a_1' + e'$
d	$t_2 + e$	

To summarize then, the molecular orbitals in tetra-hydroborate molecules may be classified as follows:

	$M(BH_4)_4\ T_d$	$M(BH_4)_3\ D_{3h}$
Boron 2s	$a_1 + t_2$	$a_1' + e'$
π-Bridging	$t_1 + t_2 + e$	$a_2'' + e''$
l.a.t.b.	$a_1 + t_2$	$a_1' + e'$
Pure terminal		$a_2' + e'$

An important feature of the electronic structure of metal tetrahydroborates is that the ratio of purely bridging electrons to electrons which are at least partially delocalized into the terminal region (*i.e.* l.a.t.b. and pure terminal electrons) is 1 : 2 for doubly bridged tetrahydro-borates and 2 : 1 for triply bridged molecules. A further feature of electronic structure which deserves comment
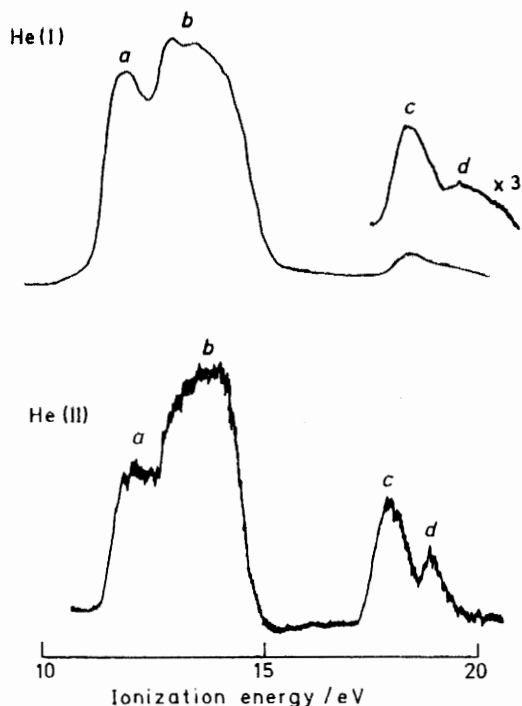

FIGURE 1   He(I) and He(II) p.e. spectra of $Zr(BH_4)_4$

is that in both tetrakis(tetrahydroborates) and aluminium tris(tetrahydroborate) one of the nominally bridging m.o. species [namely the t_1 orbitals in $M(BH_4)_4$ molecules and e'' orbitals in $Al(BH_4)_3$] can contain little or no contribution from the metal atomic orbitals. It follows that the overall covalent M–H bond orders must be lower than implied by the simple three-centre two-electron model.

Photoelectron Spectra of the Metal Tetrahydroborates.— The p.e. spectra of the metal tetrakis(tetrahydroborates) show clear family resemblances and are best discussed collectively. The spectra have in common four distinct bands [labelled (*a*)—(*d*) in Figures 1—3] which must relate to m.o.s predominantly localized on the ligand system. In the p.e. spectra of $U(BH_4)_4$ there is substantial overlap between bands (*a*) and (*b*). The peaks (*c*) and (*d*) are most clearly defined in the He(II) p.e. spectra, the low intensity of the corresponding He(I)

signals being due mainly to instrumental attenuation of low kinetic-energy p.e. flux.
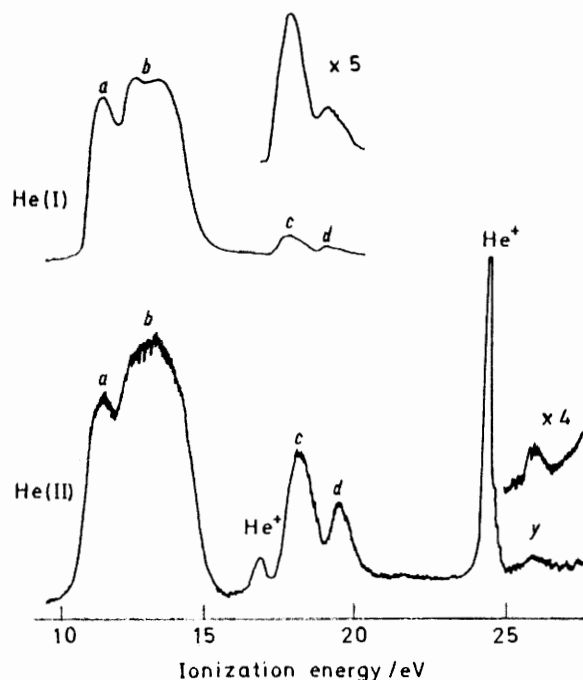

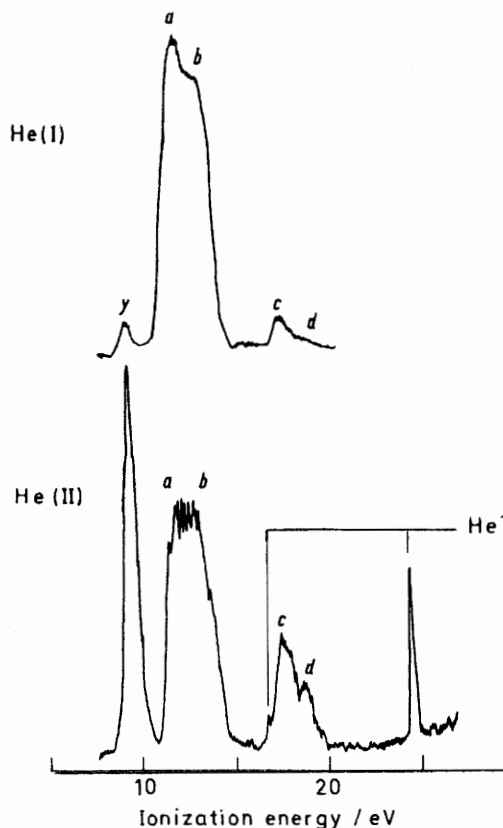FIGURE 2   He(I) and He(II) p.e. spectra of $Hf(BH_4)_4$

FIGURE 3   He(I) and He(II) p.e. spectra of $U(BH_4)_4$

A straightforward interpretation of the p.e. spectra can be given in terms of the m.o. model developed in the

previous section, as illustrated in Figure 5. Bands (c) and (d) are associated with the t_2 and a_1 molecular sub-shells having dominant boron $2s$ atomic character, the
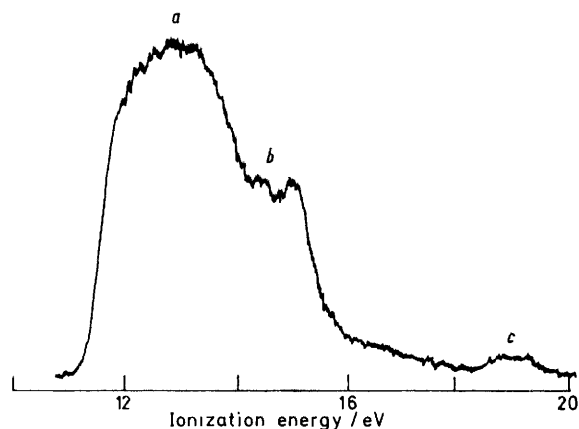

FIGURE 4 The He(I) p.e. spectrum of $Al(BH_4)_3$

intensity ratio $I_c : I_d$ being reasonably close to the statistical value of $3 : 1$ in He(II) p.e. spectra. Band (b) can then be assigned to π-bridging orbitals $(t_1 + t_2 + e)$ and band (a) to l.a.t.b. orbitals $(t_2 + a_1)$. Whilst it is difficult to obtain reliable estimates of the intensity ratio of bands (a) and (b), it is clearly of the order $1 : 2$ in the He(I) p.e. spectra, thus supporting the view that the molecular subshells are grouped energetically according to their differing localization properties in the simple m.o. scheme. Moreover, the general pattern of intensity distribution between bands (a) and (b) in the He(I) p.e. spectrum of $Al(BH_4)_3$ (Figure 4) is clearly different from that in the tetrakis(tetrahydroborates). It seems that the differences between p.e. spectra of $Al(BH_4)_3$ and the $M(BH_4)_4$ species simply reflect inversion of the ratio of bridging to terminal $(i.e.$ purely terminal or l.a.t.b.) electrons as the ligation of tetrahydroborate changes from the triply to doubly bridging mode.

Changes in the intensity ratio between bands (a) and (b) in p.e. spectra of the tetrakis(tetrahydroborates) on switching from He(I) to He(II) excitation provide further guidance regarding the assignment problem. If it is assumed that (i) terminal and bridging H $1s$ atomic orbitals contribute equally to the l.a.t.b. molecular orbitals, (ii) l.a.t.b. and bridging symmetry-adapted ligand orbitals ψ_c^γ (m.o.) can be written in the general form ψ_c^γ(m.o.) $= B\psi_c^\gamma(B\ 2p) + C\psi_c^\gamma(H\ 1s)$ where B and C are mixing coefficients and the ψ_c^γ on the right-hand side of the expression are symmetry-adapted combinations of atomic orbitals, and (iii) the metal atoms in tetrakis(tetrahydroborates) are surrounded by a regular dodecahedral array of hydrogen atoms, then it can be shown that the group overlaps between hydrogen $1s$ atomic orbitals and d orbitals on the central metal atom are as in (6)—(8) where the functions $|\gamma(L)\rangle$ and $|\gamma(\pi\text{-B})\rangle$

are respectively l.a.t.b. and π-bridging ligand orbitals belonging to the irreducible representation γ.

$$\langle t_2(L)|d\rangle = C\frac{1}{3} \cdot 2^{\frac{1}{2}}S(s,d_o) \qquad (6)$$

$$\langle t_2(\pi\text{-B})|d\rangle = C\frac{2}{3} \cdot 2^{\frac{1}{2}}S(s,d_o) \qquad (7)$$

$$\langle e(\pi\text{-B})|d\rangle = C\frac{3}{2} \cdot 2^{\frac{1}{2}}S(s,d_o) \qquad (8)$$

On this basis it is to be expected that the metal d contribution to π-bridging orbitals $(t_2 + e)$ will be significantly greater than the contribution to l.a.t.b. orbitals of t_2 symmetry. Now it has been shown[12,16] that on changing from He(I) to He(II) excitation the p.e. signals associated with metal–ligand bonding orbitals possessing substantial metal d character generally increase in intensity relative to those associated with largely non-bonding levels.[*] The observation that there is a small but significant increase in the intensity of band (b) relative to that of (a) on switching to He(II) excitation therefore lends support to the view that band (b) relates to l.a.t.b. molecular orbitals.

It is interesting to note that the proposed ordering of l.a.t.b. and bridging molecular subshells is just that which would be expected on simple electrostatic grounds. Penetration integrals of the type $\langle \phi_L|V_M|\phi_L\rangle$ (where ϕ_L,
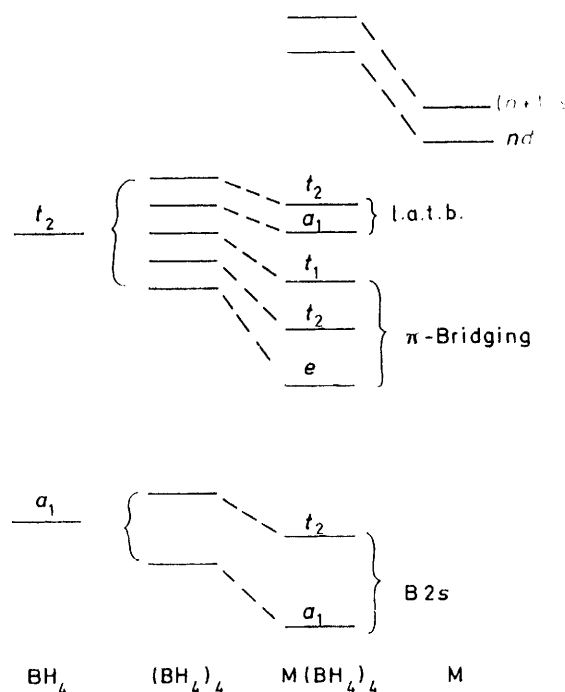

FIGURE 5 Schematic molecular-orbital diagram for a transition-metal tetrakis(tetrahydroborate)

is a ligand orbital and V_M refers to the electrostatic potential provided by the metal atom) clearly stabilize orbitals restricted to the bridging region relative to those

---

[*] This behaviour is expected whenever the metal d one-electron cross-section exceeds the one-electron cross-section for valence ligand orbitals at He(II) wavelengths.

[16] R. G. Egdell, A. F. Orchard, D. R. Lloyd, and N. V. Richardson, *J. Electron Spectroscopy*, 1977, **12**, 415.

which are at least partially delocalized into the terminal B–H region (*i.e.* l.a.t.b. or pure terminal orbitals).

There has been some speculation [2] that direct metal–boron interactions may be of importance in the bonding in metal tetrakis(tetrahydroborates). In this connection it is noteworthy that there is a small but discernible increase in the $1a_1$ (B 2s) binding energy in going from $Zr(BH_4)_4$ to $Hf(BH_4)_4$. This clearly parallels a trend found in p.e. spectra of the corresponding metal halides,[12] and invites the speculation that the increase in binding energy is mediated by direct B 2s–Hf 6s overlap. Certainly, a recent study of $Hf(BH_4)_4$ by Raman spectroscopy [17] revealed a surprisingly large M–B stretching force constant as well as a sizeable mean polarizability derivative $\bar{a}'(M–B)$, suggesting direct boron–metal interactions.

f-*Subshell Ionizations in P.e. Spectra of* $Hf(BH_4)_4$ *and* $U(BH_4)_4$.—Photoelectron spectra of both $Hf(BH_4)_4$ and $U(BH_4)_4$ contain features having no counterpart in the spectra of $Zr(BH_4)_4$. The additional peaks [labelled (*y*) in Figures 2 and 3] probably relate to ionization from metal *f* subshells.

In the case of $Hf(BH_4)_4$ an exceedingly weak band is observed in the He(II) spectrum at a binding energy just in excess of that for the helium self-ionization peak. This, it seems, corresponds to the $^2F_{\frac{7}{2}}$ final state produced by ionization of the 4f subshell of hafnium; the corresponding $^2F_{\frac{5}{2}}$ component is presumably obscured by the helium self-ionization peak, the $^2S(He^+)$ — $^2F_{\frac{5}{2}}$ separation being close to that between final-state components of the 4f ionization observed in X-p.e. spectra of hafnium dioxide.[18,19]

The ' 5f ' ionization in $U(BH_4)_4$ occurs before the onset of the ligand ionizations. On changing from He(I) to He(II) excitation there is a very pronounced increase in the intensity of the 5f band relative to that of the ligand bands (*a*) and (*b*). Moreover, by normalizing intensities in the He(II) p.e. spectra relative to the B 2s bands [(*c*) and (*d*)] it is possible to estimate the ratio of one-electron cross-sections for the 4f subshell in $Hf(BH_4)_4$ and the 5f subshell in $U(BH_4)_4$. The value of *ca.* 1/130 so obtained suggests that the *f* subshell cross-sections are rather small close to threshold and increase slowly as a function of electron kinetic energy as the continuum *g* orbitals increasingly penetrate the angular-momentum barrier provided by the $l(l + 1)/r^2$ term in the radial Hamiltonian for the continuum states. The remarkably low value for σ_{4f}/σ_{5f} indicates moreover that the growth in cross-section is much more rapid for the U 5f subshell than for the more contracted 4f subshell of hafnium. Somewhat surprisingly, calculations in which a plane wave is used to represent the continuum states yield a

cross-section ratio essentially in agreement with the experimental value.[20] Whilst it is difficult to evaluate an isolated case, our observations do appear to lend support to the view expressed by Williams and Shirley [21] that the plane-wave method should provide a ' fair ' means of calculating *f*-subshell ionization cross-sections.

Final-state Structure in P.e. Spectra of Uranium(IV) Complexes.—The pattern of final-state structure expected on ionizing a 5f electron from a uranium(IV) compound is clearly influenced by two important factors. These are, first, the nature of the atomic coupling scheme appropriate to the 5f subshell, and secondly the effects of the ligand field on the initial and final states of the system.

Some general insight into the problem is gained by considering the atomic situation in which an electron is removed from the ground ($J = 4$) term of U^{4+}. The energies of the $^2F_{\frac{7}{2}}$ and $^2F_{\frac{5}{2}}$ final states are obviously independent of the choice of atomic coupling scheme, and these two multiplet levels are separated by $7/2\zeta_{5f}$, where ζ_{5f} is the spin–orbit coupling constant for the 5f subshell. On the other hand, the p.e. intensities of the two final-state peaks are dependent on the mechanism of ground-state coupling.

Cox [22,23] has treated the problem in the Russell–Saunders ($L–S$) limit using fractional parentage methods. The ground state can then be labelled as $^3H_4$ and the $^2F_{\frac{5}{2}}:^2F_{\frac{7}{2}}$ final-state intensity ratio is $1.714:0.286$. An alternative and more general approach is to describe the initial state $|I\rangle$ in terms of a linear combination of relativistic configuration-state functions.[24] In the usual notation: *

$$|I\rangle_{J=4} = a|f_{\frac{5}{2}}^2\rangle_{J=4} + b|f_{\frac{5}{2}}f_{\frac{7}{2}}\rangle_{J=4} + c|f_{\frac{7}{2}}^2\rangle_{J=4} \quad (9)$$

For pure *j–j* coupling the ground state is characterized by $a = 1$, $b = 0$, and $c = 0$, whilst the $L–S$ limit coefficients are given by 9-*j* symbols representing the transformation between *j–j* and $L–S$ basis functions. For the general intermediate-coupling situation, coefficients must be obtained from a multiconfiguration Dirac–Fock calculation. Particular values obtained by Grant and Pyper [25] from such a calculation are listed below, together with values for $L–S$ and *j–j* limits.

	a	*b*	*c*	$^2F_{\frac{5}{2}}:^2F_{\frac{7}{2}}$ intensity ratio
j–j Limit	1.000 0	0.000 0	0.000 0	1.000 : 0.000
L–S Limit	0.865 0	0.466 6	−0.184 4	1.714 : 0.286
Intermediate coupling	0.975 3	0.213 2	−0.057 0	1.948 : 0.052

In each case the $^2F_{\frac{5}{2}}:^2F_{\frac{7}{2}}$ intensity ratio is given quite simply by $(2a^2 + b^2):(2c^2 + b^2)$ (assuming that $f_{\frac{5}{2}}$ and $f_{\frac{7}{2}}$ subshells have identical one-electron cross-sections).

* The ket $|f_{j1}f_{j2}\rangle_{J=4}$ specifies a suitably antisymmetrized eigenfunction of the angular-momentum operator $\hat{j}$ constructed from one-electron spin orbitals with *j* values j_1 and j_2.

[17] T. A. Keiderling, W. T. Wozniak, R. S. Gay, D. Jurkowitz, E. R. Bernstein, S. J. Lippard, and T. G. Spiro, *Inorg. Chem.*, 1975, **14**, 576.
[18] A. F. Orchard and G. Thornton, *J. Electron Spectroscopy*, 1977, **10**, 1.
[19] G. Thornton, D.Phil. Thesis, Oxford, 1976.
[20] R. G. Egdell, D.Phil. Thesis, Oxford, 1977.
[21] R. S. Williams and D. A. Shirley, *J. Chem. Phys.*, 1977, **66**, 2378.
[22] P. A. Cox, *Structure and Bonding*, 1975, **24**, 59.
[23] P. A. Cox, D.Phil. Thesis, Oxford, 1973.
[24] N. Beatham and A. F. Orchard, in preparation.
[25] I. C. Grant and N. C. Pyper, personal communication.

It follows that, in the j–j coupling limit, only the $^2F_{\frac{5}{2}}$ state can be reached. With the coefficients obtained by Grant and Pyper, the $^2F_{\frac{5}{2}}$ term is still expected to be dominant $(^2F_{\frac{5}{2}} : {}^2F_{\frac{7}{2}}$ intensity ratio $ca.$ 40 : 1): the coupling in the $5f^2$ configuration is evidently close to the j–j limit. Finally, with the coefficients of the L–S limit, a result identical with that derived by Cox is obtained. The behaviour expected for U^{4+} is clearly reminiscent of that observed for the lead atom, which has a ground term with $J = 2$ derived from a $6p^2$ configuration. Here the $^2P_{\frac{1}{2}} : {}^2P_{\frac{3}{2}}$ intensity ratio is 15 : 1, indicating effective j–j coupling in the $6p$ sub-shell.[26]

In order to predict energies in ionic $(5f^1)$ states of uranium(IV) complexes it is clearly necessary to take account of both spin–orbit and ligand-field perturbations. Absorption spectra of a number of cubic or pseudo-cubic uranium(IV) complexes have been analysed in terms of an effective spin–orbit coupling constant ζ_{5f} and two radial parameters related to effective values for $\langle r^4 \rangle$ and $\langle r^6 \rangle$.[10,27-30] In these cases it is possible to estimate the pattern of final-state energy levels by diagonalizing the $5f^1$ matrix of spin–orbit and ligand-field operators using initial-state parameter values for ζ_{5f}, $\langle r^4 \rangle$, and $\langle r^6 \rangle$. Calculations of this type reveal that in tetrahedral complexes the ligand field usually acts as a weak perturbation, splitting the $J = \frac{5}{2}$ level into E'' and U' components and the $J = \frac{7}{2}$ level into $E' + E'' + U'$ components. In the case of $U(BH_4)_4$, for

TABLE 2

Calculated splitting of the $^2F_{\frac{5}{2}}$ final state in p.e. spectra of some cubic uranium(IV) compounds [a]

Compound	Initial-state parameters [b] (cm⁻¹)			Final-state splitting [c] (eV)	Ref.
	ζ_{5f}	$A(\langle r^4 \rangle)$	$B(\langle r^6 \rangle)$		
$U(BH_4)_4$	1 908.0	−371.9	−261.6	−0.101	10
UCl_4	1 796.0	−593.0	−21.6	−0.170	27
UBr_4	1 796.0	−490.0	−15.2	−0.140	27
$[U(C_5H_5)_3Cl]$	1 719.0	−636.0	−261.0	−0.206	30
$[UF_6]^{2-}$	1 970.0	1 258.4	1.4	0.371	28
$[UCl_6]^{2-}$	1 800.1	901.4	85.4	0.225	29
$[UBr_6]^{2-}$	1 792.6	824.1	74.7	0.209	29
$[UI_6]^{2-}$	1 724.0	792.2	58.8	0.206	28

[a] Calculations are based on the assumption that values for ζ_{5f}, A, and B are unchanged on ionization. [b] See M. T. Hutchings, $Solid$ $State$ $Phys.$, 1964, **16**, 227, for definitions of the radial parameters A and B. [c] A negative splitting parameter implies a sequence $U' < E''$, positive parameters indicate $E'' < U'$.

example, the calculated splitting for the $J = \frac{5}{2}$ level is only 0.101 eV,* and there is little mixing between com-

ponents of $J = \frac{5}{2}$ and $\frac{7}{2}$ levels. Calculated final-state splittings for some other cubic complexes are listed in Table 2.

Although ligand-field splittings of the $5f^1$ final states are rather small (<0.4 eV), initial-state splittings inferred from absorption spectra are usually significantly greater than kT at room temperature. It appears, however, that ligand-field mixing of components of the ground atomic term $(J = 4)$ with components derived from excited terms is generally of minor importance. In these circumstances, initial-state splittings would exert important influences on the final-state intensity patterns were it possible to resolve the final-state ligand-field structure. However, Cox [23] has shown that weak-field perturbation of the initial state has no influence on final-state intensity patterns if the ligand-field structure is unresolved.

Application of these ideas to the low-energy region of the p.e. spectrum of $U(BH_4)_4$ leads clearly to the conclusion that the peak (y) (Figure 3) relates to the unsplit $^2F_{\frac{5}{2}}$ final-state component of the $5f$ ionization. It is interesting to note, moreover, that in the studies reported to date, the p.e. spectra of compounds containing U^{IV} in a cubic $\{e.g.\ UO_2(s)$ [31-33] or $K_2[UF_6](s)$ [34]$\}$ or pseudo-cubic $\{e.g.\ [U(C_5H_5)_3Cl]$ or $[U(C_5H_5)_3Br]\}$ [35] environment each contain a single uranium $5f$ peak. It seems quite plausible that the situation in these cases is essentially similar to that in $U(BH_4)_4$, with atomic coupling close to the j–j limit militating in favour of the $^2F_{\frac{5}{2}}$ final state and the ligand field insufficiently strong to produce a measurable splitting of this level.

In contrast, p.e. spectra of $[U(C_5H_5)_3(BH_4)]$ [35] do contain two U $5f$ peaks. In this species it may well be that non-cubic components of the ligand field are of major importance in lifting the six-fold degeneracy of the $^2F_{\frac{5}{2}}$ state, although it is not possible to attempt a detailed analysis of the p.e. spectrum in the absence of reliable estimates for the cubic and non-cubic ligand-field parameters.

$Conclusions.$—Photoelectron spectra of a number of metal tetrahydroborates have been interpreted tentatively in terms of a simple m.o. model using a basis set of localized bond orbitals. This model indicates that doubly and triply bridged tetrahydroborates should have qualitatively distinct p.e. spectra, a prediction borne out by the differences between spectra of the $M(BH_4)_4$ species, on the one hand, and $Al(BH_4)_3$ on the other. This encourages the view that p.e. spectroscopy may be of value not only as a probe of electronic properties but also in the diagnosis of the mode of ligation in tetrahydroborates. In a future publication we shall describe

* Throughout this paper: 1 eV ≈ 1.60 × 10⁻¹⁹ J.

[26] S. Süzer, M. S. Banna, and D. A. Shirley, $J.\ Chem.\ Phys.$, 1975, **63**, 3473.

[27] J. R. Clifton, D. M. Gruen, and A. Ron, $J.\ Chem.\ Phys.$, 1969, **51**, 224.

[28] D. R. Johnston, R. A. Satten, C. L. Schreiber, and E. Y. Wong, $J.\ Chem.\ Phys.$, 1966, **44**, 3141.

[29] W. Wagner, N. Edelstein, B. Whittaker, and D. Brown, $Inorg.\ Chem.$, 1977, **16**, 1021.

[30] H.-D. Amberger, $J.\ Organometallic\ Chem.$, 1976, **116**, 219.

[31] J. Verbist, J. Riga, J. J. Pireaux, and R. Caudano, $J.\ Electron\ Spectroscopy$, 1974, **5**, 193.

[32] B. W. Veal, in ' The Actinides: Electronic Structure and Related Properties,' eds. A. J. Freeman and J. B. Darby, jun., Academic Press, London, 1974, vol. 2, p. 73.

[33] S. Evans, $J.C.S.\ Faraday\ II$, 1977, **1341**.

[34] J. J. Pireaux, N. Mårtensson, R. Didriksson, K. Siegbahn, J. Riga, and J. Verbist, $Chem.\ Phys.\ Letters$, 1977, **46**, 215.

[35] I. Fragala, E. Ciliberto, R. D. Fischer, G. R. Sienel, and P. Zanella, $J.\ Organometallic\ Chem.$, 1976, **120**, C9.

characterization of the molecule $Ti(BH_4)_3$ by techniques including p.e. spectroscopy.[36]

[36] R. G. Egdell, A. J. Downs, P. D. P. Thomas, and A. F. Orchard, in preparation.