

Articles

Contribution from the Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

An X-ray Photoelectron Spectroscopic Study of Uranium Compounds

David B. Beach, Kenneth D. Bomben, Norman M. Edelstein, David C. Eisenberg, William L. Jolly,* Ron Shinomoto, and Andrew Streitwieser, Jr.

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The gas-phase X-ray photoelectron spectra of UF_6 , $\text{U}(\text{BH}_4)_4$, $\text{U}(\text{BH}_3\text{CH}_3)_4$, and $\text{U}(\text{C}_8\text{H}_8)_2$ have been obtained. The core binding energy data show that the bonding in UF_6 is extraordinarily ionic and that the bonding in the other compounds, especially $\text{U}(\text{C}_8\text{H}_8)_2$, is considerably more covalent. The binding energies and shake-up spectra show that the covalencies of $\text{U}(\text{BH}_4)_4$ and $\text{U}(\text{BH}_3\text{CH}_3)_4$ are comparable to that of UBr_4 , with $\text{U}(\text{BH}_3\text{CH}_3)_4$ being more covalent than $\text{U}(\text{BH}_4)_4$. By consideration of both core binding energies and literature valence ionization potentials, it is shown that the HOMO of UF_6 is the t_{1g} fluorine lone-pair orbital. A similar analysis of data for $\text{U}(\text{BH}_4)_4$, $\text{U}(\text{BH}_3\text{CH}_3)_4$, and $\text{U}(\text{C}_8\text{H}_8)_2$ is consistent with spectral features that suggest the uranium $5f$ electrons in these compounds are essentially nonbonding.

UF_6 , $\text{U}(\text{BH}_4)_4$, $\text{U}(\text{BH}_3\text{CH}_3)_4$, and $\text{U}(\text{C}_8\text{H}_8)_2$ are some of the most volatile uranium compounds known and have been the subject of numerous chemical, spectroscopic, and theoretical studies.¹⁻⁶ In the present study we have obtained the gas-phase X-ray photoelectron spectra of these four compounds. The core electron binding energies can be used to compare the relative ionicities of the bonds and to interpret previously determined ultraviolet photoelectron spectra. The core binding energy data are presented in Table I. The uranium $4f_{7/2}$ binding energies span a remarkably wide range, greater than 9 eV. As a rough approximation, the change in core binding energy ΔE_B for an element on going from one compound to another can be represented by^{7,8}

$$\Delta E_B = k\Delta Q$$

where k is a constant, approximately equal to the reciprocal of the effective atomic radius of the atom, and ΔQ is the change in atomic charge. This is one reason that the range of core binding energies observed for larger atoms is usually much smaller than for smaller atoms. For example, the carbon 1s binding energy of CCl_4 is 5.48 eV greater than that of CH_4 , whereas the tin $3d_{5/2}$ binding energy of SnCl_4 is only 2.18 eV greater than that of SnH_4 .⁹ Thus we conclude that the large increase in uranium binding energy on going from $\text{U}(\text{C}_8\text{H}_8)_2$ to UF_6 corresponds to a large increase in the effective uranium atom charge.

Uranium Hexafluoride

The uranium and fluorine binding energies reported in Table I are in fair agreement with those of Mårtensson et al.¹ Our values are 0.36 eV higher and 0.17 eV lower than theirs, respectively. The fluorine 1s binding energy, 692.33 eV, is quite low; it lies between that of sulfur hexafluoride, 695.0 eV, and that of trimethylfluorogermane, 690.5 eV (the lowest known F 1s binding energy for a gaseous compound).⁹ Apparently, the fluorine atoms of UF_6 are highly negatively charged in spite of the fact that there are six fluorine atoms competing for electron density. A recent natural orbital population analysis¹⁰ of SF_6 indicates that each fluorine atom in SF_6 has a charge of about -0.5. The present result for UF_6 suggests still greater negative charge for its fluorine atoms. Of course, this result is consistent with our conclusion (vide supra) that the uranium atom in this compound has a remarkably high positive charge.

There has been considerable discussion in the literature¹⁻⁶ regarding the assignment of the low-energy bands of the valence photoelectron spectrum of UF_6 . Most investigators³⁻⁶ have assigned the lowest energy peak (corresponding to the HOMO) to

Table I. Core Binding Energies (eV) of Uranium Compounds

compd	U $4f_{7/2}$		ligand atoms ^a	
	E_B	fwhm ^b	E_B	fwhm
UF_6	392.86 ^c		692.33 ^c	
$\text{U}(\text{BH}_4)_4$	387.88 (4) ^d	1.42 (6)	195.27 (7)	1.91 (21)
$\text{U}(\text{BH}_3\text{CH}_3)_4$	386.77 (3)	1.44 (6)	193.56 (8)	1.80 (18)
			288.56 (4)	1.41 (13)
$\text{U}(\text{C}_8\text{H}_8)_2$	383.49 (5)	1.26 (14)	290.84 (3)	1.41 (9)

^aF 1s, B 1s, and C 1s. ^bFull width at half-maximum. ^cReference 9. ^d 2σ value from least-squares fit of data indicated parenthetically.

the t_{1u} fluorine lone-pair orbital, whereas Mårtensson et al.^{1,2} have assigned this peak to the t_{1g} fluorine lone-pair orbital.

This problem can be readily resolved by use of both the core and valence ionization potentials of UF_6 and HF.¹¹ The F 1s ionization potential of UF_6 is 1.98 eV lower than that of HF. We subtract eight-tenths of this difference from the lone-pair ionization potential of HF (16.06 eV) to obtain the localized orbital ionization potential (LOIP)¹¹ of 14.48 eV for a fluorine 2p orbital of UF_6 . This is the ionization potential that a fluorine lone pair of UF_6 would have if it were completely nonbonding. The LOIP is slightly greater than the lowest ionization potential of UF_6 (14.14 eV) and is lower than all of the other ionization potentials. We assume, with previous investigators,¹⁻⁶ that the 14.14 eV peak corresponds to a single level. Hence we conclude that the HOMO has a small amount of net antibonding character and that the other lone-pair orbitals have net bonding character.

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* To whom correspondence should be addressed at the University of California.

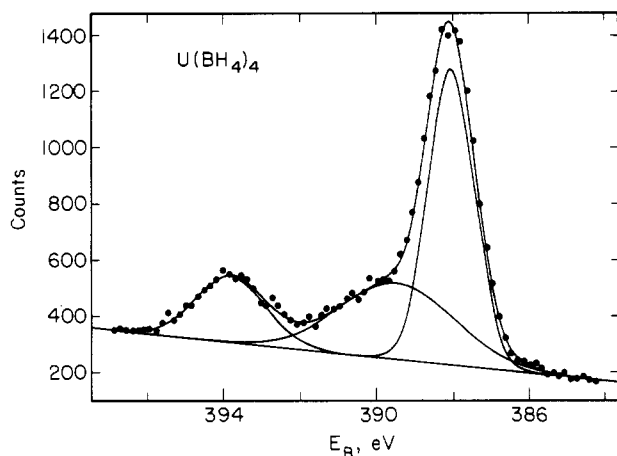


Figure 1. U $4f_{7/2}$ photoelectron spectrum of $U(BH_4)_4$.

The fluorine $2p\pi$ lone-pair orbitals of UF_6 have the symmetry species t_{1g} , t_{2g} , t_{1u} , and t_{2u} . Any significant interactions of these orbitals with uranium orbitals would be expected to be with higher lying, empty orbitals and hence would be bonding, or stabilizing, interactions. None of the lone-pair orbitals are expected to be destabilized (i.e., to acquire antibonding character) by interaction with uranium orbitals.

The HOMO, which is the only orbital with net antibonding character, cannot be the t_{2g} or t_{2u} orbital, because these orbitals have, within themselves, inherent bonding character, and interactions with uranium orbitals would give them even more bonding character. Both of the remaining two orbitals (t_{1g} and t_{1u}) have inherent antibonding character, but only the t_{1u} orbital has a symmetry that allows it to undergo a stabilizing interaction with the uranium p and f orbitals. Hence, the HOMO must be the t_{1g} orbital, which by symmetry cannot interact with the available uranium orbitals. This conclusion is the same as that of Mårtensson et al. It is significant that Hay et al.⁵ calculated, with configuration interaction (CI) wave functions without spin-orbit splitting, that the t_{1g} level lies 0.04 eV above the t_{1u} level. Pyykkö and Laaksonen¹² have discussed a possible CI explanation for this ordering.

Uranium(IV) Hydroborates

The X-ray photoelectron spectra of the $4f_{7/2}$ peaks of uranium tetrakis(tetrahydroborate) and uranium tetrakis(methyltrihydroborate) are characterized by strong satellite structure due to shake-up, as shown in Figure 1. The spectrum of the methyltrihydroborate is essentially identical with that of the tetrahydroborate, except that the peaks are shifted by approximately 1 eV to lower binding energies. This shift to lower binding energy indicates a shift of electron density from the methyl groups toward the metal ion and is consistent with the increased polarizability of the methyl group compared to that of the hydrogen atom.¹³ This effect has been seen in many gas-phase thermodynamic data, such as proton affinities¹⁴ and ionization potentials.¹⁵ In the present case the substitution occurs one to two atoms removed from the uranium. Analogous core binding energy shifts are found in ethyl vs. methyl substitutions. For example, each replacement of a methyl group by an ethyl group in methylamines,¹⁶ dimethyl ether,¹⁶ and dimethylzinc^{17,18} lowers the core binding energy of

nitrogen, oxygen, and zinc, respectively, by 0.1–0.2 eV. Since there are four methyl groups in uranium(IV) methyltrihydroborate, this effect may be of some importance.

The shake-up energies corresponding to the deconvolution in Figure 1 are 1.5 and 5.8 eV, considerably lower than the corresponding shake-up energies of UF_6 (for which the prominent shake-up peak has an energy of 10.2 eV).¹ This result is consistent with the general observation that the shake-up energy for the prominent peak increases with oxidation state.¹ As in the case of UF_6 , the lower energy shake-up peak of $U(BH_4)_4$ has an energy less than that of the optical band gap. There is no shake-up in the B 1s spectrum of $U(BH_4)_4$, indicating that the virtual orbitals involved in the shake-up of Figure 1 have mainly uranium character.

Thibaut et al.¹⁹ have proposed a correlation of the decrease of the splitting between the shake-up and the U $4f_{7/2}$ peaks and an increase of the shake-up intensities with heavier halide ions to an increase of the covalent character of the bonding orbitals. The shake-up satellites represent valence electron excitation simultaneous with the emission of a core electron. This excitation involves donation of an electron from a ligand orbital to the lowest available 5f level. They also observed a relative decrease of the U 5f peak intensity relative to the U 4f core peaks and to the U $6p_{3/2}$ peak as the halide atomic number increased. All of these observations were attributed to increasingly covalent character with heavier halides.

We cannot compare our binding energies with those of the U(IV) halides since the latter data were obtained in the solid state. The satellite splittings for $U(BH_4)_4$ and $U(BH_3CH_3)_4$ are 5.8 and 5.6 eV, respectively, while Thibaut et al. find values of 6.1 and 5.8 eV for UCl_4 and $U(Br_4)_4$, respectively.¹⁹ These data suggest that $U(BH_4)_4$ and $U(BH_3CH_3)_4$ have approximately the same covalencies as $U(Br_4)_4$, with $U(BH_3CH_3)_4$ being slightly more covalent than $U(BH_4)_4$. However, satellite intensities relative to the main peak for the hydroborates are much lower than that observed for $U(Br_4)_4$ (~20% vs. 67%). This result may be due to relaxation effects or to differences in coordination in the two compounds. Thus the correlation with differences in binding energy is consistent with the $U(Br_4)_4$ data, but discrepancies remain when the relative satellite intensities are considered. The results of the optical analysis of $U(BD_4)_4$ diluted in $Hf(BD_4)_4$ and U^{4+} diluted in $ThBr_4$ also showed that the U^{4+} -ligand covalent interactions are very similar in these two cases.¹⁹ Analysis of magnetic data for $Np(BH_4)_4$ and $Np(BH_3CH_3)_4$ showed the methyltrihydroborate compound to be more covalent than the borohydride.²⁰

The boron 1s binding energy of $U(BH_4)_4$ is 1.2 eV lower than that of B_2H_6 .⁹ The boron atoms in these compounds have similar environments: each boron atom is directly bonded to four hydrogen atoms and is connected by hydrogen bridges to an electropositive atom (uranium or boron). The lower electronegativity of uranium relative to that of boron explains the lower boron binding energy of $U(BH_4)_4$ compared with that of B_2H_6 .

Uranocene

The uranium(IV) borohydride and uranocene, bis([8]-annulene)uranium(IV), are both formally compounds of uranium(IV), but the uranium core binding energy in uranocene is more than 4 eV lower than that of the borohydride. The compounds are sufficiently different that part of the decrease could be due to a difference in relaxation energies. It seems more likely, however, that most, if not all, of the difference stems from the much greater ring-metal covalency in uranocene. For comparison, the metal core binding energies in ferrocene and nickelocene are unusually low relative to those of other compounds of these metals.²¹

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An appropriate comparison is to the Mössbauer spectrum of neptunocene, a compound isomorphous with uranocene.²² Neptunocene has the largest Mössbauer isomer shift of any Np(IV) compound studied.²³ This result is indicative of an unusually high degree of charge transfer from ligand to the central metal. The core binding energy of uranium in uranocene leads to a comparable conclusion. Both observations are in agreement with quasi-relativistic $X\alpha$ scattered-wave SCF calculations that also indicate substantial ring-metal covalency in uranocene with significant electron transfer from ligand to metal,²⁴ but are in disagreement with relativistically parametrized extended Hückel (REX) calculations that indicate an essentially ionic structure.²⁵

The 5f Electrons

The first bands in the valence photoelectron spectra of $U(BH_4)_4$, $U(BH_3CH_3)_4$, and $U(C_8H_8)_2$, at 9.58, 8.3, and 6.20 eV, respectively, have been assigned to the uranium 5f electrons in these compounds.²⁶⁻²⁸ These bands are sharp, symmetrical peaks, suggestive of orbitals with little bonding or antibonding character. Further evidence for nonbonding character of the 5f electrons is found in the similarity of the entire UPS spectra of $U(C_8H_8)_2$ and $Th(C_8H_8)_2$ ²⁸ and of $U(BH_4)_4$ and $Hf(BH_4)_4$.²⁶ It appears that the bonding in $U(C_8H_8)_2$ and $U(BH_4)_4$ is little affected by the inclusion of the 5f electrons.

If the 5f electrons in $U(BH_4)_4$, $U(BH_3CH_3)_4$, and $U(C_8H_8)_2$ are indeed nonbonding, then the differences between the 5f ionization potentials should be approximately equal to eight-tenths of the corresponding differences in uranium core binding energy.¹¹ Thus for $U(BH_4)_4$ and $U(C_8H_8)_2$, we calculate $0.8 \times 4.39 = 3.5$ eV (to be compared with the actual difference of 3.38 eV). Similarly, for $U(BH_3CH_3)_4$ and $U(C_8H_8)_2$, we calculate $0.8 \times 3.28 = 2.6$ eV (to be compared with the actual difference of 2.1 eV). The agreement between the observed and calculated differences is close enough that we may conclude that the bonding or antibonding characters of the 5f electrons in these compounds are similar. Thus the data are consistent with the conclusion that

these electrons are primarily nonbonding.

Experimental Section

The uranium(IV) hydroborate,²⁹ uranium(IV) methyltrihydroborate,³⁰ and uranocene³¹ were prepared by published procedures.

Vapor-phase X-ray photoelectron spectra were obtained with a GCA/McPherson ESCA-36 spectrometer using a magnesium anode. Spectra were calibrated with the N_2 1s (409.93 eV), Ne 1s (870.31 eV), and Ne 2s (48.47 eV) lines by a method described previously.³² Spectra were fit to Gaussian/Lorentzian line shapes by using the nonlinear least-squares program CURVY.³³ The U $4f_{7/2}$ spectrum of $U(BH_4)_4$ (Figure 1) was corrected for the $\alpha_{3,4}$ satellites of the magnesium X-rays by assuming the $4f_{5/2}$ - $4f_{7/2}$ splitting to be 10.8 eV, assuming the $4f_{5/2}$: $4f_{7/2}$ intensity ratio to be 6:8, and using the $\alpha_{3,4}$ positions and intensities from the literature.³⁴

Uranium hexafluoride was introduced into the gas cell through an all-metal inlet system. Flow was controlled by a micrometer-type stainless steel needle valve. Uranium tetrahydroborate and methyltrihydroborate were sublimed directly into the spectrometer through large-diameter (1.5-cm) tubing from a reservoir cooled to 10 °C. Uranocene was volatilized in a resistively heated gas cell of our own design.³⁵ A 200-mg sample was placed in a thin-walled glass bulb in an inert-atmosphere box, sealed under vacuum, and crushed after the spectrometer sample chamber pressure was less than 4×10^{-7} torr. The gas cell was heated to 180 °C to obtain the spectra. The reactivity of the hydroborate complexes caused some difficulty in the collection of spectra. After less than 2 h of data collection, the aluminum X-ray window became coated with uranium and the electron detector became inoperative. (The detector could be restored to its former level of performance by treatment with dilute hydrogen peroxide; thus it is reasonable to assume that its surface had undergone reduction, either by the hydroborate, by diborane, or by hydrogen.) For these reasons, it was necessary to collect the data for each element individually and to clean the X-ray tube and detector between each run.

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