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ELECTRONIC STRUCTURE OF URANYL COMPOUNDS - AN XPS STUDY

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ELECTRONIC STRUCTURE OF URANYL COMPOUNDS - AN XPS STUDY*

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ABSTRACT

X-ray photoemission spectroscopy (XPS) measurements are reported for a series of uranyl compounds in which the primary uranium-oxygen ($U-O_I$) separation varies substantially. We report the observation of crystal field splittings of the U $6p_{3/2}$ core electron energy levels. These splittings are explained with the point charge crystal field model when both first and second near uranium neighbors are considered. The systematics of charge migration (observed by monitoring electron core level shifts) associated with bonding in the uranyl series were also investigated. Core level shifts for compounds with different $U-O_I$ separations are large but essentially no relative shifts of uranium and oxygen core levels were observed within the uranyl group. Thus charge appears to flow between the uranyl group (as a unit) and the secondary uranium ligands as $U-O_I$ is varied. We have also studied U 5*f* electron participation in covalent bonding by systematically measuring XPS line intensities; U 5*f* electron occupation appears to be minimal.

I. INTRODUCTION

Many hexavalent uranium compounds contain a very stable symmetric linear chain UO_2^{++} group. Although this unit, called the uranyl group, has been studied for more than a century, the electronic structure has not been well understood. In this paper we report X-ray photoemission spectroscopy (XPS) studies on a series of uranyl compounds. We have investigated

1) crystal field effects resulting from the strong axial electric field within the uranyl ion,

2) U 5*f* electron participation in chemical bonding,

3) charge migration associated with bonding as determined by relative shifts in core level spectra.

Each of these studies relies on the systematic dependence of observed properties for a number of uranyl compounds in which the primary uranium-oxygen separation ($U-O_I$) can be varied substantially. We examined over 20 compounds with $U-O_I$ distances spanning the range between 1.7-2.1Å.

II. EXPERIMENTAL

The XPS spectra were obtained with a Hewlett-Packard 5950A X-ray photoelectron spectrometer using a monochromatized aluminum X-ray source with a resolution of ∿0.55 eV. In all cases, data were taken on powder samples pressed into indium substrates. The indium was supported in the shallow machined hole of a gold-plated stainless steel platen (holder) which could be directly inserted into the spectrometer. The indium 3*d* and 4*d* core levels were monitored to see if the XPS spectra might be influenced by any exposed indium surface. However, the samples were sufficiently thick so that no indium lines were observed through the pressed powder.

Uranyl oxalate was a reagent grade chemical which was used as received: $\gamma-UO_3$ was obtained as a granular fluidized-bed product which was ground to <325 mesh and dried to 500°C before use. Most of the remaining compounds were prepared by established procedures. [1-8]

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The uranyl group is almost always linear but the U-O_I bond lengths vary as a function of the other ligands present in the compound. Coordination of the uranyl group about the equatorial plane, usually with oxygen or halogen atoms, may be 4, 5, or 6. [9,10] The two axial or uranyl oxygen atoms form the primary bonds with uranium (U-O_I); those in the equatorial plane form secondary, weaker bonds (U-O_{II}).

Such structural information as size, geometry, and coordination properties of the hexavalent uranium-oxygen systems can best be obtained from X-ray and neutron diffraction data, but infrared spectroscopy has been shown to be useful in the estimation of U-O_I bond lengths. [11] In the present investigation, the U-O_I distances are derived from the asymmetric vibration frequency (ν) obtained from infra-red data [1-6, 12-16] using the empirical relationship (with R in Å and ν in cm^{-1})

$$R_{U-O_I} = 83.6\ \nu^{-2/3} + 0.864 \qquad (1)$$

III. ELECTROSTATIC SPLITTING OF U $6p_{3/2}$ LEVEL

The valence band XPS spectra of UO_2F_2, $Li_2U_3O_{10}$ and Na_2UO_4 are shown in Fig. 1. This series provides a reasonably clear example of the electronic structure

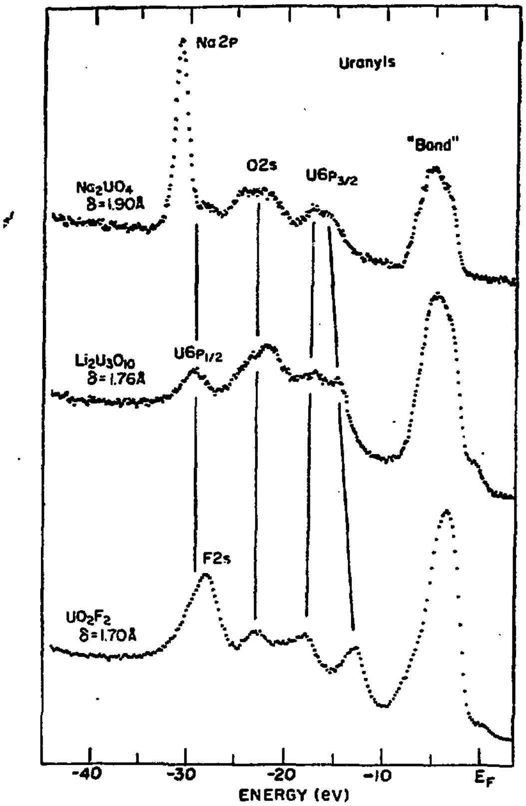

Fig. 1. XPS spectra for three hexavalent uranium compounds showing the electronic levels within 50eV of the Fermi level. The crystal field splitting of the U $6p_{3/2}$ level varies with the U-O_I separation δ.

within 50eV of the Fermi level (E_F), common to most of the compounds discussed in this paper and a demonstration of the differing degree of the U $6p_{3/2}$ level splitting. Previously reported [17] XPS studies of uranium and uranium compounds have, for the most part, established the identification of XPS spectral features in this energy range. However, doublet structure observed in oxides of uranium located near -15 eV, in the vicinity of the U $6p_{3/2}$ level, has not been unambiguously identified. We believe that the suggestion made by Verbist et al [18] that it might be due to a second bonding band between uranium and oxygen is incorrect. After systematically examining this structure, we conclude that it results from electrostatic splitting of the U $6p_{3/2}$ level. The systematic variation of the $6p_{3/2}$ level splitting with U-O_I bond length is presented graphically in Fig. 2.

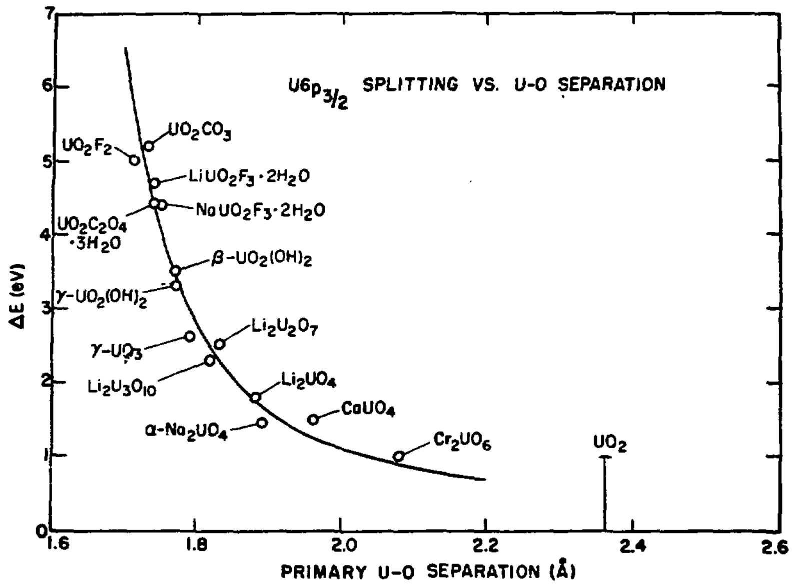

Fig. 2. XPS measurements of the crystal field splitting of the U $6p_{3/2}$ level for a series of uranium compounds plotted vs. U-O_I separation.

The XPS measurement provides a final-state observation; that is spectra are to associated with states of the n-1 electron system rather than the ground state n electron system under examination. Consequently, the p-electron energy level scheme observed is associated with the $6p^5$ configuration. A semiquantitative explanation of the observed splitting can be obtained by examining the crystal field perturbation on the spin-orbit split J = 3/2 level of the 6p electron shell. *The axial field (produced by the charge of the primary and secondary* ligands) on the uranium ion splits the J = 3/2 level into $M_J = \pm 3/2$ and $M_J = \pm 1/2$ substates; the J = 1/2 level preserves its 2-fold degeneracy in the axial field (as observed in the experiment). The splitting of the U $6p_{3/2}$ level is

$$\Delta E p_{3/2} = \langle \Gamma_b | V | \Gamma_b \rangle - \langle \Gamma_a | V | \Gamma_a \rangle \,, \tag{2}$$

where Γ denotes the appropriate crystal field wave function and V is the crystal field potential.

Now consider a simple crystal field model of a uranium ion at the origin of a three dimensional cartesian coordinate system surrounded by six ligands with charge Z. Two of the ligands are located along the z-axis. These ligands and the uranium atom represent the uranyl ion.

The separation between the uranium ion and the ligands is equal to δ. The other four ligands with charge Z are located at positions along the x- and y-axes at equal distances b from the origin. The electric potentials generated by the six point charges which influence the uranium 6p electrons are [19]

$$V = \sum_{i=1}^{6} V_i \tag{3}$$

where the terms are

$$\left.\begin{aligned} V_1 + V_2 &= \frac{2Ze^2}{\delta}\left[1 + \frac{1}{2}\left(\frac{r}{\delta}\right)^2\left(\frac{3z^2}{r^2} - 1\right)\right] \\ V_3 + V_4 &= \frac{2Ze^2}{b}\left[1 + \frac{1}{2}\left(\frac{r}{b}\right)^2\left(\frac{3x^2}{r^2} - 1\right)\right] \\ V_5 + V_6 &= \frac{2Ze^2}{b}\left[1 + \frac{1}{2}\left(\frac{r}{b}\right)^2\left(\frac{3y^2}{r^2} - 1\right)\right] \end{aligned}\right\} \tag{4}$$

Simple algebraic manipulation yields

$$\Delta Ep_{3/2} = Ze^2\left(\frac{1}{\delta^3} - \frac{1}{b^3}\right)\left[\langle\Gamma_b|r^2\left(\frac{3z^2}{r^2} - 1\right)|\Gamma_b\rangle - \langle\Gamma_a|r^2\left(\frac{3z^2}{r^2} - 1\right)|\Gamma_a\rangle e\right]$$

$$= \text{Constant}\left(\frac{1}{\delta^3} - \frac{1}{b^3}\right). \tag{5}$$

In the limit as b becomes large, we have the axial field corresponding to the isolated uranyl ion. If δ = b, as in the case of octahedral symmetry, no splitting of the $p_{3/2}$ state results.

The constant can be evaluated for this simple point charge model using atomic wave functions. We obtain

$$\Delta Ep_{3/2} = (8.98\text{A}^{\circ 3}\text{eV})Z\left(\frac{1}{\delta^3} - \frac{1}{b^3}\right). \tag{6}$$

For the uranyl series, excellent quantitative agreement is obtained between the measured XPS U $6p_{3/2}$ splitting and the predicted splitting from the point charge model when the effect of the secondary uranium ligands is included in the crystal field calculations and Z is appropriately adjusted. If we use Z = 3.4 and make use of the experimental δ and b values [1-7, 12-16, 20-24] (infra-red values for δ) to evaluate Eg. (6), we obtain the diamonds shown in Fig. 3. The circles are the XPS measurements of $\Delta Ep_{3/2}$ for the uranyl series. Some disagreement exists only for those compounds with very small $U\text{-}O_I$ separation; UO_2F_2, UO_2CO_3, $UO_2C_2O_4 \cdot 3H_2O$, $LiUO_2F_3 \cdot 2H_2O$ and $NaUO_2F_3 \cdot 2H_2O$. Unlike the assumed model, several of these compounds have secondary ligands which are a different element than the primary ligands. If, for the small δ samples, the charge on the secondary ligands is reduced to about one-half the charge (Z = 3.4) on the uranyl group oxygen, the results of theory and experiment are also in agreement.

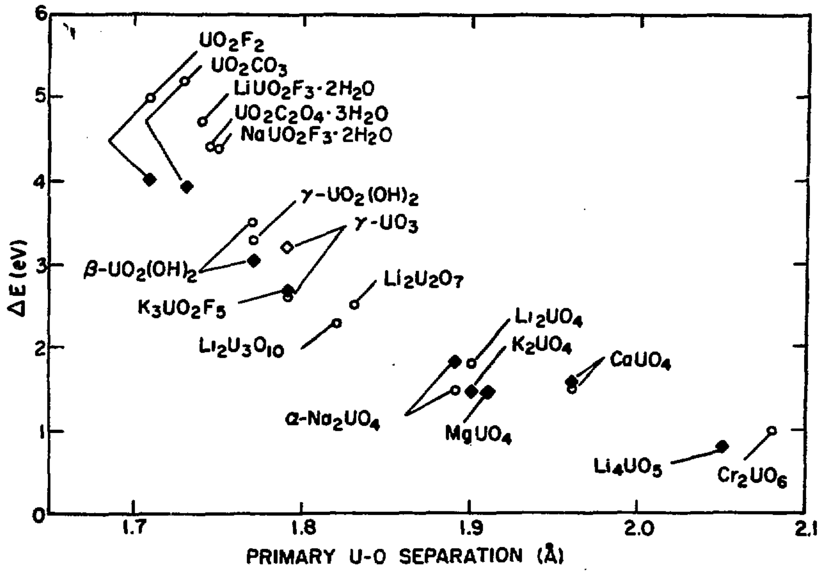

Fig. 3 - XPS measurements of crystal field splittings of the U $6p_{3/2}$ levels (circles) vs. U-O_I plotted with the crystal field theory results of Eq.6 (diamonds) using experimental measurements for δ and b.

The point charge model represents a rather crude approximation to the charge distribution in the real crystal. Thus little significance should be attributed to the magnitude of the derived Z value. Not all of the samples can be accurately represented by the distorted octahedral field since a number of them contain 6 second near neighbors in the equatorial plane. For simplicity in investigating the systematics of the series, however, only the distorted octahedral coordination was considered. [The particularly simple form of Eq. (5) is obtained only for this coordination.] In any case, use of the four second neighbors should provide a much better representation of the axial field in the real crystal than is provided by the isolated UO_2^{++} ion. The remarkably good functional agreement between theory and experiment (with a suitable estimate of the ligand charge) provides convincing evidence that the $p_{3/2}$ splitting is a crystal field effect.

IV. URANIUM 5*f* ELECTRONS AND BONDING.

It has been proposed [25] that the 5*f* electrons in the light actinides are sufficiently delocalized so that they might participate in covalent bonding. From symmetry considerations alone, one might expect such bonding to occur between the oxygen 2p electrons and the U5*f*'s. This expectation is unhanced when we recall that atomic uranium has three occuped 5*f* states and all valence electrons of hexavalent uranium must directly participate in the bond. Previous XPS studies of uranium oxides [26], however, indicated that 5*f* participation in bonding must be minimal in the oxides. In this paper we have sought to discover the role played by the U 5*f* electrons in covalent bonding in the hexavalent uranium (uranyl) compounds. Recognizing that the intensity of a given XPS line is a strong function of the quantum numbers of the energy level associated with that line, we have systematically examined intensities of a series of uranium compounds with valences spanning the range 4 to 6. In order to provide a consistent internal calibration, we have plotted the intensity of the "bond" (predominantly O2p) normalized to the U $4f_{7/2}$ core line versus the oxygen-to-uranium ratio (O/U) for a given compound. Since the intensity of the U $4f_{7/2}$ line should scale with the uranium concentration (for a given set of experimental conditions and comparably prepared samples), then the intensity of the "bond", if the bond is made up solely of p-electrons, should correspondingly scale with oxygen concentration. For this case,

$$I_{Bond}/I_{U\ 4f_{7/2}} \propto O/U \ . \tag{7}$$

On the other hand, if the *5f* electrons participate in the bond, then we can chemically modulate the number of *5f* electrons in the bond simply by varying the uranium valence. For example, in UO_2, there are two *5f* electrons remote (in energy) from the bond [27] and hence at most one *5f* in the bond. In UO_3, however, there are no *5f* electrons outside the bond so that as many as three *5f* electrons might appear in the bond. Since the intensities (cross section for photoemission) of the U *5f*'s and the O2p's are very different, Eq. (7) should fail badly for *5f* participation in bonding providing that the intensities of the *5f* <u>bonding</u> electrons were comparable to intensities of the *5f* <u>non-bonding</u> electrons.

Fig. 4 shows $I_{bond}/I_{U\ 4f_{7/2}}$ plotted versus O/U for series of compounds spanning the O/U ratio from 2 to 4. A background correction was subtracted out of the

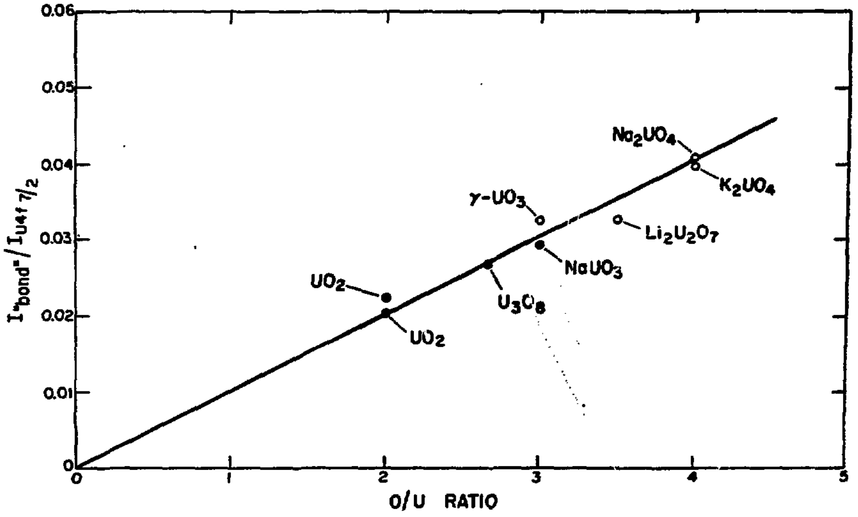

Fig. 4 - The XPS "bond" intensity (normalized to the U $4f_{7/2}$ level intensity) plotted vs. oxygen-uranium ratio. The linear result indicates that the "bond" has predominately O2p character. The solid points represent samples having occupied *5f* states.

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measured intensities. Within experimental error, we find that Eq. (7) is satisfied and even includes the point (0,0). Thus the argument seems sound that U 5*f* electrons must participate minimally in covalent bonding. Rather, it would appear that, in the compounds, all U 5*f* levels must be pushed up above the Fermi level.

V. CHARGE MIGRATION ASSOCIATED WITH BONDING

XPS is, for the most part, used to study core level binding energies and shifts associated with chemical bonding. The core level energies are sensitive to local atomic charge and, hence, charge transfer toward or away from a given atom is reflected in a relative shift in the binding energy of the core electron energy levels of that atom. Because of the similarity of the uranyl group within the series of hexavalent uranium compounds, a systematic study of relative level shifts between different uranyls should provide useful insight into the chemical bond.

For insulating materials, sample charging problems cause considerable difficulty for absolute binding energy measurements. To minimize this problem, we recorded relative core level energies of a mixed powder sample of two compounds in which one of the compounds was always present and served as a standard. The variation in the compensation of the charging effect by the electron-flood gun during the experiment can thus be minimized.

In our experiment, UO_2F_2 (δ= 1.7Å), was used as standard and was mixed with γ-UO_2 (1.79Å), Li_2UO_4(1.90Å), $CaUO_4$(1.96Å) or Cr_2UO_6 (2.08Å). In all cases the U 4*f* levels of the difluoride were easily distinguished from those of the mixed component. The O 1s levels were also recorded. A comparable shift of the O 1s and U 4*f* peaks relative to those of UO_2F_2 was observed for each mixture. For example, in $CaUO_4$, the U 4*f* shift was 3.3 eV and the O 1s shift was 3.4 eV in the same direction (toward lower binding energy). As the U-O_I distance is decreased across the uranyl series, charge apparently transfers away from the immediate vicinity of both the uranium and the oxygen atoms. This indicates that the role of the uranium second near neighbors becomes important. The second-near ligands, which are responsible for the small U-O_I distances, apparently pull charge away from the entire uranyl group as a unit, with these shifts being modulated by the second neighbor elements. The charge transfer, like the splitting of the U $6p_{3/2}$, thus appears to be controlled by the uranium second neighbors.

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