

Electronic Supplementary Information

Theoretical Analysis of the U L₃-Edge NEXAFS in U Oxides

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1. Details of calculations.

Our theoretical treatment is based on embedded cluster models of the oxides. For the octahedral UO₆ clusters, there is a central U atom and its 6 nearest neighbor O anions which are embedded in a point charge field with charges corresponding to the nominal ionicities; [1, 2] The point charges are placed at lattice sites. For the U(IV) fluorite structure of UO₂, the cluster is UO₈ with the U cation at the center of a cube and the O anions at the vertices; the point charge embedding atoms are at lattice sites, again with charges corresponding to the nominal ionicities. [3] For the ground and excited state configurations, we use optimized orbitals, four-component spinors, which are solutions of suitable Dirac-Fock self-consistent field equations, [4] The orbitals for the ground state of the clusters are optimized for the average of configurations that can be formed by distributing 0 for U(VI), 1 for U(V), or 2 for U(IV) electrons over the nearly degenerate open shell spinors of dominantly 5f character. [2-4]. However, we stress that the open shell spinors are not pure U 5f but are anti-bonding combinations of U(5f) and ligand 2p orbitals while the closed shell orbitals of suitable symmetry are bonding combinations between U and oxygen. [1, 2, 5] For the optimized four-component spinors, this covalent mixing is considerable. [1] The ground state WF is a configuration mixing, CI, WF where the determinants that can be formed by placing the electrons in all possible ways over the open shell spinors are mixed. The CI WF's and energies are determined by diagonalizing the exact Hamiltonian matrix over these determinants. For the NEXAFS excited states, the orbitals are optimized for the 2p_{3/2} ion; specifically for an average of configurations that can be formed for 3 electrons in the U 2p_{3/2} shell and the open shell valence electrons as distributed for the ground state configuration. Excitations are then made into the g or gerade symmetry virtual orbitals of the calculations

for the $2p_{3/2}$ ion. The use of virtual orbitals for the ion to describe the NEXAFS excited states has been used before successfully to treat excitations in light molecules. [6-8] For the virtual orbitals, the 22 lowest lying spinors with g symmetry are selected to form the NEXAFS excited states; only g symmetry is considered since these are the only dipole allowed transitions. An important caution is that the energies of the more diffuse orbitals in this set, the 7s and 7d orbitals, are artificially lowered in energy because of the point charge embedding which does not include effects of Pauli exclusion to compress the anion orbitals. [9] However, since the states where these orbitals are dominant do not carry significant transition intensity, the artifacts do not affect our predicted spectra. The diffuse orbitals are included to allow a more accurate representation the 6d orbitals which carry the main L_{3} -edge NEXAFS intensity. With these orbitals, we construct CI wavefunctions by mixing determinants for the following configurations or distributions of electrons over sets of shells. There are 3 electrons in the $2p_{3/2}$ shell, 1 electron in the 6d, 7d, and 7s shells, and 0, 1, or 2 in the valence open shell of 14 spinors for U(VI), U(V), and U(IV), respectively. We stress that these CI wavefunctions give reasonable descriptions of the intermediate angular momentum coupling between the different open shells [10] where the errors are small, especially compared to the lifetime broadening of the NEXAFS excitations considered. This is discussed further below for U(IV).

The relative NEXAFS intensities, I_{rel} , between the total WF's for the initial, Ψ_i , and the i^{th} final state, $\Psi_f(i)$, are computed with transition matrix elements between the many electron WF's as $I_{rel}(i) = \sum_j | \langle \Psi_i | r_j | \Psi_f(i) \rangle |^2$. For I_{rel} , we do not include the term $(\Delta E)^3$ involving the excitation energy from the ground to the NEXAFS excited state [11] because the energy range of interest for the NEXAFS is small compared to the total excitation energy and ΔE is essentially constant over this range. Since different sets of optimized orbitals are used for the initial, ground, and final, NEXAFS, excited states, the calculation of the dipole matrix elements require the evaluation of co-factors of the determinant of overlap integrals between the two sets of orbitals. [12, 13] In order to compare with experiment, we broaden our directly computed I_{rel} with a Voigt convolution where we estimate that the instrumental broadening for the

measurements is 3 eV. This estimate may be a lower bound since a considerably larger instrumental resolution of 5 eV for the L₃-edge of UF₄ has been reported. [14] Furthermore, we limit our comparison with experiment to the region around the NEXAFS maximum, or white line, and we do not consider higher excitations. The higher excitations involve excitations to the continuum [15] which we have not included in our theoretical model where the focus is on the excitations to discrete levels, important for the white line features.

The orbital optimizations and the CI wavefunction calculations were performed with the Dirac program system. [16] The Gaussian basis sets used are uncontracted and of double or triple zeta quality in the valence region; they are described elsewhere. [5] We have computed the transition dipole matrix elements rigorously with CLIPS programs [17] modified to interface with the output of the Dirac calculations. This is an extension of the program described in Ref. [18]

2. U(V) Excited States.

For U(V), where there is a valence open shell electron in the dominantly U 5f shell, the determinants for the NEXAFS final states have 3 electrons in the 2p shell, one electron in one of the 14 spin-orbit and ligand field split 5f spinors and one electron in the virtual space with 22 spinors. The angular momentum coupling of the 5f and the NEXAFS excited spinors gives rise to a large number of determinants. For example placing 1 electron in one of the 10 6d spinors and 1 electron in the 14 5f spinors leads to 140 determinants, many of which will recouple with the 2p_{3/2} hole to give rise to dipole allowed states. It is clear from Fig. 1(b) for the U(V) NEXAFS, that many terms, not just 3 as for U(VI), contribute to the total spectra. Because of the near degeneracies of the 1232 determinants that are formed by distributing electrons over the different spaces, there is significant mixing of different configurations in the final states. Despite this mixing, it is possible, as we did for U(VI), to associate the features that have the highest intensity, with excited states separated by ligand field splitting of t_{2g} and e_g orbitals.

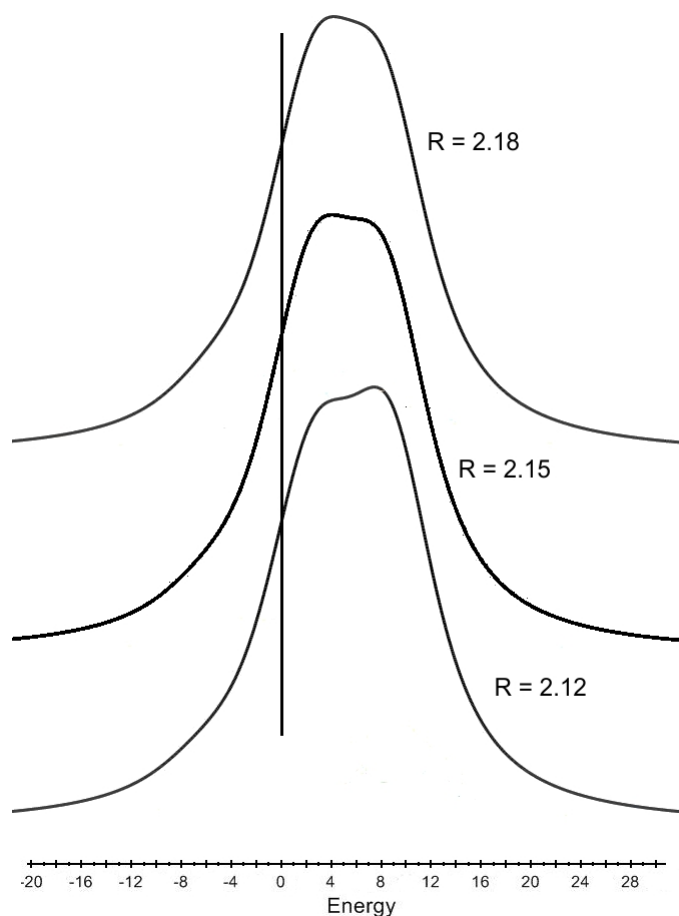
In order to better understand the influence of $d(\text{U-O})$ for the $\text{U(V)} L_3$ -edge NEXAFS, we examined two other distances, one larger, $d(\text{U-O})=2.18\text{\AA}$, and one shorter, $d(\text{U-O})=2.12\text{\AA}$, than the nominal $d(\text{U-O})=2.15\text{\AA}$. These distances represent a modest range of $d(\text{U-O})$ about the value used in the main text. The NEXAFS for these three distances are compared in Fig. S1. The change in the FWHM for U(V) is similar to that discussed in the main text for U(VI) . The FWHM are 14.45 eV for $d(\text{U-O})=2.12\text{\AA}$, 14.10 eV for $d(\text{U-O})=2.15\text{\AA}$, and 13.80 eV for $d(\text{U-O})=2.18\text{\AA}$. This variation of FWHM is fully consistent with our analysis that associates the NEXAFS broadening with distant dependent covalent mixing of the $\text{U}(6d)$ with $\text{O}(2p)$. Furthermore, all three spectra have a comparable width and all have a relatively flat top indicating that the change in the branching ratio between the e_g and t_{2g} excited is smaller for variation of $d(\text{U-O})$ for U(V) than for U(VI) .

3. U(IV) Excited States.

For U(IV) , there are now two electrons in the dominantly $\text{U } 5f$ open shell and this considerably increases the number of states that can arise from the angular momentum coupling of the dominantly $5f^2$ open shell electrons with each other, with the $2p_{3/2}$ open core shell, and with the NEXAFS excited orbitals. There are 8008 determinants for these open shell occupations. In particular, for the isolated U^{4+} cation, the 91 states for the $5f^2$ configuration couple to 13 terms. The highest $J=0$ term is not observed but the 12 terms that are observed are spread over an energy of 3 eV. [19] With our open shell CI to represent intermediate angular momentum coupling for the U^{4+} cation, we find a spread of energies 0.8 eV larger than experiment with errors for the excitation energies to higher levels of ~ 0.6 to 1.0 eV. From work on lighter atoms, the angular coupling errors can be corrected by including many-body excitations from semi-core levels. [20, 21] However, given the large lifetime and instrumental broadenings in the measured and broadened theoretical spectra, these errors should not dramatically affect the predicted spectra which is shown in Fig. 1(c). Even more individual final states contribute to the NEXAFS for U(IV) than for U(V) . The smaller number of individual contributions to the total NEXAFS spectra shown in Fig. 1(c) than shown in Fig. 1(b) is misleading since the individual contributions shown in the figure are obtained by summing intensities in groups with an energy range of 0.02 eV. Hence, each individual

contributing curve in Fig. 1 may include contributions from several nearly degenerate states. The smaller number of contributing individual curves in Fig. 1(c) is simply a reflection of there are many degenerate and nearly degenerate terms contributing to the 8008 different determinants for the open shell system. The large number of nearly degenerate states is a reason that the analysis in terms ligand field split levels is successful despite the large number of terms arising from the angular momentum coupling of these levels with the other open shells.

Figure S1. Comparison of theoretical L_3 -edge NEXAFS for octahedral U(V) modeled by an embedded UO_6 cluster for $d(U-O)=2.12, 2.15, \text{ and } 2.18\text{\AA}$. The Voigt broadening is a convolution of a 7.5 eV Lorentzian and 3.0 eV Gaussian. All curves are aligned so that their inflection points are at $E_{\text{rel}}=0$.



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17. *CLIPS is a program system to compute ab initio SCF and correlated wavefunctions for polyatomic systems. It has been developed based on the publicly available programs in the ALCHEMY package from the IBM San Jose Research Laboratory by P. S. Bagus, B. Liu, A. D. McLean, and M. Yoshimine.*
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