Charge Transfer in Uranyl(VI) Halides [UO$_2$X$_4$]$^{2-}$ (X = F, Cl, Br, and I). A Quantum Chemical Study of the Absorption Spectra

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The electronic spectra of uranyl(VI) coordinated with four equatorial halide ligands, [UO$_2$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 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 [UO$_2$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 [UO$_2$F$_4$]$^{2-}$ there is no charge transfer excitation below 50 000 cm^{-1}, while in [UO$_2$Cl$_4$]$^{2-}$ it appears around 33 000 cm^{-1} and in [UO$_2$Br$_4$]$^{2-}$ around 23 000 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 studied[5−7] 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 at room temperature.[9] Therefore, studies of these complexes have been less frequent. The absorption and luminescence spectra of the [UO$_2$F$_4$]$^{2-}$, [UO$_2$Cl$_4$]$^{2-}$, and [UO$_2$Br$_4$]$^{2-}$ have been studied experimentally, but only the spectrum of [UO$_2$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$_\delta$) and ϕ_u (f$_\phi$) orbitals. 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

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TABLE 1: Experimental Geometries of the [UO$_2$X$_4$]$^{2-}$ Complexes from EXAFS Measurements of [UO$_2$F$_4$]$^{2-}$ in Aqueous Solution,[51] [UO$_2$Cl$_4$]$^{2-}$ in Acetonitrile,[49] [UO$_2$Br$_4$]$^{2-}$ in Ionic Liquid[50] and X-ray Diffraction of [UO$_2$I$_4$]$^{2-}$ in Solid (Ph$_4$P)$_2$UO$_2$I$_4$·2NCCH$_3$[55,a]

	[UO$_2$F$_4$]$^{2-}$	[UO$_2$Cl$_4$]$^{2-}$	[UO$_2$Br$_4$]$^{2-}$	[UO$_2$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	

[a] The calculated geometry of the bare UO$_2^{2+}$ ion[56] is also shown. Distances in Ångstroms.

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 [UO$_2$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 [UO$_2$X$_4$]$^{2-}$ Complexes and Symmetry Considerations. The experimental geometry for [UO$_2$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 [UO$_2$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 $\delta_g \rightarrow b_{1g}$

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'

$+ b_{2g}$. 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 to 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 U5f6d and O2p 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 $[UO_2X_4]^{2-}$ 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, 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 50 000 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$_\delta$) 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

TABLE 3: Number of Roots Averaged in the CASSCF Calculations for Each Multiplicity and Irreducible Representation of the C_{2v} Point Group

	$^1A_1$	$^3A_1$	$^1B_1$	$^3B_1$	$^1B_2$	$^3B_2$	$^1A_1$	$^3A_2$
$[UO_2F_4]^{2-}$	4	6	5	5	4	6	5	5
$[UO_2Cl_4]^{2-}$	10	9	8	7	6	6	7	7
$[UO_2Br_4]^{2-}$	8	6	8	8	6	6	7	8
$[UO_2I_4]^{2-}$	10	9	8	8	6	6	8	8

TABLE 4: Restricted Active Space (RASSCF) Calculations in $[UO_2Br_4]^{2-}$ Including Single Excitations from the Ligand Orbitals[a]

four ligands		one ligand	
total energy	transition energy	total energy	transition energy
−38 517.511 401 68	0	−38 517.491 245 66	0
−38 517.357 841 64	33 701	−38 517.339 265 70	33 356
−38 517.319 298 93	42 162	−38 517.304 657 31	40 951
−38 517.319 298 91	42 162	−38 517.269 835 30	48 594

[a] Energies in cm^{-1}.

5p in iodine). In Table 3 are found the details of the CASSCF calculations for each complex, including the number of roots averaged in each irreducible representation. In order to assess the validity of this assumption, in which we consider only one halide ligand, we have carried out some restricted active space self-consistent-field (RASSCF) calculations[24] in the bromide complex, $[UO_2Br_4]^{2-}$, where the complete active space is now built on the distribution of 12 electrons in 10 molecular orbitals from the uranyl unit (σ_g, σ_u, π_g, π_u, ϕ_u, and δ_u) and we generate additional configuration state functions by allowing single excitations from the ligand orbitals. To ensure that the first transitions were of charge transfer type, the inactive orbitals were not allowed to mix with the active and the virtual orbitals. Thus, we can estimate the energy of ligand-to-metal charge-transfer states including the four ligands, which means taking into account single excitations of 24 electrons from the twelve 4p orbitals of the bromide ligands, and compare it with the same charge-transfer states arising from single excitations of 6 electrons from the three 4p orbitals localized in only one bromide ligand. The results of these calculations are shown in Table 4, where it is observed that the first two transitions (the first one corresponding to a $\sigma_u\delta_u$ configuration and the second one to a mixture of $\pi_g\delta_u$ with $p_z\delta_u$ configurations) appear at similar energies in both cases. The third transition is degenerated with the second one when the four ligands are included and corresponds to the same configuration but involving a different bromide ligand. Of course this transition is not observed when we allow excitations only from one ligand. Thus, we can say that is reasonably safe to take into account only one ligand in the calculation and ignore the rest, since the spectrum is not going to be excessively affected. The remaining dynamical correlation effects were included through complete active space second-order perturbation-theory (CASPT2)[25] calculations based on the CASSCF reference with the ionization potential electron affinity (IPEA)-corrected zeroth-order Hamiltonian.[26] The use of an imaginary level-shift operator technique[27] 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 and np shells from the ligands. Finally, to take into account the spin−orbit coupling, we use the variation-perturbation method RASSI-SO,[28] available in MOLCAS, with the orbital basis

TABLE 5: Comparison of Methods and Basis sets[a]

	localization				ab initio model potentials				
	MS-CASPT2		RASSI-SO		MS-CASPT2		RASSI-SO		
	triple-ζ	quad-ζ	triple-ζ	quad-ζ	triple-ζ	quad-ζ	triple-ζ	quad-ζ	exp.
F	25 705	18 984	22 458	16 269	18 331	18 347	17 272	17 256	20 000[48]
Cl	24 333	19 421	21 850	18 489	23 841	24 771	21 605	22 870	20 208[49]
Br	18 779	20 568	16 994	19 935	24 725	23 600	22 538	21 649	20 117[50]
I	12 002	21 508	10 897	20 534	27 306	28 274	23 331	24 303	

[a] Only the first transition of the spectra is shown. Energies in cm⁻¹.

TABLE 6: Electronic Spectrum of [UO₂F₄]²⁻ Including Spin-Orbit Coupling[a]

energy	configuration[b]
0	$p^6\pi_u^4\pi_g^4\sigma_g^2\sigma_u^2$
17 256	88% $\sigma_u\delta_u''$
17 339	89% $\sigma_u\delta_u''$
17 736	94% $\sigma_u\delta_u''$
22 173	48% $\sigma_u\delta_u' + 39\%\ \sigma_u\delta_u''$
24 356	82% $\sigma_u\delta_u'$
24 468	86% $\sigma_u\delta_u'$
25 808	43% $\sigma_u\bar{\delta}_u'' + 40\%\ \sigma_u\delta_u'$
29 540	95% $\sigma_u\pi_u^*$
29 733	83% $\sigma_u\pi_u^*$
29 775	81% $\sigma_u\pi_u^*$
30 305	85% $\bar{\sigma}_u\phi_u$
30 665	43% $\pi_u\delta_u'' + 30\%\ (\pi_u\bar{\delta}_u'' + \bar{\sigma}_u\pi_u^*)$
30 828	90% $\pi_u\delta_u''$
30 950	78% $\pi_u\delta_u''$
31 228	42% $\sigma_u\pi_u^* + 25\%\ \pi_u\delta_u''$
31 457	38% $\sigma_u\pi_u^* + 24\%\ \pi_u\delta_u'' + 24\%\ \pi_u\delta_u''$

[a] The composition of each state is given in terms of spin-orbit free configurations. Energies in cm⁻¹. [b] δ_u and ϕ_u are the uranium atomic f$_\delta$ and f$_\phi$ orbitals.

obtained from a state-average CASSCF calculation. 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.[29,30] Differential spinor relaxation, that is, different radial distributions for different spinor components, is not accounted for in the variation-perturbation method. This effect has been shown to be small in uranyl, but it may be significant in the main group where the outermost p orbital is more polarizable than the f orbitals in uranyl. In a previous study of the spin−orbit effect in the Tl atom,[31] the experimental spin−orbit splitting of the 5p-spinors was found to be 7793 cm⁻¹. Variation-perturbation calculations underestimated the splitting by about 1500 cm⁻¹, while a result in good agreement with experiment was obtained when the spinor components were allowed to relax. In the excited states in the uranyl-halide complexes the open p-shell on the ligands will contribute to the spin−orbit splitting. The spin−orbit splittings of the p-shells in F,[32] Cl,[33] Br,[34] and I[35] are 404, 882, 3685, and 7603 cm⁻¹, respectively. The largest error, which will occur for iodine and thus will be estimated to be 1500 cm⁻¹ below, is of limited importance in the present case.

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. Initially we made an attempt to use localization, based on the Pipek−Mezey procedure.[36] In this 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. However, as will be discussed in a subsequent section, the localization procedure did not give satisfactory results. The alternative procedure, to freeze three of the ligands, implies that the spectrum of UO₂X⁺ 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, AIMPs, 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.[37,38] 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.[39−43] When the AIMPs are used in the present context it is no longer necessary to have symmetry-independent ligands, 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][44] and on oxygen the (14s9p4d3f2g) primitive basis set contracted to a triple-ζ size [4s3p2d1f].[45] For the halide ligands we also used ANO-RCC basis sets of both triple-ζ and quadruple-ζ quality;[45] 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 (20s17p11d-4f2g) 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: Cs₂NaYF₆,[46] Cs₂NaYCl₆,[47] and Cs₂NaYBr₆.[47] The embedding potential for iodide ion was produced in this work, following the recipe for the AIMP method[37,38] 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 UO₂²⁺ unit, and the spectra were generated from excitations to the empty nonbonding δ_u and ϕ_u orbitals. Table 5 shows the first transition from the ground state for each basis set and each model, together with experimental results for fluoride,[48]

TABLE 7: Electronic Spectrum of $[UO_2Cl_4]^{2-}$ Including Spin-Orbit Coupling[a]

energy	configuration[b]
0	$p^6\pi_u^4\pi_g^4\sigma_g^2\sigma_u^2$
22 870	58% $\sigma_u\delta_u'' + 35\%\ \sigma_u\delta_u'$
22 876	58% $\sigma_u\delta_u'' + 37\%\ \sigma_u\delta_u'$
23 090	59% $\sigma_u\delta_u'' + 20\%\ \sigma_u\phi_u$
23 745	64% $\sigma_u\delta_u' + 18\%\ \sigma_u\phi_u$
24 450	43% $\sigma_u\delta_u' + 32\%\ \sigma_u\phi_u + 13\%\ \bar{o}_u\phi_u$
24 636	44% $\sigma_u\delta_u' + 30\%\ \sigma_u\phi_u + 12\%\ \sigma_u\delta_u''$
25 222	52% $\sigma_u\phi_u + 29\%\ \sigma_u\delta_u'$
26 143	51% $\sigma_u\phi_u + 26\%\ \sigma_u\delta_u''$
28 580	39% $\sigma_u\phi_u + 29\%\ \sigma_u\delta_u'' + 20\%\ \sigma_u\delta_u'$
28 746	45% $\sigma_u\phi_u + 26\%\ \sigma_u\delta_u'' + 19\%\ \sigma_u\delta_u'$
30 158	85% $\sigma_u\phi_u$
30 326	92% $\sigma_u\phi_u$
31 052	71% $\sigma_u\bar{\delta}_u'$
31 726	66% $\sigma_u\bar{\delta}_u''$
31 868	54% $\bar{o}_u\phi_u + 19\%\ \sigma_u\phi_u + 17\%\ (p_y\phi_u + \pi_u\phi_u)$
32 052	56% $\bar{o}_u\phi_u$
32 743	32% $(\sigma_g\delta_u'' + \pi_g\phi_u) + 24\%\ (\bar{p}_z\phi_u + \bar{\pi}_g\phi_u) + 21\%\ (\pi_g\phi_u' + p_z\delta_u'')$
32 794	35% $(\sigma_g\delta_u'' + \pi_g\phi_u) + 26\%\ (p_z\phi_u + \pi_g\phi_u) + 14\%\ p_z\delta_u'$
32 989	28% $(\sigma_g\delta_u'' + \pi_g\phi_u) + 22\%\ (p_z\phi_u + \pi_g\phi_u) + 19\%\ (\pi_g\bar{\delta}_u' + p_z\bar{\delta}_u')$
33 200	33% $(\pi_g\delta_u'' + p_z\delta_u'') + 27\%\ p_z\delta_u' + 11\%\ \bar{o}_u\phi_u$
33 226	59% $p_z\bar{\delta}_u' + 11\%\ (\pi_g\delta_u'' + p_z\delta_u'')$

[a] The composition of each state is given in terms of spin-orbit free configurations. Energies in cm^{-1}. [b] δ_u and ϕ_u are the uranium atomic f_δ and f_ϕ orbitals.

$[UO_2F_4]^{2-}$, chloride,[49] $[UO_2Cl_4]^{2-}$, and bromide,[50] $[UO_2Br_4]^{2-}$. 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 AIMPs, while the triple-ζ basis sets with the localization technique give remarkably different results. This is presumably due to basis set dependent differences in the admixture with orbitals on the passive ligands. The sensitivity to the basis set shows that the localization procedure is unreliable in this type of calculations, and in the following we will only refer to results obtained with AIMPs. The AIMP results obtained with both the triple-ζ and the quadruple-ζ basis sets show a trend where the first transition is blue-shifted between F$^-$ and Cl$^-$, very similar between Cl$^-$ and Br$^-$, and again blue-shifted between Br$^-$ and I$^-$. The first transition in experimental absorption spectra[48-50] 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. The agreement with experiment must in all cases be considered satisfactory. The excitation energies obtained with the AIMP model are similar and are within the expected errors for this method, thus we will only refer to results obtained with the larger quadruple-ζ basis sets.

First Excited State. Effects of the U−X Interaction. The last two columns in Table 5 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 that 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 the 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 $[UO_2Br_4]^{2-}$ compared to $[UO_2Cl_4]^{2-}$, only 0.14 Å, and in this case the transition energy actually decreases by 1221 cm^{-1} at the 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. $[UO_2F_4]^{2-}$. There is no crystal structure available for this complex, and the experimental structure is obtained from EXAFS measurements in solution.[51] The calculated vertical excitation energies including spin−orbit coupling for the first 17 states of $[UO_2F_4]^{2-}$, up to 31 500 cm^{-1}, are shown in Table 6 (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 17 256 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 22 173 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 24 356 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,[52] $[UO_2(CO_3)_3]^{5-}$, it was found that the transition to the π_u^* orbital is lowered more than 10 000 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 $[UO_2F_4]^{2-}$ the effect of the F$^-$ is more pronounced than in the carbonates because the distance to the ligands is shorter, 2.260 Å, compared to 2.552 Å in the $[UO_2(CO_3)_3]^{5-}$ complex. There are no charge-transfer excitations from the fluoride at energies lower than 50 000 cm^{-1} due to the great electronegativity of this ion. The experimental spectrum is recorded in aqueous solution[48] and consists of several weak bands with origin at about 20 000 cm^{-1}

TABLE 8: Comparison of Experimental and Theoretical Results for the Lower Part of the [UO$_2$Cl$_4$]$^{2-}$ Absorption Spectrum[a]

this work	Cs$_2$UO$_2$Cl$_4$[14]	ionic liquid[53]	acetonitrile[49]	SO-CASPT2[10]	TD-DFT[11]
22 870	20 096	20 060	20 208	21 024	20 884
23 090	20 407	20 325	20 635	21 273	20 954
23 745	21 316	20 563	22 935	22 125	21 335
24 450	22 026	20 756	26 388	22 859	22 108
24 636	22 406	21 026		24 056	22 420

[a] Energies in cm^{-1}.

TABLE 9: Electronic Spectrum of [UO$_2$Br$_4$]$^{2-}$ Including Spin-Orbit Coupling[a]

energy	configuration[b]
0	p$^6\pi_u^4\pi_g^4\sigma_g^2\sigma_u^2$
21 649	67% $\sigma_u\delta_u''$ + 25% $\sigma_u\delta_u'$
21 695	66% $\sigma_u\delta_u''$ + 25% $\sigma_u\delta_u'$
21 772	64% $\sigma_u\delta_u''$ + 31% $\sigma_u\phi_u$
22 470	58% $\sigma_u\phi_u$ + 41% $\sigma_u\delta_u'$
22 776	70% $\sigma_u\phi_u$ + 30% $\sigma_u\delta_u''$
23 200	42% $\sigma_u\delta_u'$ + 29% $\sigma_u\phi_u$ + 22% ($\bar{p}_z\phi_u + \bar{\sigma}_u\phi_u$)
23 549	48% $\sigma_u\phi_u$ + 37% ($\sigma_u\bar{\delta}_u' + p_z\bar{\delta}_u'$)
23 954	45% $\sigma_u\delta_u'$ + 21% ($\sigma_u\bar{\delta}_u'' + p_z\bar{\delta}_u''$) + 17% $\sigma_u\phi_u$
26 715	32% $\sigma_u\delta_u'$ + 23% $\sigma_u\phi_u$ + 22% $\sigma_u\delta_u''$
26 812	27% ($\bar{p}_z\phi_u + \bar{\sigma}_u\phi_u$) + 25% $\sigma_u\delta_u'$ + 20% $\sigma_u\delta_u''$
27 258	49% ($\sigma_u\bar{\delta}_u' + p_z\bar{\delta}_u'$) + 13% $\sigma_u\delta_u''$ + 12% ($\pi_g\delta_u'' + p_z\delta_u''$)
28 338	53% ($\sigma_u\bar{\delta}_u'' + p_z\bar{\delta}_u''$)

[a] The composition of each state is given in terms of spin-free configurations. Energies in cm^{-1}. [b] δ_u and ϕ_u are the uranium atomic f$_\delta$ and f$_\phi$ orbitals.

TABLE 10: Electronic Spectrum of [UO$_2$I$_4$]$^{2-}$ Including Spin-Orbit Coupling[a]

energy	configuration[b]
0	p$^6\pi_u^4\pi_g^4\sigma_g^2\sigma_u^2$
24 303	79% ($p_z\phi_u + \sigma_u\phi_u$)
24 375	80% ($p_z\phi_u + \sigma_u\phi_u$)
24 614	51% ($p_z\phi_u + \sigma_u\phi_u$) + 27% ($\bar{p}_z\phi_u + \bar{\sigma}_u\phi_u$)
24 813	40% ($\bar{p}_z\phi_u + \bar{\sigma}_u\phi_u$) + 37% ($p_z\phi_u + \sigma_u\phi_u$)
25 887	47% ($\sigma_u\underline{\delta}_u' + p_z\delta_u'$) + 35% ($\sigma_u\delta_u'' + p_z\delta_u''$) + 11% $p_x\delta_u'$
26 205	41% ($\sigma_u\delta_u'' + p_z\delta_u''$) + 39% $p_z\bar{\delta}_u'$ + 12% $p_y\delta_u'$
26 565	49% ($\sigma_u\delta_u'' + p_z\delta_u''$) + 24% ($p_z\bar{\delta}_u' + \pi_g\bar{\delta}_u''$) + 15% $p_y\delta_u'$
29 732	36% $p_x\phi_u$ + 15% $p_x\delta_u''$ + 13% ($p_z\phi_u + \sigma_u\phi_u$)
29 750	27% $p_x\phi_u$ + 14% ($\bar{p}_z\phi_u + \bar{\sigma}_u\phi_u$) + 13% $p_x\delta_u'$
29 945	19% ($p_z\phi_u + \sigma_u\phi_u$) + 17% ($\sigma_u\delta_u'' + p_z\delta_u''$) + 13% $p_z\delta_u'$ + 12% $p_x\delta_u''$

[a] The composition of each state is given in terms of spin-free configurations. Energies in cm^{-1}. [b] δ_u and ϕ_u are the uranium atomic f$_\delta$ and f$_\phi$ orbitals.

(500 nm), thus our theoretical results seem to underestimate the experiment by a few thousand cm^{-1}.

[UO$_2$Cl$_4$]$^{2-}$. Among the uranyl halides, the chloride complex has attracted the most attention, and several experimental and theoretical results are available in the literature. Our calculated absorption spectra up to 33 300 cm^{-1}, including spin−orbit coupling, is shown in Table 7 (a more complete spectrum, both at the CASPT2 and RASSI-SO levels, can be found in Tables S3 and S4 in the Supporting Information). The first transition, which corresponds to a $\sigma_u \rightarrow$ f$_\delta$ transition in the uranyl ion, is found at 22 870 cm^{-1}. This level is a mixture of σ_uf$_\delta'$ and σ_uf$_\delta''$ due to the small separation of these levels in the spin−orbit free calculations, 446 cm^{-1}. The following transitions, up to

approximately 30 000 cm^{-1}, involve both σ_uf$_\delta'$ and σ_uf$_\delta''$ mixed with σ_uf$_\phi$. At 30 158 cm^{-1} appears the pure σ_uf$_\phi$ level, and at 31 868 cm^{-1} the first level with contributions from the charge transfer from the ligands appears. At 33 226 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 the Supporting Information). These results can be compared with experiments in solutions[49,53] and in crystals,[14] and with theoretical calculations,[10,11] see Table 8. 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 calculations[10] used the active space recommended for uranyl, that is, all the bonding and antibonding orbitals, plus the two f$_\delta$ or the two f$_\phi$, 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 Besien[10] 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, 20 884 cm^{-1}, and the experiment, 20 096 cm^{-1}, the nature of the state is different. Pierloot et al. find a ground state of mainly σ_uf$_\phi$ character, rather than σ_uf$_\delta$ 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 Cs$_2$UO$_2$Cl$_4$ crystal,[12] with a first vertical transition of 20 364 cm^{-1}, which also shows good agreement with the experimental value, 20 096 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 33 000 cm^{-1}, which agrees well with our transition at 33 226 cm^{-1}.

[UO$_2$Br$_4$]$^{2-}$. The vertical spectrum including spin−orbit coupling is shown in Table 9 (see Tables S5 and S6 in the Supporting Information for the complete spectra at the spin-free and spin−orbit coupling levels, respectively). The first transition, located at 21 649 cm^{-1}, is a mixture of σ_uf$_\delta'$ and σ_uf$_\delta''$ due to the small separation of this electronic states at the spin−orbit free level, 641 cm^{-1}. The transitions at 21 772 and 22470 cm^{-1} are to levels where σ_uf$_\delta'$ and σ_uf$_\delta''$ are mixed with σ_uf$_\phi$. The next excited state, at 22 776 cm^{-1}, is still mixed but with more σ_uf$_\phi$ character, and at 23 200 cm^{-1} we find the first contribution of charge transfer from the bromide ligand, consistent with the intense absorption found at 23 000 cm^{-1} in the Cs$_2$UO$_2$Br$_4$ crystal.[54] 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 $[UO_2Br_4]^{2-}$ in an ionic liquid.[50] The spectrum has four characteristic bands at 20 117, 20 838, 21 538, and 22 232 cm^{-1}, which compares favorably with our results of 21 649, 21 772, 22 470, and 22 776 cm^{-1}, and there is an intense absorption above 23 000 cm^{-1}, again consistent with the appearance of the charge transfer band in our calculations.

$[UO_2I_4]^{2-}$. The calculated vertical spectrum for the iodide complex including spin−orbit coupling is shown in Table 10 (the complete spectra are found in Tables S7 and S8 in the Supporting Information). The main feature of the spectrum is that already the first transition, at 24 303 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, $[UO_2X_4]^{2-}$ (X = F, Cl, Br, and I), including charge-transfer excitations from the ligands, using relativistic wave function based methods of quantum chemistry. To include the charge transfer from the halides, we 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. On the basis of 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, 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 $[UO_2I_4]^{2-}$.

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). This material is available free of charge via the Internet at http://pubs.acs.org.

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