

An Investigation of the Accuracy of Different DFT Functionals on the Water Exchange Reaction in Hydrated Uranyl(VI) in the Ground State and the First Excited State

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Abstract: We discuss the accuracy of density functional theory (DFT) in the gas phase for the water-exchange reactions in the uranyl(VI) aqua ion taking place both in the electronic ground state and in the first excited state (the luminescent $^3\Delta_g$ state). The geometries of the reactant and intermediates have been optimized using DFT and the B3LYP functional, with a restricted closed-shell formalism for the electronic ground state and either an unrestricted open-shell formalism or the time-dependent DFT method for the $^3\Delta_g$ state. The relative energies have been computed with wave-function-based methods such as Møller–Plesset second-order perturbation theory, or a minimal multireference perturbative calculation (minimal CASPT2); coupled-cluster method (CCSD(T)); DFT with B3LYP, BLYP, and BHLYP correlation and exchange functionals; and the hybrid DFT–multireference configuration interaction method. The results obtained with second-order perturbative methods are in excellent agreement with those obtained with the CCSD(T) method. However, DFT methods overestimate the energies of low coordination numbers, yielding to too high and too low reaction energies for the associative and dissociative reactions, respectively. Part of the errors appears to be associated with the amount of Hartree–Fock exchange used in the functional; for the dissociative intermediate in the ground state, the pure DFT functionals underestimate the reaction energy by 20 kJ/mol relative to wave-function-based methods, and when the amount of HF exchange is increased to 20% (B3LYP) and to 50% (BHLYP), the error is decreased to 13 and 4 kJ/mol, respectively.

Introduction

Quantum chemical studies of actinides differ from those of the lighter elements in several ways. Relativistic effects are obvious, but many of the related computational problems have been mastered, at least for small complexes; the

spin–orbit problem can be handled either at the two- or four-component level, or in an LS-coupled framework by spin–orbit configuration interaction (CI) programs such as EPCISO¹ or by variation-perturbation methods as implemented in, for example, the complete active space interaction with spin–orbit, CASSI-SO,² program in the Molcas³ package. Another consideration is the large number of electrons. The core–electrons can be included in an effective core potential, but the highly polarizable outer-core orbitals make it necessary to include all shells with a principal quantum number above 4 in the valence space, which makes the

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calculations more cumbersome than those for lighter atoms. The open f-shell problem can in the scalar relativistic framework, in principle, be handled by the complete active space self-consistent field method with subsequent second-order perturbation calculation of the dynamic correlation, CASSCF^{4–6}/CASPT2^{7,8} levels, but calculations at those two levels where all valence excited states are included in the reference can only be used on small systems; already the bare uranyl ion with 12 active orbitals (six bonding and six antibonding U–O_{yl} orbitals) is approaching the limit of about 15 active orbitals for a complete CASSCF/CASPT2 treatment.⁹ It would seem that those problems are easily overcome by reverting to density functional theory (DFT) based methods, but the applicability of DFT functionals, which have been developed for lighter elements, is not obvious.

Complexes with more than one unpaired f electron give rise to multireference effects, which makes conventional unrestricted methods inaccurate.¹⁰ In some cases, such systems can be described by DFT-based methods such as time-dependent DFT (TD-DFT) or the hybrid DFT–multireference configuration interaction (DFT-MRCI).¹¹ In the latter, dynamic correlation is treated by DFT, while static correlation and multireference effects in the electronic states are accounted for in a MRCI framework. The majority of the published studies concerns the uranyl(VI) ion, for which the closed-shell structure essentially removes the problems related to spin–orbit effects and open f shells. Although the f-shell problem does not appear explicitly, the f orbitals participate actively in the bonding, and the applicability of DFT-based methods relies on the ability of the functionals to treat the f electrons properly.

DFT does not give reliable results for electron reduction processes in actinyl complexes,¹² but this is not particular for the actinides. Variable results have been reported for some complexes where the oxidation state is not changed but where the bonds between the actinide and the ligands are strong, such as in UO₃, UF₆,^{13–17} and so forth. Batista et al.^{15,16} have calculated the dissociation energy for UF₆ using both a small-core relativistic effective core potentials (RECP)¹⁸ and an all-electron approximation together with the B3LYP functional. Their spin–orbit free results are in good agreement with experiments; the difference is just a few kilojoules per mole. Peralta et al.¹⁷ have calculated the dissociation energy for UF_{*n*}, *n* = 1–6, at the B3LYP level using the all-electron approximation. Their result for the series has a deviation from the experimental value varying from –36 kJ/mol (*n* = 4) up to +43 kJ/mol (*n* = 1) and with the best result for *n* = 3 and 5, where the deviation is just a few kilojoules per mole. Considering that the dissociation reaction energy is more difficult to calculate with high accuracy than the reaction we have chosen for our study, their results are good but point out the inconsistency of DFT functionals.

The solvation of uranyl(VI) has been studied by several groups.^{19–31} Gutowski and Dixon²⁸ report differences on the order of 20 kJ/mol when calculating the relative energies of hydrated uranyl with four- and five-coordinated water at the B3LYP level compared to the Møller–Plesset second-order perturbation theory (MP2) level, using a small-core RECP

on the uranium atom. Cao and Balasubramanian²⁵ also investigated the structure and energetics of actinyl aqua ions with four-, five-, and six-coordinated water molecules. They made a comparison using the B3LYP^{32–35} hybrid density functional and MP2 and coupled cluster with single and double excitation (CCSD)³⁶ for actinyl complexes, both in the gas phase and aqueous solution. They used a large-core RECP and a smaller basis set for the uranium than we have used in the present study. However, they also noted discrepancies on the order of 20 kJ/mol in the relative energies of hydrated uranyl with varying numbers of coordinated water if computed with DFT or wave-function-based correlated methods. In a recent study of the water exchange in uranyl(VI) by Rotzinger,³¹ the same trend is observed for BLYP^{37–39} and B3LYP, using large-core effective core potentials on the uranium atom. Shamov and Schreckenbach²⁶ also noted differences between B3LYP and PBE^{32,33,40,41} functionals. All studies so far agree that the five-coordinated ion is the preferred coordination of uranyl(VI) in solution, but they disagree on the relative energies of four- and six-coordinated species. This results in different conclusions on the nature of the water-exchange mechanism. One possible explanation to the variable results may be the important contribution from the f orbitals in the binding in, for example, actinide(VI) complexes such as the actinyl ions AnO₂²⁺. Since the quality of DFT applied to actinide complexes is unclear, it is reasonable to investigate the behavior of DFT methods before launching an investigation of a new reaction.

We have previously studied ligand-exchange reactions in uranyl(VI) and uranyl(V),^{22,42–44} and this line of research has now been extended to photoexcited uranyl(VI). The first reaction we have considered is the water exchange mechanism in the first excited triplet state, which is luminescent. Before entering into the chemical properties of photoexcited uranyl, we have deemed it desirable to investigate the accuracy of different DFT functionals and hybrids for this relatively simple complex that do not exhibit any evident multireference properties. The water-exchange reaction can proceed via three pathways,²² a dissociative pathway with a four-coordinated intermediate, an associative pathway with a six-coordinated intermediate, and finally an interchange pathway. In the present investigation, we have compared the relative energies obtained with different methods between a five-coordinated reactant and the four- and six-coordinated dissociative and associative intermediates for the electronic ground state and the first excited state, the latter complexes being depicted in Figure 1. The geometries for the two states bear an overall strong resemblance to each other, naturally, with variations in bond lengths. There are experimental results for hydrated uranyl in the ground state,⁴⁵ but modeling solvent effects is outside the scope of the present study; our aim is to compare various electronic structure methods in the gas phase, and not to study the chemical problem of the solvation of the uranyl(VI) ion. Consequently, we do not have an ultimate answer to which result is “correct” for the fictitious reaction under study. However, results, which differ significantly between different methods, clearly indicate potential problems. In our experience, wave-function-based methods such as CCSD(T) or CASPT2 with a reasonably

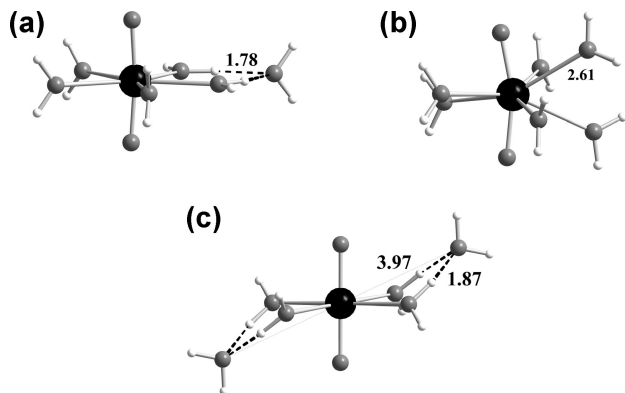
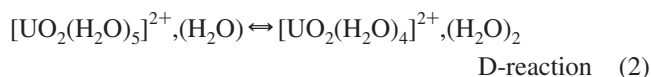
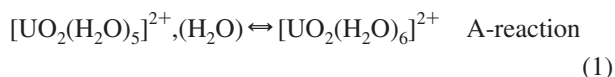


Figure 1. The geometries of the (a) reactant, (b) A-intermediate, and (c) D-intermediate water-coordinated uranyl(VI) complexes in the luminescent state. Distances in the figures are given in ångströms.

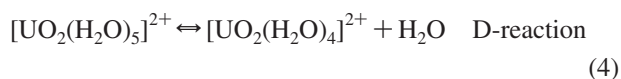
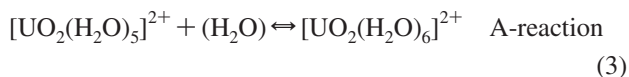
large active space are reliable, and minimal CASPT2 (MP2) methods have been shown to give reliable results when compared to those of both experiments and CCSD(T) in a number of cases. Therefore, we view the wave-function-based results as more trustworthy than DFT, although we cannot ascertain this assumption; for example, the size of the systems restricts the size of the basis sets to about triple- ζ plus polarization functions. The DFT functionals considered in the present study are the hybrid B3LYP and BHLYP and the pure DFT functionals PBE, TPSS, BP86, and BLYP used with the restricted closed-shell formalism for the ground state and the unrestricted open-shell formalism or time-dependent DFT for the first excited state. The wave-function-based methods used were CCSD(T) and MP2/minimal CASPT2.

Theory. The Model. In the present study, we have used the water-exchange reaction in uranyl(VI) in the ground state and in the luminescent state as a probe to compare results obtained with different pure DFT functionals and hybrids and with wave-function-based MP2/minimal CASPT2 and CCSD(T).^{46,47} The comparison is based on the energy of reaction starting with the five-coordinated precursor complex with one water in the outer hydration sphere, $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}, (\text{H}_2\text{O})$ (Figure 1a), to the associative and dissociative intermediates, $[\text{UO}_2(\text{H}_2\text{O})_6]^{2+}$ and $[\text{UO}_2(\text{H}_2\text{O})_4]^{2+}, (\text{H}_2\text{O})_2$, Figure 1b and c, respectively.

In the model, we consider the exchange between inner- and outer-sphere water molecules. The dissociative and associative reactions read:



An alternative model refers to the complete dissociation reactions:



As discussed in ref 48, it is preferable to use intramolecular reactions 1 and 2, rather than reactions 3 and 4, because systematic errors of the solute-solvent interactions compensate in a more efficient way.

Our aim has been to establish the accuracy of different DFT functionals and to pinpoint the problem of the description of electron correlation for the uranyl-water bonding.

Technical Details. For the ground state, we examined four generalized gradient approximation exchange-correlation functionals, PBE, TPSS,^{32,33,38,49} BP86,^{32,33,37,50,51} and BLYP; two hybrid functionals, B3LYP and BHLYP;^{32-34,52} the SAOP functional specially designed for response properties;⁵³ two wave-function-based methods, MP2 and CCSD(T); and the DFT-MRCI method proposed by Grimme and Waletzke.¹¹ The DFT-MRCI method is a combination of Kohn-Sham density functional theory and multireference CI methods and can be used for calculating excitation energies for singlet and triplet states, starting from a closed-shell reference state. In this respect, it is similar to the TD-DFT method.⁵⁴⁻⁵⁶ The wave function is expressed in terms of Kohn-Sham orbitals, obtained with the BHLYP hybrid functional (with 50% HF exchange). A selection criterion for single and double excitations, based on the energy gap between a configuration state function and the corresponding parent configuration, reduces the number of configuration state functions. Some parameters, determined from atomic calculations, are used in the method to scale the Coulomb and exchange integrals. Currently, the optimized parameter sets for the effective DFT-MRCI Hamiltonian are available with the BHLYP functional. We refer the reader to the original publication¹¹ of Grimme and Waletzke for further details on the method. For the luminescent state, we examined the same functionals and wave function methods as for the ground state. For the hybrid functionals B3LYP and BHLYP, we used both the unrestricted open-shell formalism and the time-dependent method. The exchange-correlation functionals, PBE, TPSS, BP86, BLYP, and SAOP, have been studied within the time-dependent approach. For minimal CASPT2, we used two different CASs, a minimal active space that includes the orbitals necessary for the description of the electronic states of interest, namely, the σ_u together with the two δ_u orbitals, and the slightly larger CAS where the two φ_u 's had been added to the previous CAS. The reason for including calculations with the larger CAS was to verify that our minimal CASPT2 result is not CAS-dependent. Unfortunately, it is not possible to use a nonperturbative wave-function-based method, such as for example a multireference configuration interaction, for the luminescent state due to the large number of electrons involved. For MP2, minimal CASPT2, CCSD(T), and DFT-MRCI calculations, only the valence shells, 6s, 6p, 5f of uranium and 2s and 2p of oxygen atoms, were correlated.

Calculations were performed using either RECP or an all-electron basis set with the relativistic Douglas-Kroll-Hess Hamiltonian.^{57,58} In the RECP calculations, we used a small-core RECP of the Stuttgart type¹⁸ for uranium with the corresponding basis set.⁵⁹ In the all-electron calculations, we used the (26s23p17d13f5g3h)/9s8p6d4f2g ANO-RCC basis set suggested by Roos et al.⁶⁰ with triple- ζ quality. Oxygen

and hydrogen were treated at the all-electron level in all calculations, using the TZVP basis set suggested by Schäfer et al.^{61,62} The effect of the *g* functions was investigated in the all-electron calculations; the effect was small, between 0.2 and 1.4 kJ/mol at the DFT level and at most 1.6 kJ/mol with the wave-function-based methods. This is in agreement with previous results obtained by Vallet et al.⁶³ No *g* functions on uranium were used in the RECP calculations. The DFT–SAOP calculations were performed with the ADF2006.01 code, incorporating scalar relativistic effects by means of the zeroth-order regular approximation (ZORA) method^{64–67} and with a triple- ζ Slater-type basis set enlarged by adding two polarization functions (TZ2P). This basis set is large enough to yield very similar accuracy to the Gaussian basis set used in all-electron calculations.

Effects on the ground state and the luminescent state, arising from the spin–orbit splitting of uranium, have been calculated with the EPCISO program¹ using a RECP for uranium.¹⁸ The reference space used in the calculations of the luminescent state included five orbitals, the σ_u and the two δ_u 's and two φ_u 's, while the other electrons were kept uncorrelated, whereas for the ground state, only the σ_u electrons were correlated. The resulting spin–orbit effect, including the single excitations from the active orbitals, was then added to the multiconfigurational CASPT2 energies. Spin–orbit coupling lowers the energies of all three complexes by 28.4–32.9 kJ/mol for the excited state and by 9.9–13.1 kJ/mol for the ground state. This affects the reaction energies with a lowering of 2.9 kJ/mol for the associated reaction and an increase of 2.5 kJ/mol for the dissociative reaction, for the excited state. For the ground state, it yields an increase of 0.5 kJ/mol for the associated reaction and a lowering of 2.7 kJ/mol for dissociated reaction.

It is interesting to note that, at the spin–orbit level, the luminescent state in the reactant is dominated by φ character, whereas in the A-intermediate, there is a mixture of δ and φ contributions, and in the D-intermediate, it has δ character. The mixing between δ and φ contributions is determined by the spacing between the $^3\Delta$ and $^3\Phi$ states, as discussed in detail by Réal et al. in a recent study.⁶⁸

There are no significant basis set superposition error (BSSE) effects on the computed reaction energies; the largest calculated effect on the ground-state model was 3.0 kJ/mol at the MP2 level and 1.6 kJ/mol for B3LYP using Gaussian 03.⁶⁹ Rotzinger³¹ has in a recent paper calculated the BSSE contribution to the reaction energies for the ground state and also found them insignificant, at most 4 kJ/mol. We also calculated the BSSE effect on the dissociation of the outer-sphere water in the ground-state reactant, $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$, (H_2O); the effect at the B3LYP level is 5 kJ/mol, while for the MP2, level it is close to 11 kJ/mol. The BSSE-corrected reaction energies were found to be respectively –102 and –110 kJ/mol, showing the tendency of B3LYP to underestimate reaction energies.

The optimizations of the geometries for the ground state were done at the B3LYP level with symmetry constraints using Gaussian 03.⁶⁹ For the reactant, we used C_s point group symmetry, for the A-intermediate, C_2 symmetry, and for the D-intermediate, C_{2h} symmetry. The geometries in the lumi-

Table 1. Optimized Geometries for the Reactant, A-Intermediate, and D-Intermediate in Their Electronic Ground States^a

	$d(\text{U}-\text{O}_Y)$		$d(\text{U}-\text{OH}_2)$ first coord. shell	
	B3LYP	MP2	B3LYP	MP2
ref	this work	63	this work	63
reactant	1.749	1.776	2.496	2.47(1)
A-intermediate	1.755	1.785	2.518 \times 4/2.645 \times 2	2.47 \times 2, 2.49 \times 2, 2.69 \times 2
D-intermediate	1.748	1.774	2.420	2.41

^a Distances are in ångströms.

nescent state were optimized both with TD-B3LYP using TURBOMOLE 5.7^{70,71} and with U-B3LYP using Gaussian 03, without symmetry constraints. All reaction energies have been calculated using the TD-B3LYP optimized geometries with the Gaussian 03,⁶⁹ TURBOMOLE 5.7^{70,71} the ADF2006.01^{72–74} packages.

The program packages Molcas 6.4³ and Molpro 2006.1⁷⁵ were used for the MP2/minimal CASPT2 and CCSD(T) calculations.

Results and Discussion

Water Exchange in the Electronic Ground State of Uranyl(VI) Penta Aqua Ion. The optimal ground-state geometries are shown in Table 1. The agreement between MP2 and B3LYP optimized geometries is good. It is in fact a general experience that B3LYP gives geometries in good agreement with experimental results.⁶³ As an example, the bond distances in the bare uranyl ion are 1.701 Å at the B3LYP level and 1.706 Å at the CCSD(T) level and 1.709 Å at the average quadratic coupled-cluster level.¹² Our geometries for the bare uranyl ion, the reactant, and the D-intermediate are in good agreement with those obtained by Gutowski and Dixon.²⁸ In the following, we will base our discussions on geometries optimized at the B3LYP or, for the luminescent state, TD-B3LYP level.

As expected, the bonds to the coordinated water contract or expand relative to the reactant in the D-intermediate and A-intermediate. The shortening of the uranium–water bond in the D-intermediate is sizable, 0.07 Å. In the A-intermediate, four waters are located in the equatorial plane of the uranyl unit with distances about 0.01 Å longer than in the five-coordinated reactant, while two waters lie above and below the equatorial plane at longer distances, 2.65 Å. The uranium–water bond is thus considerably stronger in the D-intermediate than in the reactant and the A-intermediate. The variation in the $\text{U}-\text{O}_Y$ distance is smaller.

For the A-intermediate, pure DFT methods yield higher reaction energies than MP2 and CCSD(T), but the differences are small; the mean value for the DFT-based RECP calculations, including DFT-MRCI, is 41.3 kJ/mol, with a largest deviation from the mean value of 4.3 kJ/mol. The largest absolute difference (between B3LYP and TPSS) is 8 kJ/mol. The MP2 and CCSD(T) results, respectively 35.6 and 36.7 kJ/mol, are about 5 kJ/mol below the DFT mean result. It is noteworthy that the largest difference between the DFT and the wave function results, 10 kJ/mol, occurs for B3LYP and for the SAOP functional, and this difference is not negligible.

Table 2. Reaction Energies in kJ/mol for A-Reaction (1) and D-Reaction (2) Computed for Uranyl(VI) in Its Electronic Ground State^a

method	HF exchange in the DFT functional	A-reaction				D-reaction			
		ECP		AE		ECP		AE	
		no g	BSSE	no g	with g	no g	BSSE	no g	with g
B3LYP	20%	44.9	44.8	41.6	42.1	20.1	17.1	21.8	21.6
BHLYP ^b	50%	42.7		41.3	41.7	29.3		31.0	30.7
BP86	0%	42.7				13.5			
PBE	0%	40.3				13.1			
TPSS	0%	37.0				15.7			
BLYP	0%	41.9				13.5			
SAOP ^b	0%				43.1				13.1
MP2		35.6	37.1	34.1	35.5	34.4	32.8	35.2	33.6
MP2 SO		36.1				31.7			
CCSD(T) ^c		36.7		31.9	33.2	34.6		37.4	36.0
DFT-MRCI	50% ^b	39.7				25.4			

^a Both an effective core potential (ECP) and an all-electron (AE) basis set were used for the uranium atom. ^b SAOP results have been obtained with the all-electron ZORA and all-electron Slater triple- ζ basis sets (see Theory section). ^c The T_1 diagnostic is between 0.0225 and 0.0239.

The all-electron and the RECP results are similar, differing by at most 5 kJ/mol, a satisfactory result. The effect of the g functions is negligible at the DFT level and below 2 kJ/mol in the wave-function-based calculations. It should be pointed out that g functions can be very important in strongly bound U(VI) complexes and in redox reactions.^{12,14} Basis set effects for actinides are discussed in a review article by Vallet et al.⁶³

The D-intermediate behaves differently. DFT consistently gives reaction energies that are lower than those obtained with MP2 and CCSD(T) (cf. Table 2), while the opposite was true for the A-intermediate. The reaction energies obtained with the pure DFT functionals are insensitive to the choice of functional, but the effect of including HF exchange is much more pronounced for the D-intermediate; the effect is depicted in the energy diagram in Figure 2. B3LYP gives a higher reaction energy by 6 kJ/mol, than the pure functionals; with BHLYP, the increase amounts to 17 kJ/mol; for MP2 and CCSD(T), the reaction energy is more than 20 kJ/mol higher than that obtained with the pure functionals. DFT-MRCI, which is based on BHLYP Kohn–Sham orbitals, also yields a value which is larger, by 12 kJ/mol, than with pure functionals and lies within the energy obtained with B3LYP and BHLYP functionals. The basis set effects and the quality of the RECP is very similar for the two intermediates.

Rotzinger⁷⁶ noted that DFT tends to overestimate the energy of transition metal complexes with a high coordination number, thus favoring associative reactions over dissociative reactions (cf. Table 2). The low reaction energy obtained for the D-intermediate at the DFT level compared to MP2 and CCSD(T) is due to the strong bonds between the four equatorial waters and the uranyl ion. It appears that the amount of HF exchange has a larger impact on the relative energies of the D-intermediate than in the reactant and in the A-intermediate. This is probably the result of the stronger bonds between the metal and the coordinated water in the D-intermediate (cf. Table 1). However, the close similarity between the reaction energies obtained with MP2 and CCSD(T) makes us confident of the reliability of wave-function-based methods as compared to DFT ones.

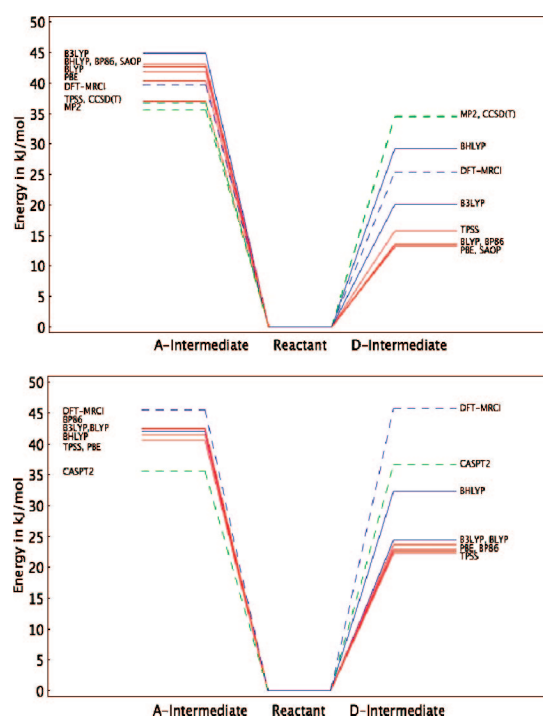


Figure 2. The reaction energies relative to the reactant for the A- and D-intermediates computed for uranyl(VI) in its electronic ground state (a) and in its first electronic excited state (b). The pure functionals are plotted in red, the hybrids in blue, and the wave-function-based methods in dashed green. The DFT-MRCI result is plotted in dashed blue.

The difference between DFT and wave-function-based methods could be caused by an inaccurate description in the DFT framework of either the hydrogen bonds and dispersion effects or the solvated uranyl. These options were investigated through calculations where the uranyl charge distribution was computed for the bare ion and kept frozen in the molecule. The differences in the MP2 and DFT reaction energies with a frozen charge distribution on uranyl were at most 1.0 kJ/mol for the A-intermediate, to be compared to 9.3 kJ/mol at the B3LYP level and 6.3 kJ/mol at the BLYP level in the fully relaxed calculation. For the A-intermediate,

we can thus conclude that the differences between the MP2 and the DFT results are due primarily to the description of uranyl. However, the differences are small. For the D-intermediate, the effects are larger both in the frozen uranyl and in the fully relaxed calculations. The differences obtained in the frozen uranyl calculations were 3.7 kJ/mol at the B3LYP level and 9.0 kJ/mol at the BLYP level. In the fully relaxed calculations, the differences were 14.3 kJ/mol at the B3LYP level and 20.9 kJ/mol at the BLYP level, which is more than twice the difference found for the frozen uranyl. Taking into consideration that not only the description of the hydrogen bonds and dispersion effects contributes to the differences between wave-function-based and the DFT-based methods for the water cage, we conclude that the differences obtained with the fully relaxed model originate primarily from the solvated uranyl ion. There are also shortcomings of DFT in the description of dispersion interactions.^{77,78}

Gutowski and Dixon²⁸ have published a study of the free energy of solvation of the uranyl(VI) ion. One of the studied reactions was reaction 4, for which the authors obtained a difference in the reaction energy of 20 kJ/mol between MP2 and B3LYP, in agreement with our results. Gutowski and Dixon also made CCSD calculations on $[\text{UO}_2(\text{H}_2\text{O})_4]^{2+}$ and $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$ and obtained T_1 diagnostics of 0.023 and 0.022, also in agreement with our results. This indicates, as pointed out by Gutowski and Dixon²⁸ and discussed in details by Vallet et al.,⁷⁹ that multireference effects caused by near-degeneracies, so-called static correlation effects, are minor in these complexes. Shamov and Schreckenbach²⁶ have in a density functional study of actinide complexes in solution, using reactions 3 and 4, made a comparison between B3LYP and PBE. They found a similar shift, 15 and 9.2 kJ/mol between the two functionals, to what we have found, for reactions 1 and 2. Bühl et al.^{27,29,30} have carried out Car–Parrinello calculations on the dissociation of one water molecule from a hydrated uranyl(VI) ion with Car–Parrinello molecular dynamics using the BLYP functional, large-core RECP, and plane-wave basis sets. In their smallest model, with only five waters and no further solvent effects, they obtain an electronic energy of reaction of -16.3 kJ/mol with a D-intermediate, with the second sphere water hydrogen bound to one water molecule (single hydrogen bond model) in the first coordination sphere.²⁹ We obtain a reaction energy at the BLYP level of 13.5 kJ/mol with a six-water model, with the water in the second sphere hydrogen bound to two waters in the first coordination sphere (double hydrogen bond model) for both the reactant and the D-intermediate (cf. Figure 1). Using the same model as Bühl et al., we obtain a reaction energy of -14.3 kJ/mol at the BLYP level and -7 kJ/mol at the B3LYP level, in good agreement with Bühl et al.²⁹ We have also investigated a six-water model, where the outer-sphere water is singly hydrogen bound to the inner-sphere water, for the D-intermediate, and found a similar reaction energy, -4 kJ/mol at the B3LYP level. Our calculated reaction energy with the double hydrogen bond model for the D-intermediate is considerably higher, 20 kJ/mol (in the optimal structure for the reactant, the outer-sphere water keeps forming two hydrogen bonds with inner-sphere water molecules). However, since the scope of this paper is

Table 3. Optimized Geometries for the Reactant, A-Intermediate, and D-Intermediate in the Luminescent Electronic State^a

	$d(\text{U}-\text{O}_\text{yl})$		$d(\text{U}-\text{OH}_2)$ first coord. shell	
	U-B3LYP	TD-B3LYP	U-B3LYP	TD-B3LYP
reactant	1.805	1.795	2.495	2.495
A-intermediate	1.812	1.804	2.520/2.613	2.525/2.619
D-intermediate	1.803	1.794	2.43	2.43

^a Distances are in ångströms.

Table 4. Reaction Energies in kJ/mol for the A-Reaction (1) and D-Reaction(2) Computed for the Luminescent State of Uranyl(VI)

method	HF exchange in DFT functional	A-reaction	D-reaction
B3LYP	20%	45.6	24.5
BHLYP	50%	42.0	32.3
TD-B3LYP	20%	42.4	24.6
TD-BHLYP	50%	42.0	32.3
TD-BP86	0%	42.6	22.7
TD-PBE	0%	40.6	23.0
TD-TPSS	0%	41.5	22.3
TD-BLYP	0%	42.4	23.7
TD-SAOP	0%	47.9	13.9
DFT-MRCI	50%	45.5	45.8
Min-CASPT2, ^a CAS = 3		35.6	36.6
Min-CASPT2 SO		32.7	39.1
Min-CASPT2, ^a CAS = 5		34.9	36.9

^a CAS = 3 and CAS = 5 refer to active spaces involving three active (σ_u and two $5f_\pi$) or five active orbitals (σ_u , two $5f_\pi$, and two $5f_\delta$), respectively.

a method study, the present investigation was done using a double hydrogen bond model for the D-intermediate.

Water Exchange in the Luminescent State of Uranyl(VI). Table 3 shows geometries for the reactant, the A-intermediate, and the D-intermediate optimized with U-B3LYP and TD-B3LYP. TD-B3LYP gives shorter bond distances than U-B3LYP, but the differences are small, particularly for the uranium–water distances. Our results show that geometries in (good) agreement with U-B3LYP can be obtained with TD-B3LYP, a result that opens the possibility of geometry optimizations in excited states of actinide complexes. The reaction energies are shown in Table 4 and Figure 2.

For the A-intermediate, pure and hybrid TD-DFT calculations give higher reaction energies, on average 42.4 kJ/mol, which is higher by about 7 kJ/mol than the two minimal CASPT2 calculations. The largest deviation, 10 kJ/mol, occurs for TD-SAOP and U-B3LYP, as in the ground state, but also for DFT-MRCI, the same difference is noticed. The spread within the reaction energies is even less than in the ground state; the standard deviation is 0.8 compared with 2.7, and the largest absolute difference, between U-B3LYP and TD-PBE, is only 5 kJ/mol.

Like in the ground state, the situation is different for the D-intermediate. Here, we can notice that the reaction energy varies with the chosen DFT functional, the largest difference with the CASPT2 value being obtained with the TD-SAOP functional, although the latter has been specially designed to describe the excited state. The effect of including HF

Table 5. The adiabatic transitions, in cm^{-1} , computed for uranyl(VI) using an effective core potential (ECP)^a

	B3LYP	BHLYP	BP86	PBE	TPSS	BLYP	SAOP ^b	MP2/min CASPT2
reactant	18704	21157	15903	15997	17179	15566	25008	30115
A-reaction	18843	20950	15847	15972	17493	15574	25009	30115
D-reaction	19021	21284	16622	16766	17700	16387	25409	30304

^b SAOP results have been obtained with the all-electron ZORA and all-electron Slater triple- ζ basis sets (See Theory section). ^a For all functionals, except the unrestricted (U-) B3LYP, the TD-DFT results have been used in the table.

exchange is not as pronounced as for the ground state. U- and TD-B3LYP give reaction energies very close to those of the pure functionals, with an average of 23 kJ/mol. As in the ground state, the use of the BHLYP functional increases the energy by 9 kJ/mol. The minimal CASPT2 reaction energy is here 14 kJ/mol higher than that obtained with the pure functionals. The DFT-MRCI, which is based on BHLYP Kohn–Sham orbitals, gives a reaction energy 10 kJ/mol higher than the one received with minimal CASPT2; for the ground state, the picture was different; DFT-MRCI was sharing the behavior of the BHLYP functional and underestimated the reaction energy at 9 kJ/mol. If we look at both the A- and D-reaction, we can see that DFT-MRCI has the same feature as the minimal CASPT2 but shifted up to 10 kJ/mol. The basis set effects and the quality of the RECP are, as expected from the ground-state result, very similar for the two intermediates.

We have reported in Table 5 the adiabatic energies of the luminescent state with respect to the ground state in the reactant and A- and D-intermediates for the DFT functionals and MP2/min CASPT2. There are differences in the absolute transition energy values, as predicted by the various methods. Our group has discussed the reasons for such discrepancies in detail in another publication.⁶⁸ In the present context, it is interesting to note that all methods predict that the adiabatic transition energies to the luminescent state are very similar, within a few hundred wave numbers, that is, within 10 kJ/mol. This implies that the reaction potential energy surfaces that connect the reactant to the D- and A-intermediates in the excited-state are essentially parallel to those of electronic ground state.

Conclusions

In this study, we have made a detailed investigation of the effect of different DFT functionals and the wave-function-based methods MP2 or minimal CASPT2 and CCSD(T) on the associative and dissociative pathways in the water exchange reaction for hydrated uranyl(VI) in the ground state and in the luminescent state. CCSD(T) is the most accurate method used in the present investigation. In our calculations, MP2 and CCSD(T) give very similar results, which provides support for the accuracy of MP2. For the luminescent state, we have, so far, no other accurate method with which to compare our minimal CASPT2 results, but the consistency between the two different CASs (three or five active orbitals) proves that our result does not depend on a wrongly chosen CAS, an argument frequently used for CASPT2 calculations deviating from other accurate methods.

DFT consistently overestimates the reaction energy compared to MP2/minimal CASPT2 and CCSD(T) for the associative pathway, both in the ground state and the

luminescent state, but the differences are minor, less than 10 kJ/mol in all cases. For the dissociative pathway, DFT consistently underestimates the reaction energy, by up to 22 kJ/mol for the pure functionals without HF exchange. This is probably an effect of the stronger uranium–water bonds in the D-intermediate. HF exchange is important in the ground-state dissociative reaction, where the difference between MP2 or CCSD(T) and the DFT reaction energies decreases monotonically with an increasing amount of HF exchange in the functionals. The same trend is noted for the luminescent state but not as “clear” as in the ground state.

Looking at the overall picture of the behavior of DFT results compared with wave function methods, see the reaction energy in Figure 2, we can notice that the consistent overestimation and underestimation of the reaction energy for, respectively, the associative mechanism and the dissociative mechanism compared to the wave function result strongly points out that, at this moment, DFT has to be used with caution when reaction mechanisms within actinide chemistry are investigated. The dissociative mechanism is always favored, with 14–29 kJ/mol for the ground state, and for the luminescent state, the corresponding numbers are 10–20 kJ/mol. For the wave function methods, this difference is a few kilojoules per mole.

All DFT functionals have been developed by comparison with lighter elements, and our results show that these functionals are not ideally suited to describe reactions involving actinides where the 5f contribution in the bonds is substantial and the charge distribution on the actinide is significantly perturbed during the reaction. Examples of this are the gas-phase reactions discussed in refs 13 and 14, but also the coordination of uranyl complexes with sulfate ligands.⁸⁰ In actinide complexes, with ligands composed of light elements, DFT should behave well as long as the charge distribution on the actinides is not significantly perturbed.

Water interacts fairly strongly with the uranyl ion. That alone has an influence on the uranyl bond distance when the number of coordinated waters is changed. This is enough to generate errors, which in some cases may be significant. The error obtained for B3LYP compared to CCSD(T) or CASPT2 is 10–15 kJ/mol. This is certainly an acceptable result in many cases, but the error can be expected to increase when a metal–ligand bond is strengthened. Moreover, the error has opposite signs for the associative and dissociative mechanisms, and DFT should thus be used with great caution when discussing reaction energetics of actinide complexes.

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