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Water Exchange Mechanism in the First Excited State of Hydrated Uranyl(VI)

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The water exchange mechanism of the uranyl(VI) aquo ion in the luminescent state, $^3\Delta_g$ in the spin–orbit free nomenclature, has been investigated using quantum chemical methods and compared to the corresponding reaction in the electronic ground state. The reaction mechanism was studied by calculation of the enthalpy of reaction of the A- and D- intermediates relative to the reactant, using a penta-aquo ion model with one additional water molecule in the second hydration sphere. The reaction barriers around the intermediates are low, and they are therefore a good approximation for the activation enthalpy. The energy of the D-intermediate is significantly larger than that of the A-intermediate both in the luminescent and in the ground states, suggesting that the water exchange is the same in both states. This suggestion is supported by the experimental rate constants for luminescence decay and water exchange in the electronic ground state that are 0.5×10^6 s^{-1} and 1.3×10^6 s^{-1}, respectively.

Introduction

The luminescent state of the uranyl(VI) ion has been extensively studied since the days of the Becquerels,[1] and there are several recent reviews of the field.[2–4] The experimental studies involve determinations of the fluorescence lifetimes, fluorescence quenching, and photoredox reactions, as well as mechanistic discussions. Mechanisms for the fluorescence quenching have been discussed in some detail by Bouby et al.,[5] but not in the extensive literature review of Yusov and Shilov.[4]

The luminescence lifetime of the UO_2^{2+}(aq) in the lowest excited state is about 2 μs,[5] and this is sufficiently long to allow experimental studies of its chemical properties. The luminescent state is $^3\Delta_g$ at the spin–orbit free level, but as a result of the spin–orbit interaction it mixes strongly with $^3\Phi_g$.[6] In a recent publication[7] we studied a possible mechanism for the labilization of the U–O$_{yl}$ bond based on the electronic structure and the geometry of the uranyl(VI) aquo ion in the ground and some excited states, including the lowest triplet state, and presented evidence that the chemical properties in the latter were very similar to those in the ground state. In the present communication we will compare the rate and mechanism for the water exchange between $UO_2(OH_2)_5^{2+}$ and solvent water with results obtained in the $^1\Sigma_g^+$ ground state,[8] for which there are experimental data.[9]

Nagaishi et al.[10] have pointed out that the fluorescence lifetime of the excited uranyl(VI) aquo ion depends strongly on temperature, but that the H/D isotope effect on the quenching is small; this is in stark contrast to the situation for the quenching of the fluorescence of Eu^{3+}(aq) that shows a strong isotope effect, but a very small temperature dependence. Farkas et al.[9] noted that the activation enthalpy for the fluorescence decay and for the water exchange were similar, observations that suggest that the mechanism for non-radiative energy transfer from the luminescent state is due to water exchange, a collision mechanism, rather than through vibronic coupling between coordinated water and solvent. In the present investigation we have tested this suggestion by a comparison of the reaction energies for the formation of the intermediates in the dissociative (D),

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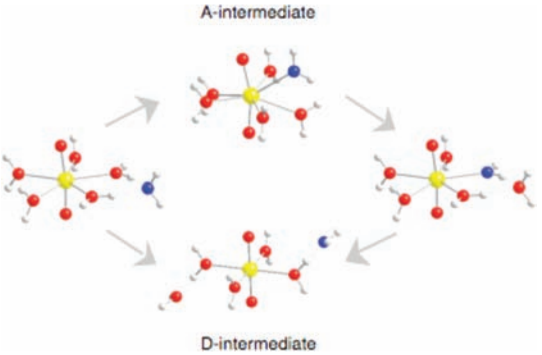

Figure 1. Water exchange reaction via associative or dissociative pathways.

associative (A) water exchange mechanisms in the lowest triplet state and the ground state. A previous study[8] shows that the intermediates are surrounded by low activation barriers, and their energies should therefore be a good approximation for the corresponding activation energies.

Theory

Chemical Model. We have used a model with a penta-aquo uranyl(VI) ion with one additional water molecule in the second coordination sphere; this unit is embedded in a polarizable continuum (CPCM) representing the bulk solvent. The reactant, and the D- and A-intermediates have the composition $[UO_2(OH_2)_5]^{2+}$,(H_2O), $[UO_2(OH_2)_4]^{2+}$,$(H_2O)_2$ and $[UO_2(OH_2)_6]^{2+}$, respectively, and the corresponding exchange pathways are depicted in Figure 1. This model is a compromise between what is chemically realistic and what is computationally possible, as described below. In a previous communication[11] we have discussed the choice of quantum chemical methods and solvation models for calculations of water exchange in uranyl(VI) aquo ion, and concluded that a six water model gives satisfactory results.

Quantum Chemical Methods. In the present study we have optimized the gas phase structures of the ground and luminescent states with the B3LYP[12] functional, using the unrestricted Kohn−Sham approach for the luminescent state. The corresponding reaction energies were obtained at the CASPT2[13,14] level. In the CASSCF[15−17] calculations, preceding the CASPT2 calculations, we used a reference space defined by all electronic configurations generated by distributing two electrons in the σ_u and the two nearly degenerate f_δ orbitals. This is the smallest possible reference space for a proper description of the electronic states of interest. The accuracy corresponds closely to a minimal CASPT2 as discussed in ref 6. The active space, the doubly occupied σ_u, σ_g, π_u, and π_g valence orbitals, plus the 6s and 6p of uranium and the 2s orbitals of the oxygen atoms were correlated in the CASPT2 calculations. For the description of the excited state we have also assessed the importance of spin−orbit coupling. All CASSCF and CASPT2 calculations were done using the Molcas 7.2 package.[18]

Solvent effects were accounted for by using the CPCM[19] with the United Atom[20] (UA0) ansatz (one spherical cavity is used to describe each water molecule). Other groups, for example, Cao et al.,[21] Shamov et al.,[22] and Gutowski et al.,[23] have investigated different solvent models and found the approach using continuum models acceptable. However, we have found significant differences between the UA0 ansatz and the one using one spherical cavity for each atom.[11] The solvent effect on the reaction energies was for technical reasons calculated using restricted open shell MP2 (ROMP2) with Gaussian03[24] and subsequently added to the CASPT2 results. We have previously found that the solvent effect is insensitive to the quantum chemical method used and in fact the difference in reaction energies in gas phase obtained at the minimal CASPT2 and ROMP2 level was less than 4 kJ/mol.

Spin−orbit effects in the luminescent state were calculated with the EPCISO1.8 program[25] interfaced with the Molcas 7.2 package,[18] as described in ref 25. The spin−orbit calculations used all singlet, triplet, and quintet states obtained from a slightly enlarged reference space that included the f_ϕ and f_δ orbitals.[26,27] The reaction enthalpies were calculated from the electronic energy and the gas phase frequencies of the reactant and the intermediates.

Calculations were performed using a RECP for uranium, a small core relativistic ECP of the Stuttgart type[28] together with the associated basis sets.[29] Oxygen and hydrogen were treated at the all electron level using the TZVP basis set suggested by Schäfer et al.[30,31] The zero point corrections were small, below 8 kJ/mol in all cases, and we found no significant Basis Set Superposition Error (BSSE) effects on the reaction energies in the ground state, see ref 6.

Results and Discussion

Geometries. The geometries for the ground- and luminescent states, optimized in the gas phase, are shown in

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Table 1. Optimized Geometries for the Reactant, A-Intermediate, and D-Intermediate in the Luminescent Electronic State and in the Ground State

		first sphere	second sphere
complex	d(U−O$_{yl}$)	d(U−OH$_2$)	d(U−OH$_2$)
		First Excited State	
reactant	1.80	2.50	4.37
A-intermediate	1.81	4 × 2.52 2 × 2.62	
D-intermediate	1.81	2 × 2.37 2 × 2.46	2 × 4.43
		Ground State	
reactant	1.75	2.50	4.26
A-intermediate	1.76	4 × 2.52 2 × 2.65	
D-intermediate	1.75	2 × 2.36 2 × 2.45	2 × 4.36

Table 2. MP2 and Minimal CASPT2 Electronic Reaction Energies/Enthalpies (in kJ/mol) for the A-Reaction (1) and the D-Reaction (2) Computed for Both the Ground and the Luminescent State of Uranyl(VI) Aquo Ion in the Solvent

	associative reaction	dissociative reaction	
		one hydrogen bond	two hydrogen bonds
		Ground State	
spin−orbit free electronic energy	18	39	62
spin−orbit free enthalpy	18	35	63
spin−orbit corrected enthalpy	16	32	61
		Excited State	
spin−orbit free electronic energy	18	43	66
spin−orbit free enthalpy	16	37	65
spin−orbit corrected enthalpy	18	44	71

Table 1. The U−OH$_2$ bond lengths are nearly identical in both states, while the U−O$_{yl}$ distances are significantly longer, typically 1.81 Å in the luminescent state compared to 1.75 Å in the ground state. The difference between the ground and the luminescent states is not surprising since the excitation takes place from a bonding U−O$_{yl}$ orbital. The uranium−water distances in the D-intermediates are up to 0.14 Å shorter than those in the reactant. The bond distances of four equatorial water ligands in the A-intermediate are very nearly the same as in the reactant, while the distances to the incoming and leaving water molecules are significantly longer.

Reaction Energies. Reaction enthalpies and electronic reaction energies in gas phase and in the solvent are given in Table 2. The results show that the values for the ground state at the MP2 level and the luminescent state at the minimal CASPT2 level are very similar, in all cases the difference is below 4 kJ/mol at the spin−orbit free level. The reaction electronic energies differ by only a few kJ/mol from the corresponding reaction enthalpies. In a previous study of the water exchange in the ground state, we obtained electronic activation barriers for the D and A reaction of 12 and 3 kJ/mol, respectively, relative to the intermediates.[8] Hence, the reaction energy/enthalpy from the reactant to the intermediates is a good approximation to the activation energy, and we have assumed that this is the case also in the luminescent state.

In the reactant and D-intermediate the second-sphere water may be linked to the first coordination sphere using one or two hydrogen bonds.[11] In the reactant, the preferred configuration has two hydrogen bonds both in the electronic ground state[11] and in the luminescent state. The D-intermediate has a single hydrogen bond in both states. This is in agreement with the results of Bühl and coworkers who used the Car−Parrinello method to study the water exchange reactions.[32] In the reactant, the preferred configuration has two hydrogen bonds both in the electronic ground state[11] and in the luminescent states, with energies of 8 and 12 kJ/mol, respectively, at the MP2 level, below the configurations with a single hydrogen bond. The D-intermediate with a single hydrogen bond is 23 kJ/mol more stable in both the ground and the luminescent states than the one with two hydrogen bonds. Tsushima[33] found, on the basis of B3LYP and a CPCM description of the solvent, that the configuration with a single hydrogen bond is preferred also in the reactant. However, we have not been able to reproduce the result of Tsushima.[11] In the following we will only consider the D-intermediate with one hydrogen bond.

In the ground state, the reaction enthalpy is 16 kJ/mol higher in the D- than the A-pathway, in the luminescent state this difference is 26 kJ/mol. These results suggest that the water exchange is associative (or possibly interchange) with very nearly the same activation enthalpy in the ground and luminescent states, 16 and 18 kJ/mol, respectively.

Looking at the spin−orbit coupled wave functions of the first excited electronic (the luminescent) state for the reactant and the A- and D-intermediates, we note that spin−orbit coupling strongly mixes the configurations arising from the $\sigma \rightarrow f_\delta$ and $\sigma \rightarrow f_\phi$ excitations; the wave functions of the reactant and the A-intermediate are equal mixtures of f_ϕ and f_δ while the D-intermediate with one hydrogen bond is more dominated by f_ϕ. The character of the states is due not only to the ligand field but also the electron correlation effects, which strongly influence the relative ordering of and its effect on the close lying f_δ and f_ϕ orbitals as has been discussed in detail by Réal et al.[34,35]

The spin−orbit effect on the reaction enthalpies is small in the closed shell ground state, with a stabilization of a few kJ/mol for all reaction enthalpies. The effect is marginally larger in the luminescent state, a destabilization of about 8.7 kJ/mol for the D-intermediates and of

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2.65 kJ/mol in the A-intermediate. The spin−orbit effect in the luminescent state is a result of local effects in all structures where the surroundings of the uranyl(VI) ion are similar.

The structures and reaction energies/enthalpies are very similar in the ground and luminescent states (see Table 1). The difference in bond distances between U and coordinated water, using the same outer-sphere model, is at most 0.03 Å, while the $U - O_{yl}$ distances are systematically 0.05 Å longer in the luminescent state. The experimental rate constants for the water exchange in the electronic ground state[9] and for the fluorescence decay in the luminescent state are 1.3×10^6 and 0.6×10^6 s^{-1}, respectively, and the corresponding activation parameters are also closely related, as seen from the isokinetic plot in ref 9. The spin−orbit free reaction energies for the associative pathway are virtually identical in gas phase and in the polarizable medium, the difference is at most 4 kJ/mol. This makes us conclude that the mechanism and activation parameters for the water exchange reaction are not strongly affected by excitation to the luminescent state, and it seems reasonable to assume that the same is true for other ligand exchange reactions involving hard inorganic ligands. This conclusion is supported by the results from Réal et al.[7] that showed only minor differences in the reaction barriers between the ground state and the luminescent state for the much more complicated yl-oxygen exchange reaction.

The chemical differences between the ground and luminescent states are much larger for electron transfer reactions. The large electron affinity of the open σ_u orbital in the luminescent state makes the photoexcited uranyl(VI) ion a powerful oxidant. Examples of such reactions are the use of photoexcited uranyl(VI) for degrading organic pollutants such as chlorophenols[36] or thiamine.[37]

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Supporting Information Available: Cartesian coordinates in Table S1. Complete citation for ref 24. This material is available free of charge via the Internet at http://pubs.acs.org.

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