Charge transfer in uranyl(VI) halides $[\text{UO}_2\text{X}_4]^{2-}$ (X = F, Cl, Br and I). A quantum chemical study of the absorption spectra

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Abstract

The electronic spectra of uranyl(VI) coordinated with four equatorial halide ligands, $[\text{UO}_2\text{X}_4]^{2-}$ (X = F, Cl, Br and I), have been calculated at the all-electron level using the multiconfigurational CASPT2 method, with spin-orbit coupling included through the variational-perturbational method. The halide-to-uranyl charge-transfer states were taken into account in the calculation by including ligand orbitals in the active space. In order to do that, it is assumed that the charge transfer takes place from only one of the four ligands. Two models which in principle can describe this were investigated: the first one makes use of a localizing technique and the second one replaces three ligands by *ab initio* model potentials (AIMPs). The basis set dependence was investigated by using two different basis sets for the halides, of triple- ζ and quadruple- ζ quality. The localization procedure turned out to be strongly basis set dependent, and the most

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stable results were obtained with *ab initio* model potentials. The ground state is a closed shell singlet state, and the first excitation is from the bonding σ_u orbital on uranyl to the nonbonding δ_u orbitals, except for the $[\text{UO}_2\text{I}_4]^{2-}$ complex, where the first excited state has a mixed character of charge transfer from the I^- and the $\sigma_u^1\phi_u^1$ configuration. In $[\text{UO}_2\text{F}_4]^{2-}$ there is no charge transfer excitation below 50000 cm^{-1} , while in $[\text{UO}_2\text{Cl}_4]^{2-}$ it appears around 33000 cm^{-1} and in $[\text{UO}_2\text{Br}_4]^{2-}$ around 23000 cm^{-1} . A blueshift of the spectra, from F^- to I^- , is observed. The calculations compare reasonably well with available experimental results.

Introduction

Uranyl halides are important compounds in the chemistry of uranium in its highest oxidation state (VI)^{1,2} and serve as highly useful starting materials for the synthesis of a wide range compounds.³ In particular, uranyl fluoride draws substantial attention in uranium chemistry since it is a product of the reaction of UF_6 with moisture.⁴ In the past, optical properties of the uranyl chloride complexes in the solid state have been extensively studied⁵⁻⁷ and thermodynamic data of U(VI) aquo chloro complexes have been reported.⁸ However, uranyl bromide and iodide are less stable than the fluoride and chloride complexes, especially in the solid state; for example bromide complexes decompose already at room temperature.⁹ Therefore studies of these complexes have been less frequent. The absorption and luminescence spectra of the $[\text{UO}_2\text{F}_4]^{2-}$, $[\text{UO}_2\text{Cl}_4]^{2-}$ and $[\text{UO}_2\text{Br}_4]^{2-}$ have been studied experimentally but only the spectrum of $[\text{UO}_2\text{Cl}_4]^{2-}$ has been studied theoretically,¹⁰⁻¹³ to our knowledge. The lower part of the spectra can be explained in terms of excitations from the bonding σ_g , π_g , π_u and σ_u orbitals to the nonbonding δ_u (f_δ) and ϕ_u (f_ϕ). Experimental data indicate that the energy of the low-lying excited states is relatively independent of the presence and nature of the equatorial ligands.^{5,7,14-17} However, theoretical calculations show a blueshift of about 2000 cm^{-1} due to the presence of chloride ligands.^{10,11} It is important to mention that the experimental spectra have always been recorded in a surrounding with equatorial ligands, and only an experimental spectrum of the bare uranyl ion would confirm the theoretically predicted effect of the equatorial ligands in the electronic spectra. To our knowledge, no experimental or theoretical

spectra for $[\text{UO}_2\text{I}_4]^{2-}$ are available. The aim of this work is the detailed analysis of the absorption spectra of uranyl complexed with the halides F^- , Cl^- , Br^- and I^- , including the halide-to-uranyl charge-transfer states, to see the influence in the spectra and the trends along the halide group.

Method and details of the calculations

Structure of $[\text{UO}_2\text{X}_4]^{2-}$ complexes and symmetry considerations

The experimental geometry for $[\text{UO}_2\text{X}_4]^{2-}$ is a square bipyramid structure with D_{4h} symmetry, with the four halide ligands coordinated in the equatorial plane of the uranyl unit. Experimental structural parameters are shown in Table 1. When the symmetry is reduced from $D_{\infty h}$ in the free UO_2^{2+} to D_{4h} in $[\text{UO}_2\text{X}_4]^{2-}$, the molecular orbitals will transform according to the irreducible representations of D_{4h} . The resolution of the $D_{\infty h}$ point group into D_{4h} is (see Table 2): $\sigma_g \rightarrow a_{1g}$, $\pi_g \rightarrow e_g$, $\sigma_u \rightarrow a_{2u}$, $\pi_u \rightarrow e_u$, $\phi_u \rightarrow e_u$, $\delta_u \rightarrow b_{1u} + b_{2u}$ and $\delta_g \rightarrow b_{1g} + b_{2g}$. In the new symmetry the nonbonding f_ϕ orbitals remain degenerate but can interact with the ligands through σ -type interactions, since they have their maximum density in the equatorial plane. These orbitals thus become slightly antibonding. The nonbonding f_δ orbitals, on the other hand, are split into b_{1u} and b_{2u} components, which can interact with the ligands through π -type interactions. Thus, the f_ϕ orbitals are more destabilized than the f_δ orbitals.¹⁰ In this work we have used for technical reasons the point symmetry groups C_{2v} and C_s . The resolution of the D_{4h} point group into C_{2v} and C_s is shown in Table 2. Finally, for simplicity and for comparisons, we keep the notation of the orbitals as in the free ion, UO_2^{2+} , although the f_δ , which are no longer degenerate, will be referred as δ'_u (or f'_δ) and δ''_u (or f''_δ).

Scalar relativistic and spin-orbit coupling calculations

All spectra have been obtained with wave-function based methods of quantum chemistry at the all-electron level; the second-order Douglas-Kroll-Hess Hamiltonian has been used to calculate

all relevant relativistic integrals.^{18,19} All the calculations were performed using the MOLCAS software.²⁰ In a first step we perform state-average complete active space self-consistent-field calculations (SA-CASSCF).²¹ A crucial step is the selection of the orbitals to be included in the active space. In the bare uranyl ion, UO_2^{2+} , the U - O bonds are formed by $\text{U}5f6d$ and $\text{O}2p$ atomic orbitals that generate the bonding molecular orbitals σ_g , σ_u , π_g and π_u , containing 12 electrons. The corresponding six antibonding that remain empty, plus the nonbonding pure uranium orbitals: ϕ_u and δ_u from the $5f$ shell and δ_g from the $6d$ shell, complete the active space.²² MOLCAS can only handle abelian symmetries and the components of doubly degenerate orbitals must thus be considered separately. Keeping this in mind, we need an active space built on the distribution of 12 electrons in 18 molecular orbitals for a proper description of uranyl. In $[\text{UO}_2\text{X}_4]^{2-}$, we should ideally include all the np^6 shells from the ligands in the active space in order to study the ligand-to-uranyl charge-transfer states, which means adding 12 orbitals and 24 electrons. This is beyond the limits of the CASSCF method, and hence we have to reduce the size of the active space. If the charge transfer can be described as involving only one of the four ligands, we have to take into account only three p orbitals with six electrons. This leads to an active space of 18 electrons in 21 orbitals, which is still not feasible from the computational point of view. However, the spectrum of the bare uranyl ion shows that excitations below 50000 cm^{-1} correspond to transitions from the bonding orbitals (σ_g , σ_u , π_g and π_u) to the empty nonbonding ϕ_u and δ_u ,^{10,23} which means that it is reasonable to ignore the antibonding σ_g^* , σ_u^* , π_g^* and π_u^* , as well as the nonbonding δ_g (d_δ) orbitals. This gives rise to 18 electrons to be distributed in 13 molecular orbitals (in an abelian symmetry), which is affordable. In this active space, 12 electrons and 10 molecular orbitals originate from the UO_2^{2+} unit (σ_g , π_g , σ_u , π_u , ϕ_u and δ_u) while the remaining 6 electrons and 3 orbitals come from the halide atom ($2p$ in the case of fluorine, $3p$ in chlorine, $4p$ in bromine and $5p$ in iodine). In order to account for the remaining dynamical correlation effects, we perform complete active space second-order perturbation-theory (CASPT2)²⁴ calculations based on this CASSCF reference with the ionization potential electron affinity (IPEA)-corrected zeroth-order Hamiltonian.²⁵ The use of an imaginary level-shift operator technique²⁶ was necessary to avoid the presence of intruder states

and achieve convergence of the CASPT2 calculations. The level shift value used is 0.15 au. At this stage we also correlate all the electrons from the fully occupied $U5d6s6p$ and $O2s2p$ shells in uranyl and the ns, np shells from the ligands. Finally, to take into account the spin-orbit coupling, we use the variation-perturbation method RASSI-SO,²⁷ available in MOLCAS, with the orbital basis obtained from a state-average CASSCF calculation. In order to include correlation effects in the spin-orbit calculations, an effective spin-orbit Hamiltonian is defined, where the diagonal matrix elements are shifted using the energy differences between the CASSCF and the CASPT2 calculations.^{28,29}

Description of the ligands

In a CASSCF calculation on a uranyl halide complex, the orbitals describing the halides will in general be delocalized, and in order to consider only excitations from one halide ligand, the active molecular orbitals must be localized on this ligand. This can be achieved either by localization or freezing the inactive ligands. Both methods were used in the present study. The localization technique used is based on the Pipek-Mezey procedure.³⁰ The localization allows us to select the orbitals from a particular halide atom to be included in the CASSCF calculations. In the Pipek-Mezey procedure the atoms involved must be independent, that is not related by symmetry, and all the calculations performed using this approximation have been carried out using C_s symmetry, with the plane containing the four ligands and the uranium atom as symmetry plane. The alternative procedure, to freeze three of the ligands, implies that the spectrum of UO_2X^+ is calculated in the presence of the field generated by the rest of the ligands. This can be achieved either directly in the all-electron basis set or by using model potentials. In the present study we have chosen to use *ab initio* model potentials, AIMP, which describe both classical (electrostatic) and quantum mechanical effects (exchange and linear independence) of the frozen ions on the rest of the system, and normally there are no associated electrons or basis sets.^{31,32} These *ab initio* model potentials are obtained for ions in a crystalline environment. The AIMP method has been successfully used in many applications related to structural and spectroscopic properties of impurities in solids.^{33–37}

When the AIMP's are used in the present context it is no longer necessary to have symmetry independent ligands, and thus we have performed the calculations in the higher C_{2v} symmetry.

Basis sets and *ab initio* model potentials

We have used the all-electron atomic natural orbitals (ANO-RCC) basis sets available in the MOLCAS library for all atoms. On uranium we used a $(26s23p17d13f5g3h)$ primitive basis contracted to a quadruple- ζ size $[10s9p7d5f3g]$ ³⁸ and on oxygen the $(14s9p4d3f2g)$ primitive basis set contracted to a triple- ζ size $[4s3p2d1f]$.³⁹ For the halide ligands we also used ANO-RCC basis sets of both triple- ζ and quadruple- ζ quality;³⁹ for fluorine the primitive basis $(14s9p4d3f2g)$ was contracted to triple- ζ $[4s3p2d1f]$ and to quadruple- ζ $[5s4p3d2f]$, for chlorine $(17s12p5d4f2g)$ was contracted to $[5s4p2d1f]$ and $[6s5p3d2f]$, for bromine $(20s17p11d4f2g)$ was contracted to $[6s5p3d2f1g]$ and $[7s6p4d3f2g]$, and for iodine the primitive basis $(22s19p13d5f3g)$ was contracted to $[7s6p4d2f1g]$ and $[8s7p5d4f2g]$. The *ab initio* embedding model potentials used in this work for the fluoride, chloride and bromide ions are available in the MOLCAS library,²⁰ and were obtained in the following crystals: Cs_2NaYF_6 ,⁴⁰ $\text{Cs}_2\text{NaYCl}_6$ ⁴¹ and $\text{Cs}_2\text{NaYBr}_6$.⁴¹ The embedding potential for iodide ion was produced in this work, following the recipe for the AIMP method^{31,32} in the NaI crystal.

Results and discussion

Models and basis sets

As described in the previous section, the calculations were carried out with two different basis sets, of triple- ζ and quadruple- ζ quality, and two different models, one based on a localization technique and the other using *ab initio* model potentials to describe the passive ligands. The active orbitals in the closed shell ground state are $p^6\sigma_g^2\pi_g^4\pi_u^4\sigma_u^2$, where the six p electrons belong to the halide ion and the rest to the UO_2^{2+} unit, and the spectra were generated from exci-

tations to the empty nonbonding δ_u and ϕ_u orbitals. Table 3 shows the first transition from the ground state for each basis set and each model, together with experimental results for fluoride,⁴² $[\text{UO}_2\text{F}_4]^{2-}$, chloride,⁴³ $[\text{UO}_2\text{Cl}_4]^{2-}$, and bromide,⁴⁴ $[\text{UO}_2\text{Br}_4]^{2-}$. The excitation energies obtained with quadruple- ζ basis sets are consistent for all complexes using *ab initio* model potentials and the localization procedure, and for the triple- ζ basis set with AIMP, while the triple- ζ basis sets with the localization technique give remarkably different results. This indicates that the localization technique can give rise to problems, since the AIMP results with both basis sets are consistent. This is presumably due to differences in the admixture with orbitals on the passive ligands, which is basis-set dependent. Comparing with experiments the agreement is good for the quadruple- ζ basis set with the localization procedure. However the lack of reproducibility when the basis set is changed suggests that this agreement may be incidental. The AIMP results obtained with the triple- ζ basis set and the quadruple- ζ results with localization show a trend where the first transition from F^- to I^- is blue-shifted. The results for the quadruple- ζ basis set using AIMP show a blueshift in going from fluoride to chloride and from bromide to iodide, but a slight redshift in going from $[\text{UO}_2\text{Cl}_4]^{2-}$ to $[\text{UO}_2\text{Br}_4]^{2-}$. In $[\text{UO}_2\text{F}_4]^{2-}$, the calculated origin is essentially the same with the two basis sets, for the $[\text{UO}_2\text{Cl}_4]^{2-}$ complex the agreement with the experiment is better using triple- ζ , while in $[\text{UO}_2\text{Br}_4]^{2-}$ the agreement is better with the quadruple- ζ basis. The first transition in experimental absorption spectra^{42–44} is quite similar for these three compounds, although with a small blueshift between fluoride and chloride, and a slight redshift between chloride and bromide, however, the differences in the transition energies are very small, about 200 cm^{-1} or less. For the reasons discussed above we will not make use of the localization model in the detailed analysis of the spectra. The excitation energies obtained with the AIMP model are similar, and within the expected errors for this method, and in the following we will only refer to results obtained with the larger quadruple- ζ basis sets.

The first excited state. Effects of the U - X interaction

The last two columns in Table 3 show the results obtained with the quadruple- ζ basis set using AIMPs and the experimental results. The transition energy to the first excited state increases from F^- to Cl^- , there is a slight decrease from Cl^- to Br^- and again an increase from Br^- to I^- . These observations can be explained in terms of the geometry and orbital interactions. As discussed in a previous section, the f_ϕ orbitals have the maximum probability in the equatorial plane so they are involved in σ -type interactions with the ligands, while the interaction with the f_δ orbitals is π -type. This implies an upward shift of the energy of the f_ϕ and the f_δ orbitals should be dominating in the first excited state. The f_δ orbitals are split by the D_{4h} symmetry, while the f_ϕ orbitals remain degenerate (see Table 2). The two δ_u components interact differently with the ligands, one of the components points between the ligands, while the other component is directed toward the ligands. The stronger the interaction with the ligand, the larger the splitting between the components, and *vice versa*. At shorter bond distances the interaction between the ligands and the uranyl will increase. The f_ϕ orbitals increase in energy, but at the same time the splitting of the f_δ orbitals increases, and if the interaction is strong it may give rise to a decrease of the energy of the more stable f_δ component. The structural parameters in Table 1 show that when substituting F^- with Cl^- the U - X bond distance is increased in 0.42 Å and the first transition energy is blue-shifted 6424 cm^{-1} at CASPT2 level and 5614 cm^{-1} when the spin-orbit coupling is accounted for. Comparing the Br and I complexes, the U - X bond length is lengthened by 0.23 Å in going from Br to I and the first excited state is 2654 cm^{-1} higher at RASSI-SO level for the iodine complex. The increase in the bond distance is smaller for $[\text{UO}_2\text{Br}_4]^{2-}$ compared to $[\text{UO}_2\text{Cl}_4]^{2-}$, only 0.14 Å, and in this case the transition energy actually decreases by 1221 cm^{-1} at RASSI-SO level. The trend observed for the F, Cl and Br complexes is in agreement with experiment, but the theoretical splittings are much larger than the experimental ones, which indicates that the ligand field is overestimated in the theoretical calculations.

Absorption spectra

$[\text{UO}_2\text{F}_4]^{2-}$

There is no crystal structure available for this complex and the experimental structure is obtained from EXAFS measurements in solution.⁴⁵ The calculated vertical excitation energies including spin-orbit coupling for the first 17 states of $[\text{UO}_2\text{F}_4]^{2-}$, up to 31500 cm^{-1} , are shown in Table 4 (the complete set of spin-free and spin-orbit coupling energies can be found in Tables S1 and S2 in the Supporting Information). The first excited state is located at 17256 cm^{-1} above the ground state, and corresponds to a transition to one of the components of the f_δ orbitals, the $\sigma_u f''_\delta$ level. The level at 22173 cm^{-1} corresponds to a mixture of $\sigma_u f'_\delta$ and $\sigma_u f''_\delta$ configurations, and we find a transition to the pure $\sigma_u f'_\delta$ level at 24356 cm^{-1} . The separation of these configurations at the spin-orbit free level is about 6000 cm^{-1} , which illustrates the strong interaction between the ligands and the UO_2^{2+} unit, due to the short fluoride-uranium bond distance. Transitions involving the antibonding π_u^* orbital appear at higher energies. Occasionally this orbital enters in the active space, replacing the f_ϕ , and again this can be explained in terms of the strong interaction existing between the fluoride ions and the UO_2^{2+} . In a recent theoretical study of the uranyl(V) ion coordinated with three carbonate ligands,⁴⁶ $[\text{UO}_2(\text{CO}_3)_3]^{5-}$, it was found that the transition to the π_u^* orbital is lowered more than 10000 cm^{-1} compared to the same transition in the bare ion. This was explained in terms of the composition of this molecular orbital, which had less yl-oxygen character in the carbonate complex than in the free uranyl(V). The π_u^* orbital is therefore less antibonding and thus less repulsive in the complex. In $[\text{UO}_2\text{F}_4]^{2-}$ the effect of the F^- is more pronounced than in the carbonates because the distance to the ligands is shorter, $2.260\text{ \AA}$, compared to $2.552\text{ \AA}$ in the $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ complex. There are no charge-transfer excitations from the fluoride at energies lower than 50000 cm^{-1} due to the great electronegativity of this ion. The experimental spectrum is recorded in aqueous solution⁴² and consists of several weak bands with origin at about 20000 cm^{-1} (500 nm), thus our theoretical results seem to underestimate the experiment by a few thousand cm^{-1} .

[UO₂Cl₄]²⁻

Among the uranyl halides, the chloride complex has attracted most attention, and several experimental and theoretical results are available in the literature. Our calculated absorption spectra up to 33300 cm⁻¹, including spin-orbit coupling, is shown in Table 5 (a more complete spectrum, both at the CASPT2 and RASSI-SO levels, can be found in Tables S3 and S4 in Supporting Information). The first transition, which corresponds to a $\sigma_u \rightarrow f_\delta$ transition in the uranyl ion, is found at 22870 cm⁻¹. This level is a mixture of $\sigma_u f'_\delta$ and $\sigma_u f''_\delta$ due to the small separation of these levels in the spin-orbit free calculations, 446 cm⁻¹. The following transitions, up to approximately 30000 cm⁻¹, involve both $\sigma_u f'_\delta$ and $\sigma_u f''_\delta$ mixed with $\sigma_u f_\phi$. At 30158 cm⁻¹ appears the pure $\sigma_u f_\phi$ level and at 31868 cm⁻¹ the first level with contributions from the charge transfer from the ligands. At 33226 cm⁻¹, the first transition with a pronounced chloride-to-metal charge transfer character appears, followed by a dense manifold of states arising both from internal uranyl and ligand-to-metal charge transfers (see Table S4 in Supporting information). These results can be compared with experiments in solutions^{43,47} and in crystals,¹⁴ and with theoretical calculations,^{10,11} see Table 6. In general, the agreement with experiments is satisfactory, with discrepancies below 3000 cm⁻¹. This is encouraging considering the model, where only one chloride atom is included, and the exclusion of antibonding orbitals from the active space. Previous *ab initio* calculations¹⁰ used the active space recommended for uranyl, that is, all the bonding and antibonding orbitals, plus the two f_δ or the two f_ϕ , but excluded the ligand orbitals and thus all charge transfer contributions to the spectrum. The agreement between our results and those presented in the work by Pierloot and Van Besien¹⁰ is good in the lower part of the spectrum where the charge transfer effects are minor, although our excitations energies are on the average 1000 cm⁻¹ above their results. The character of the excited states are also quite similar in this part of the spectrum. The agreement with the results obtained using time-dependent density functional theory (TD-DFT) by Pierloot et al.¹¹ is also reasonably good. However, it should be noted that although the agreement in the excitation energies to the first excited state is good between the TD-DFT calculations, 20884 cm⁻¹, and the experiment, 20096 cm⁻¹, the nature of the state is different. Pierloot et al. find a

ground state of mainly $\sigma_u f_\phi$ character, rather than $\sigma_u f_\delta$ as obtained by us and also in previous wave-function based calculations.^{10,12} Matsika and Pitzer have calculated the spectrum of UO_2^{2+} in the $\text{Cs}_2\text{UO}_2\text{Cl}_4$ crystal,¹² with a first vertical transition of 20364 cm^{-1} which shows also good agreement with the experimental value, 20096 cm^{-1} , obtained by Denning in the same crystal.¹⁴ Matsika and Pitzer also performed some test calculations including charge transfer from the chloride ions, and they conclude that the first excitation with substantial chlorine character starts at approximately 33000 cm^{-1} , which agrees well with our transition at 33226 cm^{-1} .

$[\text{UO}_2\text{Br}_4]^{2-}$

The vertical spectrum including spin-orbit coupling is shown in Table 7 (see Tables S5 and S6 in Supporting Information for the complete spectra at the spin-free and spin-orbit coupling levels, respectively). The first transition, located at 21649 cm^{-1} , is a mixture of $\sigma_u f'_\delta$ and $\sigma_u f''_\delta$ due to the small separation of this electronic states at the spin-orbit free level, 641 cm^{-1} . The transitions at 21772 and 22470 cm^{-1} are to levels where $\sigma_u f'_\delta$ and $\sigma_u f''_\delta$ are mixed with $\sigma_u f_\phi$. The next excited state, at 22776 cm^{-1} , is still mixed but with more $\sigma_u f_\phi$ character, and at 23200 cm^{-1} we find the first contribution of charge transfer from the bromide ligand, consistent with the intense absorption found at 23000 cm^{-1} in the $\text{Cs}_2\text{UO}_2\text{Br}_4$ crystal.⁴⁸ At higher energies all transitions involve charge-transfer states from the halides. Our results can be compared to the UV-Vis absorption spectrum recorded for $[\text{UO}_2\text{Br}_4]^{2-}$ in an ionic liquid.⁴⁴ The spectrum has four characteristic bands at 20117 , 20838 , 21538 and 22232 cm^{-1} , which compares favorably with our results 21649 , 21772 , 22470 and 22776 cm^{-1} , and there is an intense absorption above 23000 cm^{-1} , again consistent with the appearance of the charge transfer band in our calculations.

$[\text{UO}_2\text{I}_4]^{2-}$

The calculated vertical spectrum for the iodide complex including spin-orbit coupling is shown in Table 8 (the complete spectra are found in Tables S7 and S8 in Supporting Information). The main feature of the spectrum is that already the first transition, at 24303 cm^{-1} , is a strong mixture of

the $\sigma_u f_\phi$ configuration with charge-transfer excitations. At higher energies all the transitions are, as expected, mixtures of internal uranyl and ligand-to-metal charge transfer excitations. The main uranyl contribution to the four lowest levels stem from the $\sigma_u f_\phi$ configuration, while for the rest of the complexes the contributions are from almost pure uranyl states of $\sigma_u f'_\delta$ or $\sigma_u f''_\delta$ character. The ligand field from the iodines is weaker than that for the lighter halides, so that the interaction with the f_ϕ orbitals is also weaker and thus they become less antibonding than in the rest of the complexes; in the spin-orbit free spectrum the separation of $\sigma_u f'_\delta$ and $\sigma_u f''_\delta$ configurations is less than 300 cm^{-1} (Table S7 in Supporting Information). In addition, the charge transfer contribution to the excited states will favor the interaction with the f_ϕ orbitals due to the σ -type interactions between these orbitals and the ligands compared to the π -type one existing with the f_δ orbitals. There are, to our knowledge, no experimental spectra available for the iodine complex. Based on the comparisons in the rest of the complexes, we expect that our results overestimate the transition energies by about 2500 cm^{-1} .

Conclusions

In the present study we have analyzed the electronic spectra of the uranyl halides, $[\text{UO}_2\text{X}_4]^{2-}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I), including charge-transfer excitations from the ligands, using relativistic wave-function based methods of quantum chemistry. In order to include the charge transfer from the halides, we have investigated two models and two different basis sets, of triple- ζ and quadruple- ζ quality. The first model utilizes a localization technique to generate orbitals localized on each of the ligands, while the second one replaces three of the four ligands by *ab initio* model potentials (AIMPs). The results obtained using quadruple- ζ basis sets are within the expected errors in the two different approximations. However, the results using the localization technique are basis-set dependent, the results obtained with the triple- ζ basis sets are poor, and the satisfactory results obtained with localization and the quadruple- ζ basis may thus be a coincidence. Based on these findings only the results from the AIMP model were used in the final analyses. The first transition

energy is blue-shifted along the sequence F^- to I^- , with the exception of $[UO_2Br_4]^{2-}$ where the excitation energy is slightly decreased compared to the chlorine complex. A blueshift along the sequence is not unreasonable since the U-ligand bond lengths increase along the sequence and thus decreasing the splitting between the f_δ orbitals. The difference in bond length between the Cl and the Br complexes is small which may explain the reversal of the trend between these two complexes. Our results compare reasonably well with experiments and with the previous existing theoretical calculations, and the discrepancies are most likely related to the approximations performed in order to be able to include the charge transfer from the ligands. The effect of charge transfer from the equatorial ligands on the UO_2^{2+} ion is negligible for the fluorine and chlorine complexes in the lower part of the spectrum, but it increases for the bromine complex and it becomes important for the iodine complex. The charge transfer must thus be included in order to get an accurate description of the spectra of $[UO_2Br_4]^{2-}$ and $[UO_2I_4]^{2-}$.

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Supporting Information Available

Complete set of vertical transition energies at the spin-free and spin-orbit levels for $[UO_2F_4]^{2-}$ (Tables S1 and S2), $[UO_2Cl_4]^{2-}$ (Tables S3 and S4), $[UO_2Br_4]^{2-}$ (Tables S5 and S6) and $[UO_2I_4]^{2-}$ (Tables S7 and S8).

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Table 1: Experimental geometries of the $[\text{UO}_2\text{X}_4]^{2-}$ complexes from EXAFS measurements of $[\text{UO}_2\text{F}_4]^{2-}$ in aqueous solution,⁴⁵ $[\text{UO}_2\text{Cl}_4]^{2-}$ in acetonitrile,⁴³ $[\text{UO}_2\text{Br}_4]^{2-}$ in ionic liquid⁴⁴ and X-ray diffraction of $[\text{UO}_2\text{I}_4]^{2-}$ in solid $(\text{Ph}_4\text{P})_2\text{UO}_2\text{I}_4 \cdot 2\text{NCCH}_3$.⁴⁹ The calculated geometry of the bare UO_2^{2+} ion⁵⁰ is also shown. Distances in Å.

	$[\text{UO}_2\text{F}_4]^{2-}$	$[\text{UO}_2\text{Cl}_4]^{2-}$	$[\text{UO}_2\text{Br}_4]^{2-}$	$[\text{UO}_2\text{I}_4]^{2-}$	UO_2^{2+}
r(U - O)	1.800	1.770	1.766	1.763	1.715
r(U - X)	2.260	2.680	2.820	3.053	-

Table 2: Resolution of the symmetry species of the $D_{\infty h}$ point group into those of the D_{4h} , C_{2v} and C_s point groups.

$D_{\infty h}$	D_{4h}	C_{2v}	C_s
σ_g	a_{1g}	a_1	a'
π_g	e_g	$a_2 + b_2$	a''
σ_u	a_{2u}	b_2	a''
π_u	e_u	$a_1 + b_1$	a'
δ_u	$b_{1u} + b_{2u}$	$a_2 + b_2$	a''
ϕ_u	e_u	$a_1 + b_1$	a'
δ_g	$b_{1g} + b_{2g}$	$a_1 + b_1$	a'

Table 3: Comparison of methods and basis sets. Only the first transition of the spectra is shown. Energies in cm^{-1} .

	Localization				<i>Ab initio</i> model potentials				Exp.
	MS-CASPT2		RASSI-SO		MS-CASPT2		RASSI-SO		
	triple- ζ	quad- ζ	triple- ζ	quad- ζ	triple- ζ	quad- ζ	triple- ζ	quad- ζ	
F	25705	18984	22458	16269	18331	18347	17272	17256	20000 ⁴²
Cl	24333	19421	21850	18489	23841	24771	21605	22870	20208 ⁴³
Br	18779	20568	16994	19935	24725	23600	22538	21649	20117 ⁴⁴
I	12002	21508	10897	20534	27306	28274	23331	24303	

Table 4: Electronic spectrum of $[\text{UO}_2\text{F}_4]^{2-}$ including spin-orbit coupling. The composition of each state is given in terms of spin-orbit free configurations. Energies in cm^{-1} .

Energy	Configuration ¹
0	$p^6 \pi_u^4 \pi_g^4 \sigma_g^2 \sigma_u^2$
17256	88% $\sigma_u \delta_u''$
17339	89% $\sigma_u \delta_u''$
17736	94% $\sigma_u \delta_u''$
22173	48% $\sigma_u \delta_u'$ + 39% $\sigma_u \delta_u''$
24356	82% $\sigma_u \delta_u'$
24468	86% $\sigma_u \delta_u'$
25808	43% $\sigma_u \bar{\delta}_u''$ + 40% $\sigma_u \delta_u'$
29540	95% $\sigma_u \pi_u^*$
29733	83% $\sigma_u \pi_u^*$
29775	81% $\sigma_u \pi_u^*$
30305	85% $\bar{\sigma}_u \phi_u$
30665	43% $\pi_u \delta_u''$ + 30% $(\pi_u \bar{\delta}_u'' + \bar{\sigma}_u \pi_u^*)$
30828	90% $\pi_u \delta_u''$
30950	78% $\pi_u \delta_u''$
31228	42% $\sigma_u \pi_u^*$ + 25% $\pi_u \delta_u''$
31457	38% $\sigma_u \pi_u^*$ + 24% $\pi_u \bar{\delta}_u''$ + 24% $\pi_u \delta_u''$

¹ δ_u and ϕ_u are the uranium atomic f_δ and f_ϕ orbitals

Table 5: Electronic spectrum of $[\text{UO}_2\text{Cl}_4]^{2-}$ including spin-orbit coupling. The composition of each state is given in terms of spin-orbit free configurations. Energies in cm^{-1} .

Energy	Configuration ¹
0	$p^6\pi_u^4\pi_g^4\sigma_g^2\sigma_u^2$
22870	58% $\sigma_u\delta_u''$ + 35% $\sigma_u\delta_u'$
22876	58% $\sigma_u\delta_u''$ + 37% $\sigma_u\delta_u'$
23090	59% $\sigma_u\delta_u''$ + 20% $\sigma_u\phi_u$
23745	64% $\sigma_u\delta_u'$ + 18% $\sigma_u\phi_u$
24450	43% $\sigma_u\delta_u'$ + 32% $\sigma_u\phi_u$ + 13% $\bar{\sigma}_u\phi_u$
24636	44% $\sigma_u\delta_u'$ + 30% $\sigma_u\phi_u$ + 12% $\sigma_u\delta_u''$
25222	52% $\sigma_u\phi_u$ + 29% $\sigma_u\delta_u'$
26143	51% $\sigma_u\phi_u$ + 26% $\sigma_u\delta_u''$
28580	39% $\sigma_u\phi_u$ + 29% $\sigma_u\delta_u''$ + 20% $\sigma_u\delta_u'$
28746	45% $\sigma_u\phi_u$ + 26% $\sigma_u\delta_u''$ + 19% $\sigma_u\delta_u'$
30158	85% $\sigma_u\phi_u$
30326	92% $\sigma_u\phi_u$
31052	71% $\sigma_u\bar{\delta}_u'$
31726	66% $\sigma_u\bar{\delta}_u''$
31868	54% $\bar{\sigma}_u\phi_u$ + 19% $\sigma_u\phi_u$ + 17% $(p_y\phi_u + \pi_u\phi_u)$
32052	56% $\bar{\sigma}_u\phi_u$
32743	32% $(\sigma_g\delta_u'' + \pi_g\phi_u)$ + 24% $(\bar{p}_z\phi_u + \bar{\pi}_g\phi_u)$ + 21% $(\pi_g\delta_u'' + p_z\delta_u'')$
32794	35% $(\sigma_g\delta_u'' + \pi_g\phi_u)$ + 26% $(p_z\phi_u + \pi_g\phi_u)$ + 14% $p_z\bar{\delta}_u'$
32989	28% $(\sigma_g\delta_u'' + \pi_g\phi_u)$ + 22% $(p_z\phi_u + \pi_g\phi_u)$ + 19% $(\pi_g\bar{\delta}_u'' + p_z\bar{\delta}_u'')$
33200	33% $(\pi_g\delta_u'' + p_z\delta_u'')$ + 27% $p_z\delta_u'$ + 11% $\bar{\sigma}_u\phi_u$
33226	59% $p_z\bar{\delta}_u'$ + 11% $(\pi_g\delta_u'' + p_z\delta_u'')$

¹ δ_u and ϕ_u are the uranium atomic f_δ and f_ϕ orbitals

Table 6: Comparison of experimental and theoretical results for the lower part of the $[\text{UO}_2\text{Cl}_4]^{2-}$ absorption spectrum. Energies in cm^{-1} .

This work	$\text{Cs}_2\text{UO}_2\text{Cl}_4$ ¹⁴	Ionic liquid ⁴⁷	Acetonitrile ⁴³	SO-CASPT2 ¹⁰	TD-DFT ¹¹
22870	20096	20060	20208	21024	20884
23090	20407	20325	20635	21273	20954
23745	21316	20563	22935	22125	21335
24450	22026	20756	26388	22859	22108
24636	22406	21026	—	24056	22420

Table 7: Electronic spectrum of $[\text{UO}_2\text{Br}_4]^{2-}$ including spin-orbit coupling. The composition of each state is given in terms of spin-free configurations. Energies in cm^{-1} .

Energy	Configuration ¹
0	$p^6 \pi_u^4 \pi_g^4 \sigma_g^2 \sigma_u^2$
21649	67% $\sigma_u \delta_u''$ + 25% $\sigma_u \delta_u'$
21695	66% $\sigma_u \delta_u''$ + 25% $\sigma_u \delta_u'$
21772	64% $\sigma_u \delta_u''$ + 31% $\sigma_u \phi_u$
22470	58% $\sigma_u \phi_u$ + 41% $\sigma_u \delta_u'$
22776	70% $\sigma_u \phi_u$ + 30% $\sigma_u \delta_u''$
23200	42% $\sigma_u \delta_u'$ + 29% $\sigma_u \phi_u$ + 22% $(\bar{p}_z \phi_u + \bar{\sigma}_u \phi_u)$
23549	48% $\sigma_u \phi_u$ + 37% $(\sigma_u \bar{\delta}_u' + p_z \bar{\delta}_u')$
23954	45% $\sigma_u \delta_u'$ + 21% $(\sigma_u \bar{\delta}_u'' + p_z \bar{\delta}_u'') + 17\%$ $\sigma_u \phi_u$
26715	32% $\sigma_u \delta_u'$ + 23% $\sigma_u \phi_u$ + 22% $\sigma_u \delta_u''$
26812	27% $(\bar{p}_z \phi_u + \bar{\sigma}_u \phi_u) + 25\%$ $\sigma_u \delta_u'$ + 20% $\sigma_u \delta_u''$
27258	49% $(\sigma_u \bar{\delta}_u' + p_z \bar{\delta}_u') + 13\%$ $\sigma_u \delta_u'' + 12\%$ $(\pi_g \delta_u'' + p_z \delta_u'')$
28338	53% $(\sigma_u \bar{\delta}_u'' + p_z \bar{\delta}_u'')$

¹ δ_u and ϕ_u are the uranium atomic f_δ and f_ϕ orbitals

Table 8: Electronic spectrum of $[\text{UO}_2\text{I}_4]^{2-}$ including spin-orbit coupling. The composition of each state is given in terms of spin-free configurations. Energies in cm^{-1} .

Energy	Configuration ¹
0	$p^6\pi_u^4\pi_g^4\sigma_g^2\sigma_u^2$
24303	79% $(p_z\phi_u + \sigma_u\phi_u)$
24375	80% $(p_z\phi_u + \sigma_u\phi_u)$
24614	51% $(p_z\phi_u + \sigma_u\phi_u) + 27\% (\bar{p}_z\phi_u + \bar{\sigma}_u\phi_u)$
24813	40% $(\bar{p}_z\phi_u + \bar{\sigma}_u\phi_u) + 37\% (p_z\phi_u + \sigma_u\phi_u)$
25887	47% $(\sigma_u\delta'_u + p_z\delta'_u) + 35\% (\sigma_u\delta''_u + p_z\delta''_u) + 11\% p_x\bar{\delta}'_u$
26205	41% $(\sigma_u\delta''_u + p_z\delta''_u) + 39\% p_z\bar{\delta}'_u + 12\% p_y\delta'_u$
26565	49% $(\sigma_u\delta''_u + p_z\delta''_u) + 24\% (p_z\bar{\delta}''_u + \pi_g\bar{\delta}''_u) + 15\% p_y\delta'_u$
29732	36% $p_x\phi_u + 15\% p_x\delta''_u + 13\% (p_z\phi_u + \sigma_u\phi_u)$
29750	27% $p_x\phi_u + 14\% (\bar{p}_z\phi_u + \bar{\sigma}_u\phi_u) + 13\% p_x\bar{\delta}''_u$
29945	19% $(p_z\phi_u + \sigma_u\phi_u) + 17\% (\sigma_u\delta''_u + p_z\delta''_u) + 13\% p_z\bar{\delta}'_u + 12\% p_x\delta''_u$
¹ δ_u and ϕ_u are the uranium atomic f_δ and f_ϕ orbitals	