PHOTOELECTRON SPECTRA OF ACTINIDE COMPOUNDS

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Photoemission spectroscopy applied to chemistry and electronic properties studies is a fairly recent development. The x-ray photoemission spectroscopy (XPS) technique was developed, primarily to be a chemical analysis tool (1). In particular it was observed that the absolute binding energies of the atomic-like electron core levels are dependent on the chemical state of the atom under study. This observation led to the widespread use of XPS for basic and applied chemistry studies. Many studies were also undertaken to better understand the physics of the various excitation processes involved. Consequently, XPS has become a powerful tool for studying electronic structure of the outer electron states in solids.

Proceeding in parallel with XPS was the development of ultra violet photoemission spectroscopy (UPS) (2). This technique exploits low energy photons and must be confined to studies of electron states rather near the Fermi level (E_F). For investigating occupied electron states in the vicinity of E_F , UPS and XPS can serve as excellent complementary spectroscopies.

The actinide element series, like the lanthanide series, is characterized by the filling of an f-electron shell. The chemical and physical properties, however, are quite different between these two series of f-electron elements, especially in the first half of the series. The differences are mainly due to the different radial extension of the 4f- and 5f-electron wavefunctions. For the rare-earth ions, even in metallic systems, the 4f electrons are spatially well localized near the ion sites. Photoemission spectra of the f electrons in lanthanide elements and compounds always show "final state multiplet" structure (3), spectra that result from partially filled shells of localized electrons. In contrast, the 5f electrons are not so well localized. They experience a smaller coulomb correlation interaction than the 4f electrons in the rare earths and stronger hybridization with the 6d- and 7s-derived conduction bands. The 5f's thus

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have a greater tendency toward itinerancy than do the 4f's. The result is that 5f electrons in actinide elements and compounds may reveal itinerant, local, or intermediate behavior. Furthermore, the actinide ions can adopt a variable valence state in chemical compounds and the 5f electrons may participate in bonding.

In this paper, we shall present a brief overview of the application of photoelectron spectroscopy to the study of actinide materials. Some phenomenology will be discussed as will studies of specific materials. Only illustrative examples will be presented (4).

Theoretical Background

Photoemission is viewed as a process wherein an absorbed photon excites an electron within the solid to a final energy state greater than the work function. The electron then migrates to the surface and escapes. Figure 1 shows a schematic representation of the photoemission process. A photon with energy $h\nu$ may excite an electron from some initial state E_i below the Fermi level to a final state E . After moving through the solid to the sample surface, the electron escapes into the vacuum with kinetic energy E_k after having lost energy equal to the work function in overcoming the surface potential barrier. Since the electron kinetic energy E_k is monitored, one has a measure of E and E_i . Thus, with monochromatic exciting radiation, one is able to measure transition probabilities between states which are at known energies relative to E_F . The energy of the exciting radiation for these experiments varies from several electron volts to kilo electron volts. The low energy extreme is referred to as UV photoemission spectroscopy (UPS) and the high energy extreme as x-ray photoemission spectroscopy (XPS). However, the spectrum can be continuously scanned using synchrotron radiation.

Core Level and Localized Valence States

One of the most important capabilities of the XPS technique is the measurement of absolute core level binding energies as a means of probing the local charge state of the ion under study. The oxidation state of the ion can sometimes be clearly discerned. An example is the XPS measurement for the intermediate oxides of uranium, U_3O_8 and U_2O_5 , reported by Verbist et al. (5). Doublet structure in the U 4f lines was attributed to U^{4+} and U^{6+} ions since the 4f peaks appeared with nearly the same binding energies as the 4f lines in UO_2 and UO_3 .

It should be cautioned that photoemission spectroscopic measurements look at energy differences between an n-electron ground state and an n-1 electron excited state. Therefore, photoemission provides a good approximation to ground-state properties

only in the limit when Koopman's theorem is valid (6), i.e., for large electronic systems having extended one-electron wavefunctions like the valence and conduction band states in metallic and semiconducting solids. Koopman's theorem is not valid for core electrons since their wavefunctions are well-localized about the atomic site. Observed core level positions are uncertain, relative to the ground-state core-level energies, by the generally unknown final state relaxation energy. Similarly if a (localized) electron is removed from an incompletely filled outer shell of an ion, different final-state configurations of the ion can lead to experimentally observed multiplet structure (7). These different final states of the ion may be viewed as a form of relaxation which results from intra-atomic correlation effects.

Figure 2 shows XPS data for dioxides of neptunium, plutonium, and americium compared to the appropriate f^n multiplet calculations (8). These multiplet spectra do not represent the multiplet structure of either the f^n or the f^{n-1} configurations. They are, instead, the final state multiplet structure of the f^{n-1} configuration modulated by the transition probability from the f^n ground state to the f^{n-1} multiplets.

Intensities

For quantitative analysis of surface chemical compositions using the XPS technique, measurements of subshell photoionization cross-sections (SPC's) are needed. Problems involved in the determination of relative SPC's from the measurement of relative line intensities in an XPS spectrometer have been discussed by Cardona and Ley (2). The cross-section measurements require an appropriate consideration of the sample concentration, energy dependence of electron analyzer transmission, the angle of the incoming x-ray beam relative to the outgoing electrons and the energy dependence of electron escape depths. Using appropriate compounds, most reported line intensities have been measured relative to the fluorine 1s cross-section. Reference 2 contains a comprehensive tabulation of peak intensities and includes representative levels for most of the elements. Evans et al. (9) have reported the most recent intensity measurements for uranium compounds. These are integrated intensity measurements and include corrections for the experimental considerations cited above.

The multiplet calculations discussed above (see Fig. 2) determine relative intensities within excited multiplets. However, the f electron intensities are not related to s , p , or d intensities.

Calculations of the expected XPS spectra for the actinide dioxides uranium through berkelium were reported by Gubanov et al. (10). Results for UO_2 are shown in Fig. 3 along with experimental spectra. These calculations, extending about 30 eV below the Fermi level, are based on a one-electron molecular-cluster approach.

Intensities were determined using transition probabilities taken from the calculations of Scofield (11). In general, the (energy) positions of features in the calculated spectra correspond well with the experimentally observed features but some calculated intensities do not show good quantitative agreement with experiment.

5f-electrons and Bonding

A. Oxides.

Due to the photon energy dependence of the photoemission cross section for electrons with different orbital angular moments, a capability is available for investigating the role of 5f electrons in bonding. A systematic dependence of the localized 5f electron peak intensity on the degree of oxidation of the uranium atom was found in a series of uranium binary and ternary oxides (8). As the oxidation state of uranium in the oxides is increased, electrons are transferred from the localized 5f states into the "bonding" molecular orbitals which are predominately O 2p in character. Results are shown in Fig. 4 for several binary oxides. The 5f intensities (per electron) are substantially greater than the O 2p's. With increased oxidation, the uranium valence state increases and more 5f participation might be expected in the "bonding orbitals". However, Veal et al. (8) concluded, from a quantitative study of the valence band XPS intensities, that 5f electrons do not appear to significantly contribute to the bonding molecular orbitals. For the hexavalent uranium compounds, it appears that the 5f levels are pushed above E_F . However, molecular cluster calculations for actinide oxides (10) indicate that 5f states do show active participation in the metal-ligand bond.

Complementary studies of the 5f structure in UO_2 were obtained using UPS. Figure 5 shows photoemission spectra of Evans recorded at 21.2, 40.8, and 1253.6 eV (12). The 5f peak near E_F is dominant at 1253.6 eV but is barely discernable at 21.2 eV. Additional spectra of UO_2 at 21.2, 40.8, and 48.4 eV were obtained by Naegele et al. (13). A characteristic of the UO_2 spectra [noted by B. Brandow in Ref. (13)] is that the high binding energy side of the "O 2p" band grows in intensity along with the 5f peak as photon energy is increased. Since the bottom of the 2p band has the Bloch states with the strongest 2p-5f hybridization, these results support the view that 5f electrons hybridize with the O sp's in forming the metal-ligand bond.

B. Intermetallic Compounds.

Binary intermetallic compounds of the light actinides display a wide variety of magnetic and electronic properties that are not well understood. Physical phenomena associated with

itinerant electron behavior, resonance 5f-electron states, spin fluctuations and localized electron behavior can all be found. No single theoretical framework can suitably account for all phenomena observed.

Several NaCl-type binary compounds, including UN, have been analyzed (14) using both theoretical band structure (itinerant) and crystal field (localized) approaches (although the applicability of one of these approaches generally means that the other is inappropriate). UN may be an intermediate case where neither approach will yield very satisfactory results. Photoemission spectroscopy can yield valuable insights into this problem. Figure 6 shows UPS spectra for UN and ThN (15). The strong peak near E_F seen in UN is totally missing in ThN. Since ThN has no 5f occupation but is crystallographically similar to UN, the 5f nature of the peak near E_F is confirmed. Figure 7 shows UPS data at 21.2 and 40.8 eV, again work of Norton et al. (15). The 5f peak near E_F shows the same characteristically strong photon energy dependence that was observed in UO_2 . (The remaining spectral features are associated with s-p electrons.) The very narrow 5f peak seen in Fig. 7 implies that the 5f's occupy a narrow, steeply rising band or that the levels are essentially localized in which case XPS multiplet theory (see above) should be applicable. Taking the latter view in Fig. 7, the calculated multiplet spectrum appropriate for a $5f^3$ ground state is compared to experiment. There is a remarkably good correspondence between theory and experiment, particularly at 40.8 eV where the 5f peak is dominant. For further discussion of these results, see Ref. 4.

Satellite Structure

Satellites appear as peaks on the high binding energy side of the main peak in an XPS spectrum. The lines are generally associated with discrete energy losses called "shake-up" or "shake-off" processes that are attributed to sudden changes in the local atomic charge that accompany electron ejection. These processes involve excitations in the n-1 electron system and are generally described as the low energy excitation of a second electron "concurrent" with primary electron emission (16). The "shake-up" core level satellite spectra are generally sensitive to chemical bonding. Satellite spectra for binary uranium oxides and fluorides are discussed by Pireaux et al. (17). They attribute the dominant satellites to an excitation from an occupied ligand (predominantly O 2p) orbital to an empty or partially filled metal electronic level. This is a "charge transfer" excitation that accompanies the primary photoejection process.

Satellites may also be observable in photoelectron spectra if a 2-hole final state, with similar total energy and the same total angular momentum and parity as the original core hole state, can occur. Bancroft et al. (18) pointed out that there are several energetically favorable examples for such (configuration interaction) satellites in light actinides. Their computed satellite

intensity results, based on the sudden approximation, shows that the 5s, 5p and 6s levels should produce the most prominent satellites. Depending on which low lying final states are involved in the excitation, the process may or may not show chemical sensitivity. Kowalczyk (19) argues that when 5f final states are involved, the effect may be useful for investigating the degree of localization of 5f electrons.

Ligand Field Effects

In a systematic study involving more than twenty uranyl compounds, it was established that the axial ligand field within the uranyl unit can produce substantial splitting in the XPS spectra of the actinide $6p_{3/2}$ core level (8). Figure 8 shows examples of the $6p_{3/2}$ level splittings observed in a sequence of uranyl samples with different primary U-O separations ($U-O_I$). The experimental spectra of the uranyl compounds with the smallest $U-O_I$ separation, including the U $6p_{3/2}$ splitting, is well represented by the characteristic energies obtained from a relativistic molecular cluster calculation (20). An example is shown in Fig. 9. However, to obtain good agreement between theory and experiment for all the uranyls studied, the effect of the uranium second-near neighbors had to be included.

Spin-polarized Photoemission

For magnetically ordered materials, photoemitted electrons have a characteristic spin polarization that reflects the electron spin orientation occurring in the sample before the photoemission process. Recently, techniques have been developed to measure this photoelectron spin polarization (photo ESP) (21). When the measured ESP moment is aligned parallel to the total magnetization, the spin polarization is designated as positive. Because the ESP technique suffers from low measurable intensities of polarized photoelectrons, the usual electron energy distribution (EDC) curves are not measured for polarized electrons. Rather, integrated electron yields for a given photoexcitation energy are measured and the percentage of polarization of the integrated yield is determined. The photon energy dependence of the polarization gives information on the net spin of the electrons within $\hbar\omega - \phi$ (ϕ is the work function) of the Fermi level. Measurements are usually reported for photon energies between 4 and 11 eV.

Photo ESP measurements have been reported for the series of intermetallic compounds US, USe and UTe (21). The ESP for these compounds is negative for all $\hbar\omega$. The magnetic moment of uranium compounds is predominately determined by the occupied 5f electrons. However, the photoyield of the f-electrons at photon energies less than 11 eV is very small relative to s, p or d electron yields. Thus, the observed photoelectron spin

polarization must result from conduction electrons that are polarized by the electrons in the partially filled f shell. These polarization results are consistent with results derived from magnetization, nuclear magnetic resonance and neutron scattering measurements (4,22).

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Figure Captions

- Figure 1. Schematic representation of photoemission process for a metal. A monochromatic photon $\hbar \omega$ excites an electron from initial state E_i to final (vacuum) state E . The electron escapes with kinetic energy E_k after passing through sample surface having work function ϕ . For fixed $\hbar \omega$, monitoring photoemission intensity I vs. E_k measures transition probabilities between states E_i and E . Valence states as well as core states can be observed.
- Figure 2. XPS spectra of localized 5f states in three actinide oxides compared to calculated final state multiplet spectra. The calculated multiplets are broadened to simulate experiment.
- Figure 3. (a) Measured and (b) calculated UO_2 XPS spectra. The solid line in (b) has Lorentzian broadening of 0.4 eV, the dashed line 0.9 eV to simulate experiment.
- Figure 4. XPS valence spectra of several uranium oxides. The U 5f peak near E_F is attenuated with increasing uranium oxidation.
- Figure 5. Photoemission spectra for UO_2 taken at photon excitation energies of 21.2 eV (He I), 40.8 eV (He II) and 1253.6 eV ($\text{MgK}\alpha$). The U 5f electrons (peak A) have a very different dependence on photon energy than the O 2p's (peak B).
- Figure 6. UPS spectra for UN and ThN. The strong peak in UN which appears near E_F corresponds to U 5f electrons.
- Figure 7. UPS spectra for UN at 21.2 and 40.8 eV. The lower curve is a calculation of the final state multiplet structure for the $5f^2$ final state.
- Figure 8. XPS spectra of three uranyl compounds taken within 40 eV of E_F . The "U $6p_{3/2}$ splitting" varies with U-O_I separation δ .
- Figure 9. Comparison between experimental XPS spectrum and calculated energy levels for the uranyl compound UO_2CO_3 .

BINDING ENERGY (eV)

a

UO₂

b

UN

$h\nu = 40.8 \text{ eV}$

$h\nu = 21.2 \text{ eV}$

$f^3 \rightarrow f^2$

12

8

4

$E_f = 0$

BINDING ENERGY (eV)