

An ab Initio Theoretical Study of the Electronic Structure of  $\text{UO}_2^+$  and  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ Fernando Ruipérez,<sup>\*,†</sup> Cécile Danilo,<sup>‡</sup> Florent Réal,<sup>‡</sup> Jean-Pierre Flament,<sup>‡</sup> Valérie Vallet,<sup>‡</sup> and Ulf Wahlgren<sup>†,§</sup>

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The electronic spectra up to  $50000\text{ cm}^{-1}$  of uranyl(V) both as a bare ion,  $\text{UO}_2^+$ , and coordinated with three carbonate ligands,  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ , are presented. Solvent effects were treated by a nonequilibrium continuum solvent model. The transition energies were obtained at the spin-orbit level using relativistic wave function based multiconfigurational methods such as the complete active space self-consistent field method (CASSCF) and the complete active space with second-order perturbation theory (CASPT2) followed by a calculation of the spin-orbit effects at the variation-perturbation level. Earlier relativistic intermediate Hamiltonian Fock space coupled-cluster calculations on the spectrum of the bare uranyl(V) ion were extended to investigate the influence of electron correlation effects on spacings between the electronic states. This study is an attempt to contribute to an enhanced understanding of the electronic structure of actinyl ions. Both spectra show transitions within nonbonding orbitals and between nonbonding and antibonding orbitals as well as charge transfers from the uranyl oxygens to uranium. The ground state in  $\text{UO}_2^+$  is found to be  ${}^2\Phi_{5/2u}$ , corresponding to the  $\sigma_u^2\phi_u^1$  configuration, while in  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ , it is  ${}^2\Delta_{3/2u}$ , arising from the  $\sigma_u^2\delta_u^1$  configuration. It is remarkable that the excited state corresponding to an excitation from the nonbonding  $\delta_u$  to the uranyl antibonding  $3\tau_u^*$  molecular orbital is significantly lower in energy in the carbonate complex,  $6623\text{ cm}^{-1}$ , than that in the bare ion,  $17908\text{ cm}^{-1}$ . The first ligand (carbonate) to metal charge-transfer excitation is estimated to occur above  $50000\text{ cm}^{-1}$ . The reported results compare favorably with experiment when available.

## Introduction

Early actinides in high oxidation states have been extensively studied during the last 10 years. The spectrum of six-valued uranyl is experimentally well-known,<sup>1–3</sup> and several theoretical studies both in the gas phase<sup>4–6</sup> and in solution<sup>7</sup> have been reported, as well as experimental and theoretical studies on five- and six-valued neptunyl.<sup>8,9</sup>

While five-valued neptunyl is stable in solution, this is generally not the case for uranyl(V), which disproportionates into uranyl(VI) and U(IV). Consequently, data on the spectrum of five-valued uranyl is more scarce. Spectroscopic properties of U(V) species in aqueous<sup>10,11</sup> and in nonaqueous solvents<sup>12–15</sup> have been investigated by various groups by means of photochemical and electrochemical reduction of U(VI) complexes to U(V) ones. These studies showed that the U(V) species have characteristic absorption bands in visible and near-infrared regions, that is, 650, 750, 1000, and 1500 nm. However, in most of the previous reports, sample solutions were mixtures of U(IV), U(V), and U(VI) species, and the absorption bands of U(V) were assigned by comparing them with those of U(IV) and U(VI) species. This made these assignments rather uncertain. On the other hand, the recent use of cyclic voltametric cells allowed stabilization of U(V) species without the presence of the two other oxidation states.<sup>16</sup> The spectral studies confirmed the presence of absorption bands in the visible/near-infrared

region, that is, at around 640, 740, 860, 1470, and 1890 nm for  $[\text{U}^{\text{V}}\text{O}_2(\text{dbm})_2\text{DMSO}]^-$ , 650, 750, 900, 1400, and 1875 nm for  $[\text{U}^{\text{V}}\text{O}_2(\text{saloph})\text{DMSO}]^-$ , and 760, 990, 1140, 1600, and 1800 nm for  $[\text{U}^{\text{V}}\text{O}_2(\text{CO}_3)_3]^{5-}$  in  $\text{D}_2\text{O}$  containing  $\text{Na}_2\text{CO}_3$ . The fact that the spectral features are similar to each other despite the differences in the ligands coordinated in the equatorial plane of the  $\text{U}^{\text{V}}\text{O}_2^+$  moiety indicates that these bands are attributable to the electronic transitions in the  $\text{U}^{\text{V}}\text{O}_2^+$  core.<sup>17</sup> However, the assignment of the nature of the observed transitions remains unclear and calls for theoretical investigations, the goals being to clarify the electronic structure of both the isolated and coordinated uranyl(V) ions and to quantify the influence of complexing ligands and solute-solvent interaction on the energy levels.

The theoretical study of actinides still remains a challenging task, given the large number of electrons to be included in the calculations, the dense manifold of low-lying states, and the need to include relativistic effects. Because of the large number of electrons which must be correlated, the methods must, at least approximately, be both size-consistent and size-extensive, and the dynamical and nondynamical electronic correlation must be treated in a balanced way. Applicable spin-free methods include complete active space with second-order perturbation theory (CASPT2), Davidson-corrected multireference single and double configuration interaction (MRCI), average coupled pair functional (ACPF)<sup>18</sup> or average quadratic coupled-cluster (AQCC)<sup>19</sup> MRCI methods, and linear response coupled-cluster with single and double excitations (CCSD). All of these methods, with the exception of the CASPT2 method, are limited

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to rather small species in the gas phase if a wide range of transitions are to be studied.

The study of isolated molecules such as  $\text{UO}_2$ ,  $\text{UO}_2^+$ , and  $\text{UO}_2^{2+}$  is important from a fundamental point view as it can provide an understanding of the electronic structure and bonding in simple models.<sup>4,20–23</sup> The only previous theoretical study on  $\text{UO}_2^+$  was carried out by Infante et al. using relativistic Dirac–Coulomb intermediate Hamiltonian Fock space coupled-cluster (DC-IHFSCC) calculations.<sup>22</sup> The first computed transition at  $2736\text{ cm}^{-1}$  that corresponds to a transition from the ground state  $5f_{5/2}^0$  to the excited state  $5f_{3/2}^1$  is in excellent agreement with the experimental value measured with high accuracy,  $2678\text{ cm}^{-1}$ , by the pulsed field ionization zero electron kinetic energy (PFI-ZEKE) technique.<sup>23</sup> Infante et al. report five other transitions between  $5751$  and  $19774\text{ cm}^{-1}$  which correspond to the distribution of the unpaired electron in the virtual orbitals of the closed-shell reference  $\text{UO}_2^{2+}$ , that is, the nonbonding  $5f_\phi$ ,  $5f_\delta$ , and antibonding U–O orbitals of gerade and ungerade symmetries. However, the present implementation of the DC-IHFSCC method can only treat open-shell states with up to two unpaired electrons; thus, electronic states that would involve excitations from  $\sigma_u$  into the  $5f$  nonbonding space are not included. It might thus be possible that more states appear in the  $0$ – $20000\text{ cm}^{-1}$  energy window. Nevertheless, these calculations might be improved by increasing both the number of orbitals included in the coupled-cluster expansion (so-called  $Q$  space in the DC-IHFSCC theory) and the number of correlated electrons, considering in particular the effect of the correlation of the inner  $5d$  electrons. As discussed later in the article, we report extended DC-IHFSCC results that include some more electronic transitions above  $20000\text{ cm}^{-1}$  that were not reported by Infante et al.<sup>22</sup>

In order to clarify and assign the spectrum of uranyl(V), we have studied the vertical excitations of  $\text{UO}_2^+$  and  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  below  $30000\text{ cm}^{-1}$ . The calculations were performed in the gas phase for both systems and also within a continuum solvent model for the tricarbonate complex. We have included the  $5f_{\delta,\phi} \rightarrow 5f_{\phi,\delta}$ ,  $5f_\pi$ , and  $5f_\sigma$ , the  $5f_{\delta,\phi} \rightarrow 6d_\delta$ ,  $6d_\pi$ , and  $6d_\sigma$ , and the charge-transfer excitations from  $\sigma_u$  into the  $5f$  nonbonding space. The spin-free calculations were done at the CASPT2 level as this is the only correlated method that can be used with reasonable computational cost for the uranyl–tricarbonate complex. Spin–orbit effects were calculated using complete active space self-consistent field (CASSCF) wave functions with correlation effects included using the CASPT2 results.

## Details of the Calculations

**Details of the DC-IHFSCC Calculations.** The excitation energies at the DC-IHFSCC<sup>24–27</sup> level were obtained using the same basis sets as those used by Infante et al.,<sup>22</sup> that is, the uranium basis set optimized by Fægri<sup>28</sup> and the uncontracted correlation-consistent polarized valence triple- $\zeta$  (cc-pVTZ) basis set on oxygen.<sup>29</sup> The valence space ( $P$ ) defined for these calculations comprises the (a)  $\sigma_u$ ,  $\sigma_g$ ,  $\pi_u$ , and  $\pi_g$  bonding and antibonding orbitals; (b) the nonbonding  $f_\delta$  and  $f_\phi$  orbitals; (c) the  $6s$  and  $6p$  of the uranium and  $2s$  of the oxygen atoms; as well as (d) the virtual orbitals with energies inferior to  $\epsilon \leq 0.35$  au. The  $P$  space thus includes (22g, 30u) out of which (5g, 7u) are doubly occupied. The  $P_m$  model space is defined with the energy limits of about  $-1.50$  and  $-0.18$  au, which corresponds to (9g, 14u), out of which (3g, 4u) are doubly occupied. The buffer  $P_i$  is the remaining  $P$  space. The  $Q$  space includes virtual orbitals up to an energy value of  $20$  au; the lower limit was changed to include or not the inner  $5d$  electrons in the correlation

treatment. For a detailed account of the DC-IHFSCC method, see refs 24–27. To separate the influence of electron correlation and spin–orbit coupling on the computed spectra, we have also used the four-component spin–orbit-free Dirac–Coulomb Hamiltonian.<sup>30,31</sup> All calculations were run with a development version of Dirac<sup>32</sup> using  $D_{2h}$  symmetry.

**Methodology for Scalar Relativistic and Spin–Orbit Coupling Calculations. Details on the Methods.** The spin-free relativistic calculations were done at the all-electron level with relativistic effects included through the second-order Douglas–Kroll–Hess Hamiltonian.<sup>33,34</sup> The wave functions were obtained from state-average CASSCF, SA-CASSCF,<sup>35</sup> which included all states of interest. Dynamic correlation contributions were estimated using perturbative multistate CASPT2 (MS-CASPT2)<sup>36</sup> using the ionization potential electron affinity (IPEA)-corrected zeroth-order Hamiltonian.<sup>37</sup> In all CASPT2 calculations, we used an imaginary level shift<sup>38</sup> of  $0.15$  au to prevent the appearance of intruder states.

The effect of spin–orbit coupling was obtained by using either an uncontracted determinantal effective Hamiltonian-based spin–orbit configuration interaction method (EPCISO),<sup>39</sup> where a model space including a set of reference configurations which represent the states of interest is defined, or by using variation-perturbation calculations with the CASPT2-corrected, restricted active space state interaction with spin–orbit coupling method, RASSI-SO.<sup>40</sup> In all cases, the orbital basis was obtained from state-average CASSCF calculations. An effective spin–orbit Hamiltonian where the energy differences between the CASSCF and the SA-CASSCF/MS-CASPT2 states were used to shift the diagonal matrix elements of the initial CASSCF Hamiltonian<sup>39,41</sup> was employed in the spin–orbit calculations.

All calculations were performed with the MOLCAS<sup>42</sup> program system, except for the spin–orbit calculations on the bare uranyl(V) ion where we used the EPCISO<sup>39</sup> program interfaced with MOLCAS. Transition dipole moments between the gerade and ungerade spin–orbit eigenstates were computed with the TRANSO program.

**Basis Sets.** We have used atomic natural orbitals relativistic core correlation basis sets for all atoms. On uranium, we used a (26s23p17d13f5g3h) primitive basis contracted to a quadruple- $\zeta$  size [10s9p7d5f3g],<sup>43</sup> and on oxygen and carbon, the (14s9p4d3f2g) primitive basis set contracted to a triple- $\zeta$  size [4s3p2d1f] was used.<sup>44</sup>

**The Bare Uranyl(V) Ion.** In the calculations on the bare uranyl(V) ion, the active space in the CASSCF calculations is defined by the distribution of 3 electrons in 13 molecular orbitals,  $3\sigma_u$ ,  $1\delta_u$ ,  $1\phi_u$ ,  $3\pi_u^*$ ,  $4\sigma_u^*$ ,  $4\sigma_g$ ,  $1\delta_g$ , and  $2\pi_g^*$ , which are mainly composed of uranium  $6p$ ,  $5f$ ,  $6d$ , and  $7s$  and oxygen  $2p$  atomic orbitals. The states corresponding to the configurations with the  $3\sigma_u$  either doubly or singly occupied were considered. In the CASSCF step, the number of doublet states converged is 42 of u and 41 of g symmetry, and the number of quartet states is 15 u and 18 g. All CASSCF calculations were done with the inversion symmetry  $C_i$  to be able to describe all states in a common (averaged) orbital basis, keeping the u or g symmetry. In the CASPT2 step, the uranium atomic orbitals below the  $5d$  were kept frozen as well as the  $1s$  oxygen atomic orbitals, so that 35 electrons were correlated in this step.

**$[\text{UO}_2(\text{CO}_3)_3]^{5-}$ .** In the case of the  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  complex, it was not possible to include the carbonate ligand orbitals in the CASSCF calculation since the ligand orbitals could not be prevented from entering the CAS. To increase the CAS by including the ligand-to-metal charge-transfer (LMCT) states was not possible. Instead, we used a model where the uranyl ion

was enclosed in a ligand “cage”. This was achieved by calculating the wave function of the ligands in the full molecular basis with the  $\text{UO}_2^+$  fragment represented as ghost atoms, followed by a calculation on the complex where the uranyl ion was allowed to relax but where the ligand cage was kept frozen from the previous step. In order to allow some charge transfer to occur, the calculation was repeated with a frozen uranyl, allowing the cage to relax, and finally in the third step, the cage was frozen and the uranyl allowed to relax. The spectrum was obtained from the last cycle.

This model only gives, by construction, the internal uranyl excitations. In order to obtain an estimate of the onset of the LMCT excitations, the HOMO of the ligand cage was included in the active space and allowed to relax. This excitation energy was obtained both in the gas phase and in a water solvent described by the equilibrium conductor-like polarizable model<sup>45,46</sup> (CPCM) at the CASSCF level. This certainly only gives a rough estimate of the onset of the charge-transfer excitations, but it does provide a measure on how high it is worth calculating excitation energies using the cage model.

The geometry of the ground state was optimized in a continuum CPCM solvent<sup>45,46</sup> with the B3LYP density functional<sup>47,48</sup> using the Gaussian package.<sup>49</sup> The inclusion of solvent effects is essential for the ground-state geometry since the complex carries a large negative charge.

The spectra calculations were carried out at the CASPT2 level using the same active space as in the bare ion, that is 3 electrons distributed in 13 molecular orbitals corresponding to the uranium 6p, 5f, 6d, and 7s and oxygen 2p orbitals. In the CASPT2 step, 35 electrons were correlated. The orbitals from the carbonate ligands were frozen in this step. Only Abelian symmetry groups are used in the MOLCAS program, and in order to avoid a wave function with broken symmetry, which may influence the spin-orbit splitting significantly, we used the point group  $C_1$  (no symmetry). The number of doublet states was 53, and the number of quartets was 28. Solvent effects were accounted for by the nonequilibrium CPCM model.<sup>50</sup> In general, one should optimize the slow component of the reaction field of the solvent for the ground state and the fast component for each electronic state of interest by running as many CASSCF calculations as the number of roots. However, this approach is computationally expensive and numerically unstable because of convergence problems in the CASSCF step. We have thus used a simpler approach in which both the fast and slow components are optimized for the ground-state wave function.

## Results

$\text{UO}_2^+$ . The uranyl(V) equilibrium bond distance has been optimized at the multireference configuration interaction (MRCI) single and double spin-free Davidson corrected level. Previous method comparisons performed on uranyl(VI) geometries<sup>6,51</sup> have shown that the MRCI and CASPT2 methods yield U–O bond distances that agree within 0.01 Å. The uranyl(V) optimal bond length is 1.742 Å, which is about 0.04 Å longer than that in uranyl(VI).<sup>6,51</sup> The major reason for this is probably the decreased population in the bonding  $\sigma$  orbital, which is 1.5 in uranyl(VI) but only 1.0 in uranyl(V), induced by the repulsion of the extra electron placed in a uranium 5f orbital. As in uranyl(VI), the bonds are best described as triple bonds with one  $\sigma$  and two  $\pi$  bonds to each oxygen. At the spin-free level, the occupied valence orbitals, in increasing energy order, are  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 1\pi_u^4 2\sigma_u^2 1\pi_g^4 2\pi_u^4 3\sigma_g^2 3\sigma_u^2 5f_\phi^4$ , that is, a  ${}^2\Phi_u$  ground state.

The CASPT2 spin-free excitation energies below 30000  $\text{cm}^{-1}$  are shown in Table 1. The complete set of spin-free energies

**TABLE 1: Electronic Spectrum of  $\text{UO}_2^+$  in the Gas Phase from Spin-Free Scalar Relativistic SA-CASSCF/MS-CASPT2 Calculations at the MRCI Equilibrium Bond Distance  $r(\text{U}-\text{O}) = 1.742 \text{ \AA}^a$**

state	configuration <sup>b</sup>	energy
${}^2\Phi_u$	$\sigma_u^2 \phi_u$	0
${}^2\Delta_u$	$\sigma_u^2 \delta_u$	915
${}^2\Pi_u$	$\sigma_u^2 \pi_u^*$	17908
${}^2\Sigma_g$	$\sigma_u^2 \sigma_g$	18467
${}^2\Delta_g$	$\sigma_u^2 \delta_g$	18622
${}^4\text{H}_u$	$\sigma_u \phi_u \delta_u$	20996
${}^4\Sigma_u$	$\sigma_u \delta_u \delta_u$	21501
${}^4\Pi_u$	$\sigma_u \phi_u \delta_u$	24419
${}^2\text{H}_u$	$\sigma_u \phi_u \delta_u$	28724
${}^2\Pi_u$	$\sigma_u \phi_u \delta_u$	28750
${}^2\Sigma_u$	$\sigma_u \delta_u^2$	29163
${}^2\Gamma_u$	$\sigma_u \delta_u \bar{\delta}_u + \sigma_u \delta_u^2$	29500

<sup>a</sup> Energies are in  $\text{cm}^{-1}$ . <sup>b</sup> Configurations with two electrons occupying the same  $\phi_i$  orbital are denoted as  $\phi_i^2$ .

**TABLE 2: Composition (absolute values of the orbital coefficients) of the  $\text{UO}_2^+$  Molecular Orbitals in Increasing Energy Order**

MOS <sup>a</sup>	composition
$1\sigma_g$	0.95 U s; 0.11 O s
$1\sigma_u$	0.48 U p; 0.66 O s; 0.19 O p
$2\sigma_g^*$	0.32 U s; 0.13 U d; 0.93 O s
$1\pi_u$	0.97 U p
$2\sigma_u^*$	0.68 U p; 0.81 O s; 0.32 O p
$1\pi_g$	0.28 U d; 0.83 O p
$2\pi_u$	0.28 U p; 0.28 U f; 0.89 O p
$3\sigma_g$	0.19 U s; 0.36 U d; 0.34 O s; 0.83 O p
$3\sigma_u$	0.53 U p; 0.62 U f; 0.68 O p
$1\phi_u$	0.99 U f
$1\delta_u$	0.99 U f
$3\pi_u^*$	0.13 U p; 0.96 U f; 0.41 O p
$4\sigma_g$	0.85 U s; 0.40 U d; 0.22 O p
$1\delta_g$	0.99 U d
$4\sigma_u^*$	0.84 U p; 0.80 U f; 0.62 O s; 0.89 O p
$2\pi_g^*$	0.91 U d; 0.60 O p

<sup>a</sup> All orbitals up to the  $3\sigma_u$  are doubly occupied, and the  $1\phi_u$  is singly occupied.

can be found in Table S2 of the Supporting Information. While the  $5f_\phi$  and the  $5f_\delta$  orbitals are nonbonding and almost pure f orbitals, the  $5f_\pi$  and the  $5f_\sigma$  are antibonding and strongly mixed with the oxygen and uranium p orbitals (see Table 2). Similarly, the  $6d_\delta$  orbitals are nonbonding, while the  $6d_\pi$  and the  $6d_\sigma$  orbitals are antibonding and strongly mixed with oxygen p and uranium 7s. The first excited state is  $\sigma_u^2 5f_\delta^1 - {}^2\Delta_u$ , at 915  $\text{cm}^{-1}$ , and the next excitation is to the antibonding  $\pi_u^*$  orbital, which is dominated by  $5f_\pi$  (with a coefficient of 0.96; see Table 2), at 17908  $\text{cm}^{-1}$ . The excitation from the  $5f_\phi$  to the antibonding orbital corresponding to  $5f_\sigma$  does not appear until about 62000  $\text{cm}^{-1}$ , but in this case, the identification with a 5f orbital is meaningless. The excitation from  $5f_\phi$  into  $6d_\delta$  occurs at 18622  $\text{cm}^{-1}$ . The excitation into the first  $\sigma_g$  orbital, which might have been expected to correspond to the  $6d_\sigma$ , is at 18467  $\text{cm}^{-1}$ . However, this orbital is predominantly 7s on uranium. No  $5f_\phi \rightarrow \pi_g^*$  excitation (corresponding to  $6d_\pi$ ) could be identified. The first oxygen-to-uranium charge-transfer excitation,  $\sigma_u \rightarrow 5f_\delta$  ( ${}^4\text{H}_u$ ), occurs at 20996  $\text{cm}^{-1}$ . There are only u states with a singly occupied  $\sigma_u$  up to 34729  $\text{cm}^{-1}$ . The first g state with a singly occupied  $\sigma_u$  orbital is at 34803  $\text{cm}^{-1}$  (see Table S2 of the Supporting Information).

The spin-orbit calculations were done separately in the g and u symmetries and included all doublet and quartet states

**TABLE 3: Electronic Spectrum of  $\text{UO}_2^+$  in the Gas Phase Computed at the SO-CASPT2 Level (EPCISO) with the MRCI Equilibrium Bond Distance  $r(\text{U}-\text{O}) = 1.742 \text{ \AA}^a$** 

state	energy	$f$	configuration <sup>b</sup>
$5/2_u$	0		$88\% \sigma_u^2 \phi_u + 12\% \sigma_u^2 \delta_u$
$3/2_u$	2277		$\sigma_u^2 \delta_u$
$7/2_u$	6407		$\sigma_u^2 \phi_u$
$5/2_u$	7218		$88\% \sigma_u^2 \delta_u + 12\% \sigma_u^2 \phi_u$
$7/2_u$	19049		$\sigma_u \phi_u \delta_u$
$1/2_u$	19675		$\sigma_u^2 \pi_u^*$
$3/2_g$	20092	0.00032	$\sigma_u^2 \delta_g$
$1/2_u$	21347		$60\% \sigma_u \delta_u \delta_u + 28\% \sigma_u \phi_u \delta_u + 8\% \sigma_u \delta_u^2$
$9/2_u$	21582		$83\% \sigma_u \phi_u \delta_u + 11\% \sigma_u \bar{\phi}_u \delta_u$
$1/2_g$	21994		$\sigma_u^2 \sigma_g$
$3/2_u$	22665		$53\% \sigma_u \delta_u \delta_u + 30\% \sigma_u \phi_u \delta_u + 15\% \sigma_u \bar{\phi}_u \delta_u$
$3/2_u$	23226		$\sigma_u^2 \pi_u^*$
$5/2_g$	24153	0.04407	$\sigma_u^2 \delta_g$
$11/2_u$	25392		$\sigma_u \phi_u \delta_u$
$1/2_u$	25779		$76\% \sigma_u \phi_u \delta_u + 8\% \sigma_u \bar{\phi}_u \delta_u$
$3/2_u$	27240		$45\% \sigma_u \delta_u \delta_u + 29\% \sigma_u \phi_u \delta_u + 22\% \sigma_u \bar{\phi}_u \delta_u$
$3/2_u$	28040		$66\% \sigma_u \phi_u \delta_u + 18\% \sigma_u \delta_u \delta_u + 8\% \sigma_u \delta_u^2$
$5/2_u$	28410		$\sigma_u \phi_u \delta_u$
$13/2_u$	28874		$\sigma_u \phi_u \delta_u$
$9/2_u$	29172		$64\% \sigma_u \bar{\phi}_u \delta_u + 16\% \sigma_u \phi_u \delta_u + 15\% (\sigma_u \delta_u \delta_u + \sigma_u \delta_u^2)$
$1/2_u$	31675		$34\% \sigma_u \delta_u^2 + 33\% (\sigma_u \phi_u \phi_u + \sigma_u \bar{\phi}_u \delta_u) + 12\% \sigma_u \delta_u \delta_u + 9\% \sigma_u \bar{\phi}_u \delta_u$
$3/2_u$	31808		$56\% \sigma_u \phi_u \delta_u + 34\% \sigma_u \phi_u \delta_u$
$7/2_u$	32923		$89\% (\sigma_u \delta_u \delta_u + \sigma_u \delta_u^2) + 5\% \sigma_u \phi_u \delta_u$

<sup>a</sup> The composition of each state is given in terms of spin-free configurations. Oscillator strengths ( $f$ ) greater than  $10^{-5}$  are reported. Energies are in  $\text{cm}^{-1}$ . <sup>b</sup> Configurations with two electrons occupying the same  $\phi_i$  orbital are denoted as  $\phi_i^2$ .

generated in the CAS. The excitation energies up to  $33000 \text{ cm}^{-1}$  are shown in Table 3, and the complete set of values is in Table S3 of the Supporting Information. The spin-free ground state,  $^2\Phi_u$ , gives rise to  $u$  states with  $\Omega = 7/2$  and  $5/2$ , while the  $^2\Delta_u$  gives rise to  $\Omega = 5/2$  and  $3/2$ . The ground state,  $5/2_u$ , is thus a mixture of  $^2\Phi_u$  and  $^2\Delta_u$ , while the next two states,  $\Omega = 7/2$  and  $3/2$ , correspond to single LS states. The excitation energies for these two states are  $2277$  and  $6407 \text{ cm}^{-1}$ , respectively, a clear indication that the spin-orbit effect is larger in the spin-free ground state  $^2\Phi_u$  than in the first spin-free excited state  $^2\Delta_u$ . The fourth state,  $5/2_u$ , is again a mixture of  $^2\Phi_u$  and  $^2\Delta_u$ . The next state,  $7/2_u$ , at  $19049 \text{ cm}^{-1}$ , is the first oxygen-to-uranium charge-transfer state. The corresponding spin-free state ( $\sigma_u \phi_u^1 \delta_u^1$ ,  $^4H_u$ ) at  $20996 \text{ cm}^{-1}$  is reasonably close to the spin-orbit result. Above  $19000 \text{ cm}^{-1}$ , there is a band of strongly mixed states with a spacing which is normally below  $1000 \text{ cm}^{-1}$ . The  $u \rightarrow u$  transitions are strictly forbidden by parity selection rules. In the case of the  $u \rightarrow g$  transitions, the highest oscillator strengths correspond to the transition  $\sigma_u^2 \phi_u - ^2\Phi_{5/2u} \rightarrow \sigma_u^2 \delta_g - ^2\Delta_{3/2g}$ , with  $f = 0.00032$ , and to the transition  $\sigma_u^2 \phi_u - ^2\Phi_{5/2u} \rightarrow \sigma_u^2 \delta_g - ^2\Delta_{5/2g}$ , with  $f = 0.04407$ .

$[\text{UO}_2(\text{CO}_3)_3]^{5-}$ . The structure of  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  is hexagonal bipyramidal, with the three  $\text{CO}_3^{2-}$  ligands coordinated in the equatorial plane, and the symmetry is  $D_{3h}$ . For simplicity, we use the symmetry notations of the bare ion also for the complex. However, it should be noted that while the  $5f_\delta$  and the  $5f_\pi$  orbitals remain degenerate when the symmetry is lowered from  $D_{\infty h}$  to  $D_{3h}$ , this is not true for the  $5f_\phi$  orbitals, which split into two nondegenerate components,  $a'_1$  and  $a'_2$ , which we will denote, for simplicity, as  $\phi'$  and  $\phi''$ , respectively. The geometry of the

**TABLE 4: Composition (absolute values of the orbital coefficients) of the  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  Molecular Orbitals**

MOs <sup>a</sup>	composition
$1\sigma_g$	1.00 U s; 0.11 O s
$1\sigma_u$	0.52 U p; 0.50 O s
$2\sigma_g^*$	0.16 U s; 0.11 U d; 0.66 O s
$1\tau_u$	1.00 U p
$2\sigma_u^*$	0.71 U p; 0.53 O s; 0.20 O p
$1\tau_g$	0.23 U d; 0.70 O p
$2\tau_u$	0.20 U p; 0.20 U f; 0.70 O p
$3\sigma_g$	0.20 U s; 0.40 U d; 0.27 O s; 0.54 O p
$3\sigma_u$	0.51 U p; 0.50 U f; 0.58 O p
$1\phi_u$	1.00 U f
$1\delta_u$	1.00 U f
$3\tau_u^*$	0.99 U f; 0.24 O p
$4\sigma_g$	1.00 U s; 0.64 U d; $\text{CO}_3^{2-}$
$1\delta_g$	1.00 U d; $\text{CO}_3^{2-}$
$4\sigma_u^*$	0.50 U p; 0.88 U f; 0.25 O s; 0.50 O p
$2\tau_g^*$	1.00 U d; 0.48 O p; $\text{CO}_3^{2-}$

<sup>a</sup> All orbitals up to the  $3\sigma_u$  are doubly occupied and the  $1\phi_u$  is singly occupied.

ground state was optimized in a water solvent described by the continuum CPCM model, relaxing all orbitals, and the results are reported in Table S1 of the Supporting Information. The  $\text{U}-\text{O}_{\text{yl}}$  (uranyl) bond length is significantly longer in the complex ( $1.898 \text{ \AA}$ ) than that in the bare ion ( $1.742 \text{ \AA}$ ) due to a weakening of the uranyl bond that can also be explained in terms of the populations of the  $5f$  and  $6d$  orbitals in the bonding  $\sigma$  and  $\pi$  molecular orbitals, which are reduced in the carbonate complex as compared to the bare uranyl ion, the same way as it happened when comparing uranyl(VI) with uranyl(V). The computed  $\text{U}-\text{O}_{\text{yl}}$  bond distance,  $1.898 \text{ \AA}$ , agrees well with the value,  $1.933 \text{ \AA}$ , computed by Gagliardi et al.<sup>52</sup> with the Møller–Plesset perturbation (MP2) method and a reaction field solvent model and with the EXAFS value of  $1.90 \pm 0.02$  reported by Docrat et al.<sup>53</sup> However the  $\text{U}-\text{O}_{\text{carb}}$  distance,  $2.603 \text{ \AA}$ , is  $0.07 \text{ \AA}$  longer than the previously reported MP2 value,<sup>52</sup> a difference that should be attributable not only to the different correlation methods used but also to the different solvent model. The fact that our B3LYP-CPCM  $\text{U}-\text{O}_{\text{carb}}$  bond distance is  $0.1 \text{ \AA}$  longer than the EXAFS value,<sup>53</sup>  $2.50 \pm 0.02$ , results from the absence of counterions in our chemical model to neutralize the large negative charge of the complex. Tsushima et al.<sup>54</sup> have noticed that  $\text{Ca}^{2+}$  or  $\text{Ba}^{2+}$  counterions shorten the  $\text{U}-\text{O}_{\text{carb}}$  bond lengths in uranyl(VI)–tricarboxylate complexes by about  $0.1 \text{ \AA}$ .

The composition of the molecular orbitals is shown in Table 4. The occupied uranyl orbitals remain fairly pure in the complex and do not mix significantly with the carbonate orbitals. The  $5f_\phi$  and  $5f_\delta$  orbitals remain essentially nonbonding, and the antibonding  $\pi_u^*$  and  $\sigma_u^*$  orbitals have more  $5f$  character than in the bare ion (see Table 2) and less  $\text{yl}$ -oxygen  $2p$  character. The uranyl orbitals with appreciable carbonate character are  $4\sigma_g$ ,  $1\delta_g$ , and  $2\tau_g^*$ , which are mostly uranium  $6d$  and  $7s$ .

As explained in the section “Details of the Calculations”, the spectrum of the complex was calculated for the uranyl ion in a ligand “cage”, where no rotations between the (mainly) uranyl and the (mainly) ligand orbitals were allowed during the CASSCF step. The computed spectrum thus only describes internal uranyl excitations.

The spin-free spectrum in the gas phase below  $30000 \text{ cm}^{-1}$  is shown in Table 5 (a more complete spectrum, up to  $50000 \text{ cm}^{-1}$ , can be found in Table S4 of the Supporting Information). The model ceases to be meaningful at energies above the first LMCT state due to mixing between the carbonate-to-uranyl

**TABLE 5: Electronic Spectrum of  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  in the Gas Phase from Spin-Free Scalar Relativistic SA-CASSCF/MS-CASPT2 Calculations with the B3LYP/CPCM Geometry<sup>a</sup>**

configuration <sup>b</sup>	energy
$\sigma_u^2 \delta_u$	0
$\sigma_u^2 \phi_u$	403
$\sigma_u^2 \phi_u''$	2766
$\sigma_u^2 \pi_u^*$	6623
$\sigma_u \delta_u \delta_u$	19172
$\sigma_u \phi_u \delta_u$	19547
$\sigma_u^2 \sigma_u^* + \sigma_u \delta_u^2$	20591
$\sigma_u \phi_u \delta_u + \sigma_u \delta_u \pi_u^*$	22614
$\sigma_u \phi_u' \delta_u + \sigma_u \delta_u \pi_u^*$	23173
$\sigma_u \phi_u \delta_u$	24867
$\sigma_u \delta_u \pi_u^* + \sigma_u \phi_u'' \delta_u$	25236
$\sigma_u \delta_u \pi_u^* + \sigma_u \phi_u \delta_u$	25639
$\sigma_u \delta_u \delta_u$	26753
$\sigma_u \delta_u^2$	26973
$\sigma_u \delta_u \delta_u$	27045
$\sigma_u \phi_u \delta_u + \sigma_u \phi_u' \delta_u + \sigma_u \delta_u \pi_u^*$	27625
$\sigma_u \phi_u \delta_u + \sigma_u \phi_u' \delta_u + \sigma_u \delta_u \pi_u^*$	27806
$\sigma_u \phi_u \pi_u^*$	28490
$\sigma_u \delta_u \pi_u^*$	28563
$\sigma_u \phi_u \pi_u^*$	28661
$\sigma_u \delta_u \pi_u^*$	28814
$\sigma_u \phi_u \delta_u + \sigma_u \phi_u'' \delta_u$	29431
$\sigma_u \phi_u \pi_u^*$	29512
$\sigma_u \delta_u \pi_u^*$	29536
$\sigma_u \delta_u \pi_u^*$	29833

<sup>a</sup> Energies are in  $\text{cm}^{-1}$ . <sup>b</sup> Configurations with two electrons occupying the same  $\phi_i$  orbital are denoted as  $\phi_i^2$ .

charge-transfer states and the uranyl states. However, the first LMCT was estimated to occur above  $50000 \text{ cm}^{-1}$  ( $52000 \text{ cm}^{-1}$  in a continuum solvent using equilibrium CPCM for both states and  $70000 \text{ cm}^{-1}$  in the gas phase) using the simplified model described in the section “Details of the Calculations”. It should be noted that the equilibrium CPCM would be expected to yield slightly too low excitation energies as compared to those from using a nonequilibrium CPCM approach.<sup>50</sup> The spectrum up to  $30000 \text{ cm}^{-1}$  and possibly somewhat higher should thus be reasonably well described by the cage model.

## Discussion

**Spectroscopy of Isolated  $\text{UO}_2^+$ .** The only available experimental results on the spectroscopy of  $\text{UO}_2^+$  in the gas phase reported in the literature have been obtained from vibronically resolved spectra using the PFI-ZEKE technique (pulsed field ionization zero electron kinetic energy)<sup>23</sup> since previous results were limited to a low-resolution photoelectron spectrum.<sup>55</sup> In these experiments, only the first peak of the spectrum that corresponds to an adiabatic excitation energy is reported at  $2678 \text{ cm}^{-1}$ , which agrees well with our vertical CASPT2 value ( $2277 \text{ cm}^{-1}$ ). In fact, the authors claim that there are uncertainties in the experiment and that the excitation energy could be as low as  $2545 \text{ cm}^{-1}$ . Since this excited state corresponds to a nonbonding-to-nonbonding excitation, we do not expect the U–O bond length to change between the ground and the first excited state. It is thus proper for the lowest states to compare the computed vertical values to the experimental adiabatic ones.

Infante et al.<sup>22</sup> have computed the spectrum of uranyl(V) with the Dirac–Coulomb intermediate Hamiltonian Fock space coupled-cluster approach (DC-IHFSCC). In that method, the so-called model space or determinantal reference space includes one electron distributed over the uranium  $7s$ , two of the five

$6d$ , and six of the seven  $5f$  spinors. As was mentioned in the Introduction, the present implementation of the DC-IHFSCC method does not allow for reference configurations with three unpaired electrons (defined as the sector (1,2), allowing one hole and two particles in addition to the uranyl(VI) closed-shell electronic configuration) that would be needed to describe oxygen-to-uranium charge-transfer states. Infante’s results are reported in Table 6 along with our SO-CASPT2 and extended DC-IHFSCC results.

Our DC-IHFSCC calculations should be superior to that of Infante et al.<sup>22</sup> as we considered not only a larger valence  $P$  space but also a larger  $Q$  space of virtual orbitals that extends to 20 au in energy, beyond the 6 au limit used by Infante et al. We have also reported in Table 6 the transitions to the  $5f \pi_u^*$  and  $5f \pi_u^{3/2u}$  since they occur slightly above the highest state,  $6d_{3/2g}^{\delta}$ , reported by Infante et al. With the  $5d$  inner electrons frozen, the extension of the coupled-cluster correlation space shifts slightly downward the first three transitions to the nonbonding orbitals, by up to  $570 \text{ cm}^{-1}$ . However, the transitions to the three  $g$  states reported by Infante et al. at 15999, 17635, and  $19774 \text{ cm}^{-1}$  are all increased by about  $1430 \text{ cm}^{-1}$ . The correlation of the  $5d$  inner electrons tends to increase all transition energies. The first three transitions are shifted upward by  $575 \text{ cm}^{-1}$ , the  $7s_{1/2g}^{\delta}$  state by  $319 \text{ cm}^{-1}$ . The largest effect, about  $1000 \text{ cm}^{-1}$ , is observed for the two components of the  $6d^{\delta}$  state. In summary, while the effects of the larger virtual space and that of the  $5d$  correlation roughly compensate for the lowest  $u$  states, it adds to a total upward shift of about  $2400 \text{ cm}^{-1}$  for the two components of the  $6d^{\delta}$  state.

Comparing the SO-CASPT2 and the DC-IHFSCC results, we observe that both methods agree on the ordering and on the nature of the four lowest states of uranyl(V). If one takes the newly reported  $5d$  correlated DC-IHFSCC values as reference, the computed transition energies differ by at most  $323 \text{ cm}^{-1}$ . This indicates that both methods equally accurately predict the spin–orbit coupling among the nonbonding  $5f_{\delta}$  and  $5f_{\phi}$  orbitals. However, there are differences in the assignments of the higher excited states. While the DC-IHFSCC method predicts the next three excited states to have  $6d_{3/2g}^{\delta}$ ,  $7s_{1/2g}^{\delta}$ , and  $6d_{5/2g}^{\delta}$  character, with transition energies of 18394, 19415, and  $22222 \text{ cm}^{-1}$ , the SO-CASPT2 places them about  $2000 \text{ cm}^{-1}$  higher in energy, at 20092, 21994, and  $24153 \text{ cm}^{-1}$ , respectively, but with some oxygen-to-uranium charge-transfer states in between. It is noteworthy that the discrepancies with earlier DC-IHFSCC values of Infante et al. were significantly larger, about  $4300 \text{ cm}^{-1}$ . The SO-CASPT2 places the  $1/2_u$  ( $\sigma_u \pi_u^*$ ) state at the bottom ( $19675 \text{ cm}^{-1}$ ) of the dense manifold starting at  $19049 \text{ cm}^{-1}$  and below the states with  $6d$ ,  $7s$ , while DC-IHFSCC places it at about  $20245 \text{ cm}^{-1}$ ,  $1851 \text{ cm}^{-1}$  above the lowest component  $3/2_g$  of the  $6d^{\delta}$  state. The difference between the values computed by SO-CASPT2 and DC-IHFSCC for the  $1/2_u$  and  $3/2_u$  ( $\sigma_u \pi_u^*$ ) does not exceed  $1283 \text{ cm}^{-1}$ . The discrepancy in the states’ ordering is thus essentially related to the larger difference for the transitions to the  $g$  states. These differences are visible in the spin-free transition energies reported in Table 1 and Table S5 of the Supporting Information. This indicates that they originate from differences in the treatment of dynamical correlation for the  $g$  states and therefore require further investigation in a forthcoming study. It is, however, important to stress that these differences remain within the expected accuracy of the CASPT2 correlation method.<sup>56</sup>

It is interesting to compare the results for uranyl(V) with those obtained in similar systems, like the isoelectronic neptunyl(VI),  $\text{NpO}_2^{2+}$ , which has been studied using the multireference

**TABLE 6: Comparison of the Low-Lying States in Uranium(V),  $\text{UO}_2^+$ , Computed at the SO-CASPT2 Level with  $r(\text{U}-\text{O}) = 1.742 \text{ \AA}$  (this work) and at the DC-IHFSCC with  $r(\text{U}-\text{O}) = 1.739 \text{ \AA}$  (this work and ref 22), and the Isoelectronic Neptunyl(VI)  $\text{NpO}_2^{2+}$  (ref 9)<sup>a</sup>**

		$\text{UO}_2^+$						$\text{NpO}_2^{2+}$	
exp. ref 23		SO-CASPT2				DC-IHFSCC		DGCI	
state	energy	energy	conf. <sup>b</sup>	24e	34e	24e	conf.	energy	conf.
5/2 <sub>u</sub>	0	0	88% $\sigma_u^2\phi_u + 12\% \sigma_u^2\delta_u$	0	0	0	5f <sub>5/2u</sub> <sup>φ</sup>	0	68% $\sigma_u^2\phi_u + 17\% \sigma_u^2\delta_u$
3/2 <sub>u</sub>	2545	2277	$\sigma_u^2\delta_u$	2166	2452	2736	5f <sub>3/2u</sub> <sup>δ</sup>	447	$\sigma_u^2\delta_u$
7/2 <sub>u</sub>		6407	$\sigma_u^2\phi_u$	5715	6082	5751	5f <sub>7/2u</sub> <sup>φ</sup>	6565	$\sigma_u^2\phi_u$
5/2 <sub>u</sub>		7218	88% $\sigma_u^2\delta_u + 12\% \sigma_u^2\phi_u$	6593	7168	6567	5f <sub>3/2u</sub> <sup>δ</sup>	5515	69% $\sigma_u^2\delta_u + 17\% \sigma_u^2\phi_u$
7/2 <sub>u</sub>		19049	$\sigma_u\phi_u\delta_u$					12622	$\sigma_u\phi_u\delta_u$
1/2 <sub>u</sub>		19675	$\sigma_u^2\pi_u^*$	20183	20245		5f <sub>1/2u</sub> <sup>π*</sup>		
3/2 <sub>g</sub>		20092	$\sigma_u^2\delta_g$	17429	18394	15999	6d <sub>3/2g</sub> <sup>δ</sup>		
1/2 <sub>u</sub>		21347	60% $\sigma_u\delta_u\delta_u + 28\% \sigma_u\phi_u\delta_u + 8\% \sigma_u\delta_u^2$						
9/2 <sub>u</sub>		21582	83% $\sigma_u\phi_u\delta_u + 11\% \sigma_u\bar{\phi}_u\delta_u$						
1/2 <sub>g</sub>		21994	$\sigma_u^2\sigma_g$	19096	19415	17635	7s <sub>1/2g</sub> <sup>σ</sup>		
3/2 <sub>u</sub>		22665	53% $\sigma_u\delta_u\delta_u + 30\% \sigma_u\phi_u\delta_u + 15\% \sigma_u\bar{\phi}_u\delta_u$						
3/2 <sub>u</sub>		23226	$\sigma_u^2\pi_u^*$	24314	24509		5f <sub>3/2u</sub> <sup>π*</sup>		
5/2 <sub>g</sub>		24153	$\sigma_u^2\delta_g$	21178	22222	19774	6d <sub>5/2g</sub> <sup>δ</sup>		

<sup>a</sup> In the DC-IHFSCC calculation, the 5d inner electrons were kept either frozen (24 electrons correlated in the uranyl(VI) electronic configuration) or correlated (34 electrons correlated). Energies are in  $\text{cm}^{-1}$ . Changes in the ordering of the states are marked in italics.

<sup>b</sup> Configurations with two electrons occupying the same  $\phi_i$  orbital are denoted as  $\phi_i^2$ .

spin-orbit configuration interaction method by Matsika and Pitzer,<sup>9</sup> see Table 6. The transitions in the neptunyl ion occur at lower energies, except for 5/2<sub>u</sub> to 7/2<sub>u</sub> at 6565  $\text{cm}^{-1}$  in neptunyl(VI), compared to 6407  $\text{cm}^{-1}$  in uranyl(V). It is noteworthy that the charge-transfer states appear at significantly lower energy in neptunyl(VI), 12622  $\text{cm}^{-1}$ , than those in uranyl(V), 19049  $\text{cm}^{-1}$ . These deviations in the spectra are related to the different nuclear charge of the actinide ion, which affects the relative positions of the 5f and the 6d orbitals.

We can also compare our results with the ones obtained for the uranyl(VI),  $\text{UO}_2^{2+}$ , which has been the aim of experimental and theoretical investigation for decades due to the central role that it has played in uranium chemistry. Uranyl(VI) is a closed-shell ion with the  $3\sigma_u$  orbital as the highest occupied molecular orbital (HOMO). Thus, the lowest excited states correspond to excitations from this molecular orbital to the nonbonding 5f<sub>φ</sub> and 5f<sub>δ</sub> and, as previously mentioned, can be regarded as ligand-to-metal charge excitations. At the spin-free level with perturbative methods (CASPT2), the first charge-transfer transition appears at 22477<sup>5</sup> or 23639  $\text{cm}^{-1}$ ,<sup>6</sup> depending on which zeroth-order Hamiltonian is used. This is at least 1500  $\text{cm}^{-1}$  higher than the first charge-transfer state in  $\text{UO}_2^+$ , 20996  $\text{cm}^{-1}$  (see Table 1). At the spin-orbit level, the first charge-transfer transition appears at 19195  $\text{cm}^{-1}$  in  $\text{UO}_2^{2+}$ ,<sup>5</sup> which is very close to the first charge-transfer transition in  $\text{UO}_2^+$ , 19049  $\text{cm}^{-1}$  (see Table 6). It should be noted that Pierloot and van Besien<sup>5</sup> and Réal et al.<sup>6</sup> used a slightly larger active space than we do, including all U–O bonding orbitals. However, the computed values are partly surprising since one might have expected a blue shift of the first charge-transfer states when reducing uranyl(VI) to uranyl(V), as a result of the smaller charge on the uranium center. At the same time, the uranium–oxygen bond distance is longer in the latter than that in the former, inducing a reduction of the bonding/antibonding separation. These two effects certainly compensate each other, leading us to the

conclusion that the expected blue shift of the charge-transfer transitions may not be expected in all actinyl complexes upon reduction from oxidation state (VI) to (V). This supports the need for systematic theoretical investigations of the actinyl spectra.

**Comparison between the Spectra  $\text{UO}_2^+$  and  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ .** There are some important differences between the spin-free spectrum of the complex and that of the bare ion (see Tables 1 and 5). The ground state of the bare ion is  $\sigma_u^2 5f_\delta^1$ , and the first excited state, at 915  $\text{cm}^{-1}$ , is  $\sigma_u^2 5f_\delta^1$  in the spin-free level. In the complex, the ground state is instead  $\sigma_u^2 5f_\delta^1 - ^2\Delta_u$ . The symmetry of the complex is  $D_{3h}$ , and the first excited state, corresponding to  $\sigma_u^2 5f_\phi^1$ , is split by the ligand field into two nondegenerate components. The first two excited states correspond to excitations into these two components and occur at 403 and 2766  $\text{cm}^{-1}$  (see Table 5). The third excited state is, as in the  $\text{UO}_2^+$ , an excitation to the antibonding  $3\pi_u^*$  molecular orbital. The same change in the character of the ground state has been observed by Matsika and Pitzer for the isoelectronic neptunyl(VI) ion when coordinated to five water molecules.<sup>57,58</sup> The same argument as the one they invoked applies here, namely, that since  $\phi_u$  orbitals are localized in the equatorial planes, they are destabilized by the repulsive interaction with the carbonate ligands, while  $\delta_u$  orbitals have lobes above and below the equatorial plane.

It is remarkable that this excitation appears at 6623  $\text{cm}^{-1}$ , while in the bare ion, it is at 17908  $\text{cm}^{-1}$ . This can be explained by considering the composition of the  $3\pi_u^*$  molecular orbital in the carbonate complex, which has much lower yl-oxygen 2p character than the corresponding orbital in the bare  $\text{UO}_2^+$  ion (see Tables 2 and 4). This makes the orbital less antibonding (or more nonbonding), with more 5f character, and the excitation energy is thus lower in the complex than that in the bare ion. The next level in the tricarbonate complex, at 19172  $\text{cm}^{-1}$ , corresponds to a  $\sigma_u \rightarrow 5f_\delta$  excitation and, as in  $\text{UO}_2^+$ , is followed

**TABLE 7: Electronic Spectrum of  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  in the Gas Phase from CASPT2-Corrected Restricted Active Space State Interaction with Spin–Orbit Coupling Calculations (RASSI-SO)<sup>a</sup>**

energy	configuration <sup>b</sup>
0	$\sigma_u^2\delta_u$
119	74% $\sigma_u^2\phi_u' + 22\%$ $\sigma_u^2\delta_u$
5072	73% $\sigma_u^2\delta_u + 26\%$ $\sigma_u^2\phi_u'$
6920	$\sigma_u^2\phi_u''$
7467	$\sigma_u^2\pi_u^*$
10755	$\sigma_u^2\pi_u^*$
17389	$\sigma_u\phi_u\delta_u$
18539	60% $\sigma_u\delta_u\delta_u + 18\%$ ( $\sigma_u\phi_u''\delta_u + \sigma_u\delta_u\pi_u^*$ )
18958	57% $\sigma_u\phi_u\delta_u + 26\%$ $\sigma_u\delta_u\delta_u$
19969	35% $\sigma_u\delta_u\delta_u + 10\%$ ( $\sigma_u\phi_u\delta_u + \sigma_u\delta_u\pi_u^*$ ) + 10% $\sigma_u\phi_u\delta_u$
21621	54% $\sigma_u\phi_u\delta_u + 18\%$ ( $\sigma_u\phi_u''\delta_u + \sigma_u\delta_u\pi_u^*$ )
23104	45% ( $\sigma_u^2\sigma_u^* + \sigma_u\delta_u^2$ ) + 22% $\sigma_u\phi_u'\delta_u +$ 12% ( $\sigma_u\phi_u''\delta_u + \sigma_u\delta_u\pi_u^*$ )
23614	30% ( $\sigma_u^2\sigma_u^* + \sigma_u\delta_u^2$ ) + 22% ( $\sigma_u\phi_u''\delta_u + \sigma_u\delta_u\pi_u^*$ ) + 20% ( $\sigma_u\delta_u\pi_u^* + \sigma_u\phi_u''\delta_u$ )
23909	66% ( $\sigma_u\delta_u\pi_u^* + \sigma_u\phi_u'\delta_u$ )
24113	29% $\sigma_u\delta_u\delta_u + 21\%$ ( $\sigma_u\phi_u'\delta_u + \sigma_u\delta_u\pi_u^*$ ) + 14% $\sigma_u\phi_u\delta_u$
24656	30% $\sigma_u\phi_u\delta_u + 11\%$ ( $\sigma_u^2\sigma_u^* + \sigma_u\delta_u^2$ ) + 11% $\sigma_u\delta_u\delta_u + 11\%$ ( $\sigma_u\delta_u\pi_u^* + \sigma_u\phi_u''\delta_u$ )
24984	67% ( $\sigma_u\phi_u'\delta_u + \sigma_u\delta_u\pi_u^*$ )
25300	38% ( $\sigma_u\phi_u'\delta_u + \sigma_u\delta_u\pi_u^*$ ) + 10% $\sigma_u\phi_u'\delta_u$
25504	35% ( $\sigma_u\phi_u''\delta_u + \sigma_u\delta_u\pi_u^*$ ) + 24% $\sigma_u\phi_u\delta_u$
26526	47% ( $\sigma_u\phi_u'\delta_u + \sigma_u\delta_u\pi_u^*$ )
26589	34% $\sigma_u\phi_u\delta_u + 11\%$ ( $\sigma_u\delta_u\pi_u^* + \sigma_u\phi_u''\delta_u$ ) + 11% $\sigma_u\delta_u\delta_u$
26938	15% $\sigma_u\delta_u^2 + 13\%$ ( $\sigma_u\delta_u\pi_u^* + \sigma_u\phi_u''\delta_u$ ) + 10% $\sigma_u\phi_u\delta_u + 10\%$ $\sigma_u\delta_u\delta_u$
27296	60% $\sigma_u\phi_u\pi_u^* + 16\%$ $\sigma_u\delta_u\pi_u^*$
27580	27% ( $\sigma_u\phi_u'\delta_u + \sigma_u\delta_u\pi_u^*$ ) + 17% $\sigma_u\delta_u^2 +$ 16% $\sigma_u\delta_u\delta_u$
27635	49% ( $\sigma_u\phi_u'\delta_u + \sigma_u\delta_u\pi_u^*$ ) + 12% $\sigma_u\phi_u\delta_u$

<sup>a</sup> The composition of each state is given in terms of spin-free configurations. Energies are in  $\text{cm}^{-1}$ . No oscillator strengths are included since all of the transitions in the table are parity-forbidden.

<sup>b</sup> Configurations with two electrons occupying the same  $\phi_i$  orbital are denoted as  $\phi_i^2$ .

by a dense manifold of states arising from excitations from the uranyl  $\sigma_u$  orbital. Compared to the bare ion, the states in this region are closer in energy, with gaps of only few hundred  $\text{cm}^{-1}$  because of the small splitting between  $\delta_u$ ,  $\phi_u$ , and  $\pi_u^*$  orbitals in the complex.

The transition to the pure  $\sigma_u^2\sigma_u^*$  state appears at 32700  $\text{cm}^{-1}$  (see Table S4 of the Supporting Information), which again is much lower than the corresponding transition in the bare  $\text{UO}_2^+$  (62000  $\text{cm}^{-1}$ ), and this is again caused by less antibonding character of this orbital in the complex. The excitation into the  $6d_\delta$  orbital appears at about 51000  $\text{cm}^{-1}$ , and the one into  $6d_\pi$  is at around 60000  $\text{cm}^{-1}$ , which is at much higher energies than that in the bare ion. However, this is in the region where the first ligand-to-uranyl charge-transfer transitions are expected, and the energies are thus unreliable. No  $5f_\delta \rightarrow \sigma_g$  transitions could be identified. When the solvent effects are taken into account in the  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  calculation through the nonequilibrium CPCM model, it is observed that all transitions are shifted to higher energies in a range of 500–1500  $\text{cm}^{-1}$ .

The spectrum which includes spin–orbit effects is shown in Table 7 (the complete set is reported in Table S6 of the Supporting Information). The first four states (the ground state and the first three excited states) would correspond to the two fine-structure components of  $\sigma_u^25f_\phi^1 - {}^2\Delta_u$ , with  $\Omega = 3/2$  and

$5/2$ , and the  $\Omega = 5/2$  and  $7/2$  states of  $\sigma_u^25f_\phi^1 - {}^2\Phi_u$ , if we keep the same notation as that in the bare ion. The ground state in this notation is  ${}^2\Delta_{3/2u}$ . The mixing between these states due to the spin–orbit interaction is larger in the complex than that in the bare ion since the spin-free levels are closer in energy in the complex. The excitation to the first  $\sigma_u^25f_\phi^1$ , with some contribution of  $\sigma_u^25f_\delta^1$ , takes place at 119  $\text{cm}^{-1}$ . The second excited state, which appears at 5072  $\text{cm}^{-1}$ , corresponds to  $\sigma_u^25f_\delta^1$  mixed with  $\sigma_u^25f_\phi^1$ , and the third one, at 6920  $\text{cm}^{-1}$ , corresponds to the second  $\sigma_u^25f_\phi^1$  state. The following two states arise from the splitting of the  $\sigma_u^2\pi_u^* - {}^2\Pi_u$  state into  $\Omega = 1/2$  and  $3/2$ , at 7467 and 10755  $\text{cm}^{-1}$ , respectively. The first charge-transfer excitation from the  $\sigma_u$  bonding orbital, which is from the uranyl oxygen to the uranium, appears at 17389  $\text{cm}^{-1}$ . Above this state, there is an onset of a manifold of states of the same nature with very small energy differences.

The nonequilibrium CPCM results including spin–orbit coupling reported in Table 8 reveal that the spectrum of  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  in a solvent presents the same pattern as that in the gas phase, but the transitions are shifted to higher energies, the same way as it was found in the spin–orbit free step, this shift being smaller in the lower part of the spectrum. Besides, it is observed that the spin–orbit mixture is somewhat different when comprising solvent effects. All transitions in this part of the spectrum arise from  $\text{UO}_2^+$ -like  $u \rightarrow u$  transitions, which are essentially parity-forbidden.

**Comparison between the Computed Spectrum of  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  and Experimental Data.** We can compare these numbers with the experimental results found in the literature.<sup>10,17</sup> These results consist of absorption spectra of the following complexes:  $[\text{UO}_2(\text{saloph})\text{DMSO}]^-$ ,  $[\text{UO}_2(\text{dbm})_2\text{DMSO}]^-$ , and  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  in solution. The spectra have characteristic absorption bands in the visible and near-infrared regions. These bands, quoting the authors, are attributable to electronic transitions in the  $\text{UO}_2^+$  core because the spectral features are similar to each other despite the difference in the ligands coordinated in the equatorial plane.<sup>17</sup> In Table 8, we show the experimental data together with the corresponding theoretical results (the complete set is reported in Table S6 of the Supporting Information), both in the gas phase and in solution, and a good agreement is observed among them. As mentioned earlier, all computed transitions in the near-infrared region correspond to  $u \rightarrow u$  transitions of the  $\text{UO}_2^+$  core, in agreement with the low molar absorptivity measured experimentally. The first band recorded for  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  appears at 5560  $\text{cm}^{-1}$  and could be assigned as a transition between the two multiplets of the  ${}^2\Delta_u$  state, whose calculated value is 5072  $\text{cm}^{-1}$  in the gas phase and 5172  $\text{cm}^{-1}$  in solution. The second band is located at 6250  $\text{cm}^{-1}$  compared to the theoretical value of 6920  $\text{cm}^{-1}$  (7444  $\text{cm}^{-1}$  in solution), which corresponds to a  ${}^2\Delta_u \rightarrow {}^2\Phi_u$  transition. It is noteworthy that the next transitions appear at lower energies in  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  than those in the spectrum of the other two complexes. Comparing the recorded bands of the former to the computed values enables us to assign the transitions at 8770 and 10100  $\text{cm}^{-1}$  to the two components of the  $\sigma_u^2\pi_u^*$  state. There is no computed value in the vicinity of the next observed transition at 13200  $\text{cm}^{-1}$ . The most likely reason is that it corresponds to the next computed level at 17389  $\text{cm}^{-1}$  (17883  $\text{cm}^{-1}$  including solvent effects). This state has charge-transfer character and corresponds to an excitation from an  $\text{yl}$ -oxygen to uranium. The possible explanation to why this state appears at a too high energy in the calculations is that the cage model will most likely yield too high excitation energies in the higher part of the spectrum, although it seems unlikely that this error

**TABLE 8: Comparison between Theoretical Calculations of  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  in the Gas Phase and in Solution and Experimental Results in Solution for Uranium(V) ( $[\text{UO}_2(\text{dbm})_2\text{DMSO}]^-$ ,  $[\text{UO}_2(\text{saloph})_2\text{DMSO}]^-$ , and  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ , ref 17) and for Uranium(V) in Aqueous Solution ( $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ , ref 10)<sup>a</sup>**

configuration	$[\text{UO}_2(\text{CO}_3)_3]^{5-}$		$[\text{UO}_2(\text{CO}_3)_3]^{5-}$	$[\text{UO}_2(\text{CO}_3)_3]^{5-}$	$[\text{UO}_2(\text{dbm})_2\text{DMSO}]^-$	$[\text{UO}_2(\text{saloph})_2\text{DMSO}]^-$
	gas	solution	ref 17	ref 10	ref 17	ref 17
$\sigma_u^2\delta_u$	0	0	0	0	0	0
$\sigma_u^2\phi_u$	119	175				
$\sigma_u^2\delta_u$	5072	5172	5560		5290	5330
$\sigma_u^2\phi_u$	6920	7444	6250		6800	7140
$\sigma_u^2\pi_u^*$	7467	8674	8770	8930	11600	11100
$\sigma_u^2\pi_u$	10755	11704	10100	10100	13500	13300
$\sigma_u\phi_u\delta_u$	17389	17883	13200	13100	15600	15400

<sup>a</sup> Energies are in  $\text{cm}^{-1}$ . No oscillator strengths are included since all of the transitions in the table are parity-forbidden.

should be as large as  $4000 \text{ cm}^{-1}$ . It might also be that more extensive treatment of electron correlation is needed to improve these transition energies, but this is beyond present computing capacities. Furthermore, to achieve more accurate results, solvent effects should be included by using more sophisticated methods than the CPCM model, such as molecular dynamics or QM/MM methods. The results presented by Infante et al. in the bare ion were significantly lower than ours in this part of the spectrum, although they did not include charge-transfer excitations in their calculations. The first calculated band, at  $119 \text{ cm}^{-1}$ , is not observed in the experiments. From our results, it is reasonable to conclude that the observed transitions in the complexes all correspond to transitions in the  $\text{UO}_2^+$  core.

## Conclusions

In this paper, we have studied the electronic spectrum of uranyl(V) as a bare ion,  $\text{UO}_2^+$ , and as a carbonate compound,  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ , in the gas phase by means of relativistic multiconfigurational methods of quantum chemistry, in an attempt to contribute, from the point of view of ab initio calculations, to the knowledge of the electronic structure and spectroscopic properties of actinyl ions.

The ground state of the  $\text{UO}_2^+$  ion is  $^2\Phi_{5/2u}$ . In the lower part of the spectrum, the transitions between  $\phi_u$  and  $\delta_u$  nonbonding orbitals, up to  $7218 \text{ cm}^{-1}$ , correspond to transitions among 5f uranium atomic orbitals, the ground state being  $^2\Phi_{5/2u}$ . The next transition, at notably higher energy, corresponds to a ligand-to-metal charge transfer at  $19049 \text{ cm}^{-1}$ , certainly close to the first transition to antibonding  $\pi_u^*$  orbitals at  $19675 \text{ cm}^{-1}$  and to the first transition to nonbonding 6d atomic-like  $\delta_g$  orbitals at  $20092 \text{ cm}^{-1}$ . Going up in energy, we find a manifold of states corresponding to transitions between different nonbonding orbitals, as well as charge-transfer states. In  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ , the first transition from the carbonate ligands to the central uranyl ion is estimated to appear at energies larger than  $50000 \text{ cm}^{-1}$ . The spectrum shows the same basic picture as the bare ion at energies lower than  $50000 \text{ cm}^{-1}$ , which is expected since no carbonate-to-uranyl charge transfers occur in this region, and the absorption bands in this compounds are due to transitions in the  $\text{UO}_2^+$  core. However, important differences are found in the relative energies and distribution of the states. The ground state is now  $^2\Delta_{3/2u}$ , and the transition to the antibonding  $\pi_u^*$  orbitals appears at  $7467 \text{ cm}^{-1}$  in gas phase, significantly lower than that in the bare  $\text{UO}_2^+$  ion in which it was placed at  $19049 \text{ cm}^{-1}$ . It is noteworthy that this excitation is far below the first charge transfer from the uranyl oxygens, at  $17389 \text{ cm}^{-1}$  (gas-phase result). Above this state begins a very dense manifold of states mainly arising from charge transfers from the uranyl oxygens, with very small energy differences among them.

The experimental results available in the literature are obtained from  $\text{UO}_2^+$  complexes in solution and from bare  $\text{UO}_2^+$  in the gas phase. We find a good agreement in both the  $\text{UO}_2^+$  and the  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  cases between theoretical and available experimental results, with discrepancies of few hundreds of  $\text{cm}^{-1}$ , with the exception of the missing transition at  $13500 \text{ cm}^{-1}$ .

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**Supporting Information Available:** Cartesian coordinates of  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$ ; calculated and experimental bond distances for  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  (Table S1); complete set of vertical transition energies for  $\text{UO}_2^+$  computed at the spin-free (Table S2) and spin-orbit levels (Table S3); complete set of spin-free vertical transition energies for  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  (Table S4); spin-free DC-IHFSCC transition energies of  $\text{UO}_2^+$  (Table S5); complete set of spin-orbit vertical transition energies for  $[\text{UO}_2(\text{CO}_3)_3]^{5-}$  (Table S6). This material is available free of charge via the Internet at <http://pubs.acs.org>.



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