Many-body effects in the $4f$ x-ray photoelectron spectroscopy of the U^{5+} and U^{4+} free ions

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A strictly *ab initio* many-electron theory was used to calculate the $4f$ x-ray photoelectron spectroscopy (XPS) of the free U^{5+} and U^{4+} ions. The calculations, based on relativistic Dirac-Fock self-consistent field (DF-SCF) and Dirac configuration interaction (DCI) wave functions (WF's), indicate that the atomic spectra have a considerable multiplet structure. However, the multiplet splitting, which is mainly manifest as a broadening of the $4f_{5/2}$ and $4f_{7/2}$ lines, is not as strong as for the first-row transition metals. As expected, the U^{4+} primary peaks are broader and have more associated satellite structure than does U^{5+}. A comparison of a synthetic spectrum for U^{4+} with the observed XPS of UO_2 indicates that interatomic, solid-state, effects may decrease the multiplet and spin-orbital splitting, relative to the free ion. Notably, the 7 eV satellite characteristic of UO_2 is absent from the calculated XPS of U^{4+}.

I. INTRODUCTION

Identification of the oxidation states of U with x-ray photoelectron spectroscopy (XPS) normally relies on some combination of determining the $5f$ intensity, the binding energies (BEs) of the $4f$ core level, and the BE separations of the $4f$ satellites and core peaks. In particular, satellites at 6.5–7, ~ 8.5, and both ~ 4 and ~ 10 eV higher BE than both the $4f_{7/2}$ and $4f_{5/2}$ primary peaks are associated with the tetravalent, pentavalent, and hexavalent oxidation states of U, respectively.[1–3] Quantitative values for U^{4+}-U^{5+}-U^{6+} concentrations are usually obtained by curve fitting the main $4f$ peaks with 2 or 3 components of equal full width at half maximum (FWHM) or, more rarely, by curve fitting both satellite and core peaks in a coherent model.[4] At least two issues are apparent in such analyses: first, to what extent are the satellite features dependent on the bonding environment and, second, is the assumption of equal component FWHM appropriate? The use of U^{4+} and U^{6+} components of equal FWHM appears justified from numerous XPS and BIS studies of monovalent uranium oxides which indicate that the multiplet splitting (MS) is small relative to the open-shell $3d$ metals. Still, one would expect that the extent of MS, and hence peak broadening, should depend on oxidation state; in particular, when comparing closed shell U^{6+}, $5f^0$, to the open shell lower valence states of U. Consequently, the extent to which the U$4f$ spectra (core plus satellites) depends on intra and inter atomic effects is an open question.

One starting point for investigating these issues is with theoretical calculations for the XPS spectra of U free ions that explicitly include many-body effects. In this paper, we present *ab initio* many-body calculations for the $4f$ XPS of the free U^{5+} and U^{4+} ions; no parameters in these calculations have been adjusted to fit experimental data. To the best of our knowledge, this is the first rigorous theoretical study of atomic many-body effects for the XPS of U. Our *ab initio* theoretical XPS spectra for the $U^{5+}(5f^1)$ and $U^{4+}(5f^2)$ atomic cations are determined from Dirac-Fock wave functions (WF's).[5] Our theoretical procedure is similar to that used by

Gupta and Sen[6,7] for describing the atomic effects important for the XPS of transition metal (TM) systems. The calculated spectrum for U^{4+} is then compared to an experimental spectrum for UO_2. Differences between the theoretical and observed spectra likely highlight interatomic contributions to the XPS.

II. MATERIALS AND EXPERIMENTAL METHODS

The experimental data for UO_2 was obtained with a Scienta ESCA-300, housed at Lehigh University, which employs a high flux of monochromatic Al $K\alpha$ x-rays. The analyzer operating parameters of 150 eV pass energy and a 1.1 mm slit yielded a Fermi level width of 0.41 eV for Ag metal. A monochromatic low-energy electron flood gun was used to help neutralize charge build up at the sample surface. Spectra were acquired at a 90° takeoff angle and consisted of high-resolution regional scans over line positions of the elements of interest. The analytical area was about 8 mm $\times 300$ μm. U peak positions were referenced to the BE of C$1s$, for adventitious carbon, at 285.0 eV.[8]

A single crystal of UO_2 was scraped under UHV and analyzed. The resulting XPS is shown in Fig. 1 and it reveals for the main U$4f_{7/2}$ peak a FWHM of 2.0 eV, and a BE of 380.0 eV. Satellites occurred at ~ 6.7 eV higher BE than and with about 15% of the intensity of the main U$4f_{7/2}$ and U$4f_{5/2}$ peaks. The BE of the primary peaks and satellite positions are consistent with UO_2 values from the literature and a FWHM of 2 eV is well within the range of previously reported values for UO_2. A small asymmetry on the high BE side of the U$4f_{5/2}$ satellite might indicate minor nonstoichiometry as UO_{2+x}.

III. THEORY: METHODS AND RESULTS

A. Theoretical methods

The relative energies, E_{rel}, and the relative intensities, I_{rel}, for the $4f$ XPS of $U^{5+}(5f^1)$ and $U^{4+}(5f^2)$ are based on relativistic Dirac-Fock self-consistent field (DF-SCF) and Dirac
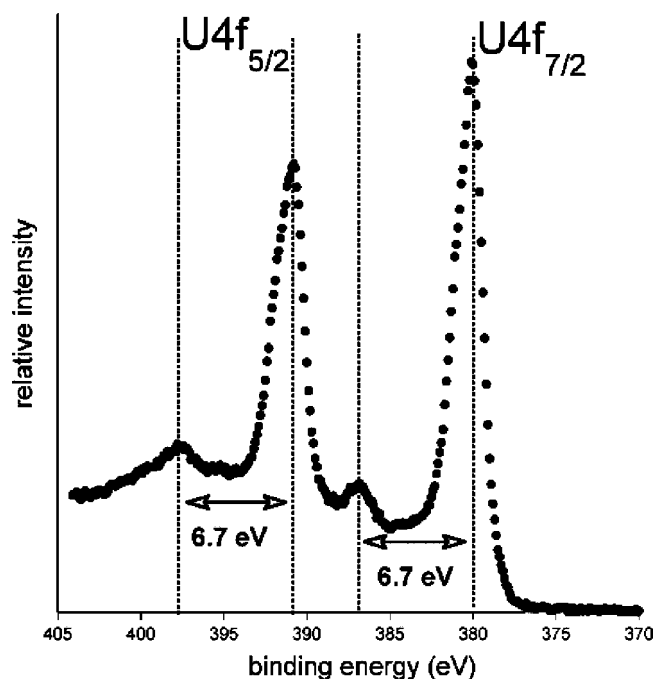
FIG. 1. Experimental XPS of UO_2 as described in Sec. II of the text.

configuration interaction (DCI) WF's. These atomic WF's were computed with the MOLFDIR program package developed at the University of Groningen.[5] The four-component relativistic spinors used for the DCI WFs were optimized with DF-SCF calculations for the average of configurations for the $5f^1$ and $5f^2$ open shell occupations of U^{5+} and U^{4+}, respectively. The differences between WF's using spinors optimized separately for each level of interest and those using spinors optimized for the average of configurations is likely to be small for open d and open f shell systems.[9,10] Here, we used the spinors optimized for the ground state to describe the $4f$ core-hole states. This approach, also taken by Gupta and Sen,[6,7] does not take into account the contraction of the atomic outer orbitals due to the presence of the core hole. These orbital contractions lead to substantial decreases of absolute core level BE's.[11] However, previous work[9,12] suggests that contracted, final state, orbitals yield only small, ~0.25 eV, increases in the E_{rel} of the various multiplet split peaks compared to calculations[6,7] using only the initial state orbitals.

The ground state spinors for each U cation are then used to determine DCI WF's for the ground and $4f$ core-hole levels of the cation. For the ground state DCI WF's, the one or two $5f$ electrons for U^{5+} and U^{4+}, respectively, are distributed in all possible ways over the 14 $5f$ spinors. This CI allows for mixed, or intermediate, j-j and Russell-Saunders L-S coupling in the $5f$ shell.[13] Of course, for U^{5+}, the configurations are either pure $5f^1_{5/2}$ or pure $5f^1_{7/2}$; where the spin-orbit splitting makes the $J=7/2$ level an excited level at 0.9 eV above the lowest $J=5/2$ level. For U^{4+}, the $5f^2_{5/2}$ configuration contributes 96% of the WF's for the lowest level, $J=4$; the next higher level is $J=5$ at 0.7 eV above the lowest $J=4$ level. Thus the $J=4$ level is the clear choice for the initial states of the XPS. For the $4f$ ionized DCI WF's,

the configurations considered have 13 electrons distributed over the 14 $4f$ spinors coupled with one (U^{5+}) or two (U^{4+}) electrons distributed over the 14 $5f$ spinors. This CI includes two types of atomic many-body effects.[12] The first, as we noted above, is the intermediate j-j and L-S angular momentum coupling within the $5f$ shell. The second is the angular momentum recoupling within the $5f$ shell to form configurations that can couple with the open $4f$ shell to give a total J level of the correct value for XPS ionization.[6,7,9,10,12] Roughly, this recoupling can be viewed as a spin flip within the open $5f$ shell and a simultaneous spin flip within the $4f$ shell that preserves the total symmetry of a state. While Clebsch-Gordon algebra is required to compute diagonal and off-diagonal Hamiltonian matrix elements,[6,7] this analogy provides a physical way to understand the angular momentum recoupling. These many-body effects are the dominant intra-atomic contributions for the $2p$ and $3p$ XPS of $3d$ TM's and it is reasonable to expect that they will also be the dominant effects for the atomic contributions to the U($4f$) XPS.

The role of the atomic many-body effects is best understood if it is recalled that the two XPS allowed ionic configurations involve removing either a $4f_{7/2}$ or a $4f_{5/2}$ electron while leaving the $5f$ electrons as determined for the ground state before core ionization. This results from the one-electron character of photoexcitation and photoionization processes.[14] For these two allowed distributions, or configurations, there is a multiplet splitting where the $4f$ core hole and the open $5f$ shell couple to different possible total J values: a $4f_{7/2}$ or $4f_{5/2}$ core hole with $5f^1_{5/2}$ ($J=5/2$) angular momentum couples to values of $J=6,5,4,3,2,1$ or $J=5,4,3,2,2,1,0$, respectively, where all these couplings are XPS allowed final J levels. Similarly, a $4f_{7/2}$ or $4f_{5/2}$ core hole couples with $5f^2_{5/2}$ ($J=4$) to give rise to $J=15/2,13/2,11/2,9/2,7/2,5/2,3/2,1/2$ or $J=13/2,11/2,9/2,7/2,5/2,3/2$ allowed final J levels, respectively. We show below that the multiplet splitting of these levels is not especially large (~2 eV). However, the angular momentum recoupling within the $5f$ shell leads to a further redistribution of intensity into XPS forbidden configurations that can carry intensity because they mix with the XPS allowed multiplet split levels.[6,7,9,12]

The spinors are expanded in an extended basis set of contracted Gaussian type orbitals where separate functions are used to describe the large and small components of the spinors. The parameters for this basis set were optimized by deJong, Visscher, and Nieuwpoort[15] for calculations on UO_2^{2+}. The other parameters for the DF-SCF and DCI calculations are as described in Ilton *et al.*[9] The I_{rel} for the XPS peaks are obtained using the sudden approximation[16] (SA) with suitable extensions for the ionization of open shell systems,[17,18] which involve summations of the intensity over degenerate final states and averages of intensity over degenerate initial states.

B. Theoretical results and discussion

The calculated XPS peaks and synthetic spectra representing their summed contributions for the $4f$ XPS of U^{4+} and U^{5+} are shown in Figs. 2(a) and 2(b), respectively. The cal-
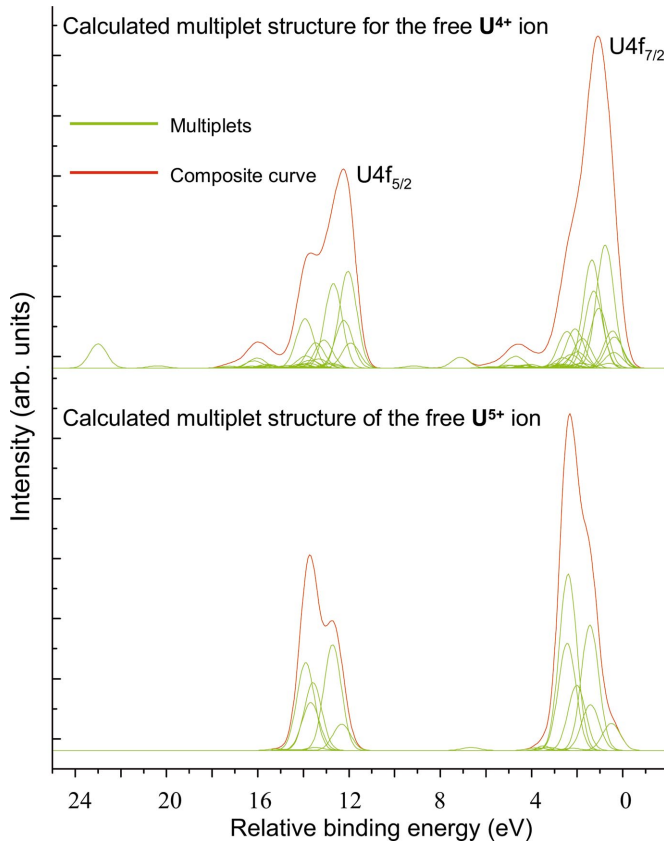
FIG. 2. (Color) Theoretical U(4f) XPS for the free U^{4+} ion, upper curves, and for the free U^{5+} ion, lower curves; the theoretical I_{rel} are broadened with a Gaussian function; see text. The contributions of individual 4f-hole final states are shown in green while the sum of these individual contributions is the composite curve in red. The lowest BE 4f final hole states for U^{4+} and U^{5+} were set to the same BE.

culated peaks are represented by Gaussians broadened to 0.9 eV FWHM. The underlying data for Fig. 2 is presented in Tables I and II. I_{rel} values were normalized so that the sum of the I_{rel} for all final 4f-hole states is 14. This arbitrary normalization indicates that any one of the 14 4f electrons may be ionized. The threshold relative intensity for including a final state in the tables is $I_{rel} \geq 0.05$. For each of the peaks, the J values of the final state levels are also given; the degeneracy of a level with quantum number J is $2J+1$. If the mixing of XPS forbidden configurations with the allowed multiplet levels is neglected, then the XPS SA intensity of a given level is proportional to $2J+1$.[9,17] The deviations from this proportionality provide an indication of the importance of the intensity stolen by forbidden configurations through configuration mixing, or configuration interaction, with the allowed final state ionic levels. We also give sequential numbers in the tables for each of the final ionic levels shown; this permits individual peaks to be referenced in the following discussion.

The E_{rel} and I_{rel} for the simpler case of the $U^{5+}(5f^{1}_{5/2})$ XPS, presented in Table I, are considered first. The first six levels are dominated by the XPS allowed configuration $4f^{-1}_{7/2}5f^{1}_{5/2}$ where $4f^{-1}_{7/2}$ is shorthand for the occupation $4f^{6}_{5/2}4f^{7}_{7/2}$. The angular momentum coupling of $4f^{-1}_{7/2}$ with

TABLE I. E_{rel}, in eV, and SA I_{rel} for the 4f hole levels of $U^{5+}(5f^{1}_{5/2})$. The levels with $I_{rel} \geq 0.05$ are listed; the J angular momentum quantum numbers are given for the levels listed. Each level listed is numbered consecutively. For selected levels that form the "main" $4f_{7/2}$ peak, a renormalized I_{rel}(renorm) is given to show how the intensity reflects the multiplicity of the peaks; this multiplicity is given in parenthesis after the I_{rel}(renorm); the same information is given for selected levels that form the "main" $4f_{5/2}$ peak.

Level	J	E_{rel}	I_{rel}	$4f_{7/2} - I_{rel}$(renorm) and $(2J+1)$	$4f_{5/2} - I_{rel}$(renorm) and $(2J+1)$
1	1	0	0.46	2.8(3)	
2	2	0.93	0.78	4.7(5)	
3	6	0.94	2.14	13(13)	
4	3	1.52	1.11	6.7(7)	
5	4	1.92	1.48	9.0(9)	
6	5	1.96	1.83	11.1(11)	
7	3	2.77	0.05		
8	2	2.99	0.05		
9	0	6.17	0.05		
10	1	11.83	0.45		2.7(3)
11	5	12.24	1.81		11(11)
12	1	13.00	0.05		0.3(3)
13	3	13.08	1.16		7.0(7)
14	2	13.18	0.82		5.0(5)
15	4	13.42	1.50		9.1(9)
16	0	26.13	0.12		0.7(1)

$5f^{1}_{5/2}$ leads to total J values of 1 to 6. For ease of comparison, the relative intensities of these six levels are arbitrarily renormalized in Table I so that I_{rel}(renorm)=13 for the J=6 level; this choice is the multiplicity, $2J+1$, of this level. If configuration mixing that allows forbidden configurations to steal XPS intensity could be neglected, the other levels of the first six would have I_{rel}(renorm)=$2J+1$. For level numbers 1, 2, and 4, the I_{rel}(renorm) are ~5% smaller than the multiplicities of these levels. This indicates that configuration mixing allows more intensity to be stolen by forbidden configurations for the J=1, 2, and 3 levels than for the J=6 level. The J=4 level, level 5, has I_{rel}(renorm)=9.0 or the same as the multiplicity of this level indicating that the same intensity is stolen for J=4 and 6. Level 6, with J=5, has I_{rel}(renorm) ~1% larger than it multiplicity indicating that slightly less intensity is stolen for J=5 than for J=6 and 4. The sum of the SA intensities, before the renormalization, for these six levels is 7.8 or almost the 8 that would occur if there were no intensity stolen because of configuration mixing; only ~2.5% of the intensity is stolen. Level 3 with J=6 is out of the energetic order of the J levels that would be expected from the coupling of $4f^{-1}_{7/2}$ with $5f^{1}_{5/2}$;[13] this change of energetic order is another indication that XPS allowed and forbidden configurations mix. The relatively small multiplet splitting of $4f^{-1}_{7/2}$ with $5f^{1}_{5/2}$ leads to an energy spread of ~2 eV. Thus these levels produce a broadening of the composite XPS peak rather than a distinct satellite structure (Fig. 2, bottom); there is, however, a shoulder on the low

TABLE II. E_{rel}, in eV, and SA I_{rel} for the $4f$ hole levels of $U^{4+}(5f^2_{5/2})$. The levels with $I_{rel} \geq 0.05$ are listed; the J angular momentum quantum numbers are given for the levels listed. Each level listed is numbered consecutively.

Level	J	E_{rel}	I_{rel}	Level	J	E_{rel}	I_{rel}
1	3/2	0	0.34	20	5/2	6.75	0.12
2	1/2	0.03	0.17	21	3/2	11.55	0.27
3	5/2	0.09	0.40	22	13/2	11.66	1.05
4	7/2	0.25	0.52	23	7/2	11.86	0.52
5	15/2	0.41	1.33	24	11/2	12.31	0.92
6	9/2	0.70	0.65	25	9/2	12.44	0.56
7	11/2	0.92	0.84	26	15/2	12.74	0.30
8	13/2	0.99	1.17	27	7/2	12.94	0.10
9	7/2	1.40	0.05	28	7/2	13.09	0.27
10	7/2	1.42	0.32	29	3/2	13.32	0.09
11	9/2	1.44	0.06	30	9/2	13.41	0.05
12	5/2	1.64	0.18	31	11/2	13.42	a
13	9/2	1.73	0.43	32	1/2	13.50	0.13
14	7/2	1.92	0.15	33	13/2	13.51	a
15	3/2	1.92	a	34	9/2	13.55	0.53
16	11/2	2.09	0.40	35	5/2	15.66	0.11
17	11/2	2.25	0.11	36	9/2	15.79	0.08
18	7/2	4.33	0.13	37	5/2	23.42	0.26
19	11/2	4.44	0.08				

a The I_{rel} for this peak is included with the I_{rel} given for the preceding peak.

binding energy side of the $4f_{7/2}$ peak. The levels numbered 7–9 are XPS satellites and have low I_{rel}; the $J=0$ satellite level at $E_{rel}=6.2$ eV, level 9, will be discussed further below.

The final $4f$ hole levels numbered 10, 11, 13, 14, 15, and 16 are dominated by the $4f^{-1}_{5/2}5f^1_{5/2}$ configuration. Level 12 is a $J=1$ satellite with low I_{rel}. As we did for the $4f^{-1}_{7/2}$ ionic levels, we renormalize the I_{rel} for the levels numbered 10–16 in order to show how closely the relative intensities follow the multiplicities of the states. Again, we choose to have a relative intensity for the highest multiplicity, $J=5$, level that is the same as the multiplicity, $I_{rel}(renorm)=11$. The $I_{rel}(renorm)$ for the levels numbered 10, 13, 14, 15 are close to the multiplicities of these levels, Table I, consistent with these WF's being dominated by the XPS allowed $4f^{-1}_{7/2}5f^1_{5/2}$ configuration. The $J=1$ level at 13.0 eV, level 12, is a low energy satellite embedded within the dominantly XPS allowed levels. Indeed, if the intensity stolen by level 12, $I_{rel}(renorm)=0.3$, is added to the $I_{rel}(renorm)$ for level 10, the main $J=1$ level, the sum is 3.0 or $2J+1$. The $J=0$ level at $E_{rel}=26.1$ eV, level 16, has lost almost 30% of the intensity that it should receive. The level is also higher in energy by more than 10 eV than the other $4f^{-1}_{5/2}$ levels. Both the loss of intensity and the large energy shift indicate a large configuration mixing. The $J=0$ satellite at $E_{rel}=6.2$ eV, level 9, recovers the intensity lost by level 16. There are only two configurations that can couple to $J=0$; these are the XPS allowed $4f^{-1}_{5/2}5f^1_{5/2}$ and the XPS forbidden $4f^{-1}_{7/2}5f^1_{7/2}$ configurations. The large proportion, ~30%, of the intensity

going into forbidden $J=0$, level 9, clearly indicates a major mixing of the XPS allowed and forbidden $J=0$ configurations. This large mixing is also consistent with a major displacement of the energy of the dominantly allowed $J=0$ level, at $E_{rel}=26.1$ eV, above the manifold of the other dominantly allowed levels that range between 11.8 to 13.4 eV. However, since the $J=0$ levels, with multiplicity 1, carry only a small fraction of the XPS intensity in the $4f^{-1}_{5/2}$ ionic states, the effect of this configuration mixing is not large. The manifold of peaks in the range $E_{rel}=11.8$ to 13.4 eV carry 96.5% of the total $4f^{-1}_{5/2}$ intensity which produces some broadening and a noticeable doublet structure (Fig. 2, bottom).

The XPS E_{rel} and I_{rel} for the $U^{4+}(5f^2_{5/2})$, given in Table II, are more complicated than the U^{5+} spectrum discussed above. This is because the additional $5f$ electron leads to many more ways to form XPS forbidden configurations that couple to allowed J values. The levels numbered 1 to 8 are dominated by the XPS allowed $4f^{-1}_{7/2}5f^2_{5/2}(J=4)$ configuration where the $4f^{-1}$ and $5f^2$ shells can couple to total $J=1/2$ through $J=15/2$; these levels cover an energy range of 1 eV. The levels numbered 21 to 26 form the "main" $4f_{5/2}$ peaks dominated by the allowed $4f^{-1}_{5/2}5f^2_{5/2}$ ($J=4$) configuration with total J values from $J=3/2$ to $J=13/2$; these cover an energy range of 1.2 eV. The I_{rel} roughly reflect the multiplicities of these levels, although the deviations are greater than for the U^{5+} XPS, reflecting the greater importance of configuration mixing for U^{4+}. The remaining peaks are satellites. For three pairs of ionic levels, levels 14 and 15, levels 30 and 31, and levels 32 and 33, the energy spacing is so small that we have combined I_{rel} for these pairs. In general, the calculated U$4f$ XPS for U^{4+} indicates broader multiplet splitting of the primary peaks and greater satellite intensity than for U^{5+} (Fig. 2). The next section compares the calculated U$4f$ spectra of U^{4+} with the observed XPS of UO_2.

IV. COMPARISON OF THEORY TO EXPERIMENT

Figure 3 compares the calculated $4f$ XPS of the free U^{4+} ion to the experimental spectrum for UO_2 that was described in Sec. II and Fig. 1. The calculated XPS multiplet-split peaks were Gaussian broadened, their peak heights normalized, and their energies rigidly shifted to match the FWHM, intensity, and BE of the $4f_{7/2}$ peak, respectively. We emphasize that the relative multiplet energies and intensities have not been altered to fit experiment. Clearly, the theory does a good job predicting the spin orbital splitting and relative intensities for the $4f_{7/2}$ and $4f_{5/2}$ peaks, although the overall spin orbital splitting is predicted to be about 0.5 eV too large. The shape of the $4f_{7/2}$ peak is also well represented by theory; differences include a minor shoulder on the high BE side of the synthetic spectrum that is not apparent in the experimental spectrum and a broader, more Lorentzian appearance to the lower part of the experimental compared to calculated spectrum. The latter difference may simply be a function of not taking core-hole lifetime effects into account. The calculated $4f_{5/2}$ peak shows a somewhat larger deviation from experiment; theory yielded a large multiplet feature on
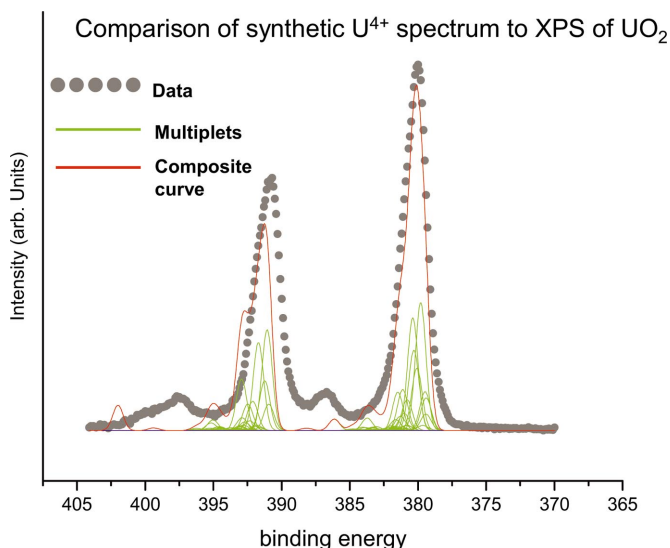
Comparison of synthetic U⁴⁺ spectrum to XPS of UO₂

FIG. 3. (Color) Theoretical U(4f) XPS for the free U^{4+} ion compared to the XPS of UO_2; the UO_2 XPS data is given by gray dots while the broadened theoretical curves are as described in the caption for Fig. 1. The calculated E_{rel} have been rigidly shifted so that the composite theoretical curve has the best fit to experimental data.

the high energy side which was not resolved in the experimental spectrum.

The most conspicuous difference between theory and experiment occurs for the satellite structure. The experimental spectrum records satellites with roughly 15% intensity of and at ~6.7 eV higher BE than both the $4f_{7/2}$ and $4f_{5/2}$ primary peaks. In contrast, the synthetic spectrum describes lower intensity satellites that do not closely match the experimentally determined satellite positions. Similarly, the synthetic spectrum for the free U^{5+} ion does not show the 8.4 eV satellite recorded for U^{5+}-containing oxides.[1–4]

If we have included all the important atomic configurations, then differences between theory and experiment have an interatomic origin. The prediction of the high BE shoulders on the core peaks (particularly for $U4f_{5/2}$), not seen in the experimental XPS, is likely due to differences in the exchange interaction between the core hole and unpaired 5f electrons. For UO_2, we would expect covalent bonding ($U5f$-$O2p$) to reduce the exchange interaction;[10] this interatomic screening should reduce the MS of the 4f core-hole peaks compared to the free U^{4+} ion and likely accounts for the symmetrical appearance of the experimental core peaks.

The difference in satellite structures between experiment and the atomic calculations is consistent with previous theoretical and experimental work indicating that the 7 eV satellite in the XPS of UO_2 is a function of charge transfer from $O2p$ to $U5f$.[19,20] In particular, Gunnarsson et al.,[19] based on an Anderson impurity model and neglecting multiplet splitting, argued that hybridization of nearly degenerate 5f and $5f^{n+1}\underline{L}$ configurations, where $\underline{L}$ denotes a ligand 2p hole, produces the necessary ~7 eV difference in final states. Obviously, the $5f^{n+1}\underline{L}$ configuration is not possible for the free U^{4+}. Consequently, the atomic calculations provide the necessary negative results to complement these previous studies.

Both covalent bonding ($U5f$-$O2p$) and photoionization induced charge transfer from $O2p$ to $U5f$ could explain the difference between the calculated and experimentally measured 4f spin orbital splitting. As noted above, covalent bonding will tend to narrow the MS of both the $U4f_{7/2}$ and $U4f_{5/2}$ peaks for U^{4+} in oxides relative to the isolated U^{4+} atom. This can produce a difference between the calculated and measured spin orbit splitting if the reduction in MS causes a differential shift in the centers of gravity of the $4f_{5/2}$ and $4f_{7/2}$ peaks. Alternatively, or perhaps in addition, a different degree of mixing of the charge transfer configuration, $5f^{n+1}\underline{L}$, in the $4f_{7/2}$ and $4f_{5/2}$ wave functions could contribute to the discrepancy between the calculated and measured spin orbital splitting. Calculations on embedded U-oxide cluster models are required to provide support for such speculation.

Finally, we caution that not all possible atomic configurations were included in the atomic calculations. Frustrated Auger configurations (FAC's) could steal intensity from the allowed configurations in the U(4f) XPS, provided that the off-diagonal matrix element between a FAC and an XPS allowed configuration is sufficiently large compared to the difference of their diagonal energies, an effect well known in the multiplet theory for 3d TM compounds.[21,22] In particular, the FAC that involves promotion of a 5d shell electron into the 5f shell while a 5s electron is dropped to fill the 4f core hole, $5s5d \rightarrow 4f5f$, has the correct parity and may have a correct J value so that it can mix with and steal intensity from XPS allowed configurations. However, a rough estimate, based on the DF-SCF orbital energies for U^{5+}, indicates that the diagonal energies of the FAC's will be ~50 eV above the diagonal energies of the XPS allowed 4f-hole configurations. Given this large excitation energy, the satellites that might arise from the mixing of the FAC's and the XPS allowed configurations would be at a high energy; approximately ⩾50 eV above the main XPS peaks.[21] This is not the proper energy range to account for the observed satellites at ~6−8 eV above the primary U4f peaks. Consequently, intra-atomic FAC's are not likely to be responsible for these satellites.

V. CONCLUDING REMARKS

Strictly *ab initio* calculations indicate that the U^{4+} and U^{5+} free ions have a non-negligible U4f XPS multiplet splitting. Theory shows that the U^{4+} 4f XPS is broadened relative to that for U^{5+}, which raises an important concern about the common practice of using components of equal FWHM for curve fitting the XPS of multivalent U compounds. However, comparison of the calculated and observed XPS of U^{4+} and UO_2, respectively, suggest that interatomic effects diminish the MS of the free U ions, create more symmetrical U4f peaks, and account for the observed satellite structure. In sum, we show that, although the MS is intrinsically small for the free U atoms compared to first row TM's, it is not negligible, and that interatomic effects are important for decreasing the MS further. In addition, the atomic calculations do not predict the 7 or 8.4 eV satellites characteristic of UO_2 or U^{5+}-containing oxides, respectively, which is consistent with the consensus that these satellites have an interatomic charge-transfer origin.

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