DOI: 10.1002/chem.201000408

Photoluminescence of Uranium(VI): Quenching Mechanism and Role of Uranium(V)

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Abstract: The photoluminescence of uranium(VI) is observed typically in the wavelength range 400–650 nm with the lifetime of several hundreds μs and is known to be quenched in the presence of various halide ions (case A) or alcohols (case B). Here, we show by density functional theory (DFT) calculations that the quenching involves an intermediate triplet excited state that exhibits uranium(V) character. The DFT results are consistent with previous experimental findings suggesting the presence of photoexcited uranium(V) radical pair during the quenching process. In the ground state of uranyl(VI) halides, the ligand contributions to the highest occupied molecular orbitals increase with the atomic number (Z) of halide ion allowing larger ligand-to-metal charge transfer (LMCT) between uranium and the halide ion. Consequently, a larger quenching effect is expected as Z increases. The quenching mechanism is essentially the same in cases A and B, and is driven by an electron transfer from the quencher to the UO_2^{2+} entity. The relative energetic stabilities of the triplet excited state define the "fate" of uranium, so that in case A uranium(V) is oxidized back to uranium(VI), while in case B uranium remains as pentavalent.

Keywords: density functional calculations • halides • luminescence • photochemistry • uranium

Introduction

The photochemistry of uranium(VI) has attracted not only the interests from chemists and physicists. Once, uranium glass was a popular household item in Europe and its use dates back as far as 79 A.D. in the Roman Empire.[1] Yet, the interest in uranium(VI) photochemistry today is mainly focused on its potential applications in the nuclear industry. Its application to nuclear fuel reprocessing by selective reduction of uranium(VI) to uranium(IV) had been a subject of a number of investigations in the 1970s and 1980s, and uranium(VI) photoreduction has also been a subject of investigation during the last ten years.[2–6] Uranyl(VI) photochemistry further forms the basis for uranium(VI) detection and determination of its speciation by laser-induced luminescence spectroscopy.[7] Photoreduction and photoinduced luminescence of uranium(VI) are closely related to each other, because in both cases the first process is photoexcitation of uranium(VI) to higher excited states.

Uranium(VI) has a dense manifold of states in the UV/Vis absorption range. These states occur mainly by the excitations from the bonding σ_u, σ_g, π_g, and π_u orbitals to the non-bonding U $5f_\delta$ and $5f_\phi$ orbitals, and include both singlet and triplet states.[8–11] The lowest-lying excited state is generally a triplet state and is transferred back to the ground state with an emission of luminescent light that has a modestly long lifetime of several hundreds μs (phosphorescence). Spectroscopic studies typically find uranium(VI) luminescence bands between 400 and 650 nm.[7] It is known that luminescence of the uranyl(VI) ion in aqueous solution may be quenched in the presence of some types of organic substances as well as by halide ions.[12] In a very recent study,[6] we demonstrated that density functional theory (DFT) calculations can properly model the mechanism of photoreduction of uranium(VI). Here, we extend these calculations to gain further insights into the photochemistry of uranium(VI) and studied the quenching of uranium(VI) luminescence in the presence of halide ions.

The quenching of uranium(VI) luminescence has been a subject of extensive experimental studies, and major contributions have come from the work by Burrows and co-workers from the 1970s to the present day,[3,12–14] and from others.[15,16] Here, we focus on the uranium(VI) lumines-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201000408.

cence quenching by halide ions. In previous experimental studies, the quenching of luminescence was interpreted as an electron-transfer process involving a uranium(V) radical pair.[13] In order to understand the mechanism of uranium(VI) luminescence quenching and also to assess the previous experimental findings with the help of modern quantum chemistry, five examples were examined by DFT calculations: the UO_2^{2+} aquo ion bound to F^-, Cl^-, Br^-, I^-, and methanol, which represent systems of UO_2^{2+} without (F^-) and with quenching (Cl^-, Br^-, I^-, methanol). The luminescence and photochemical quantum yields of uranyl complexes are counter-related. Therefore, we expected that the DFT approach will allow identifying those physical features that govern the branching into the two competing deactivation processes. We show that the calculated spin density of the excited triplet state of the complexes is the key parameter from which experimentally observed luminescence and photochemical properties can be predicted qualitatively and to a certain degree quantitatively.

Computational Methods

The calculations on uranium halides were performed in the gas phase using the Gaussian 03 program,[17] employing the DFT method with Becke's three-parameter hybrid functional[18] and the Lee–Yang–Parr gradient-corrected correlation functional (B3LYP)[19] and applying C_{2v} symmetry constraints. Symmetry constraints were used in order to make the orbital and bond analysis more comprehensible. The calculations on uranium in the presence of methanol, which was taken from previous study,[6] was performed using the same theory, but in methanol through the use of the conductor-like polarizable continuum model (CPCM)[20] using UAHF radii.[21] In both halide and methanol systems, the first coordination sphere of U was saturated with water molecules assuming the total coordination number (CN) of 7 (CN 5 in the equatorial plane). The energy-consistent small-core effective core potential (ECP) and the corresponding basis set suggested by Dolg et al.[22] were used on U, I, Br, Cl, F, O, and C. The most diffuse basis functions on uranium with the exponent 0.005 (all s, p, d, and f type functions) were omitted to make the convergence of the electronic wave function much faster, which generally has only little effect (less than 1 kJ mol^{-1}) on the total energy, according to the previous study.[23] The d function on oxygen and the g function on uranium were included. For hydrogen, a 6-311++G** basis was used. The convergence criteria of geometry optimization calculations were set as maximum and root mean square of the force of 0.00045 and 0.00030 a.u., respectively. Default integration grid of Gaussian 03 program was used, which was a pruned grid with 75 radial shells and 302 angular points per shell for all atoms except uranium. For uranium, an unpruned grid was used. The Gibbs energy correction to the electronic energy was calculated at the B3LYP level from the vibrational energy levels in aqueous phase and the molecular partition functions. Spin-orbit effects and the basis set superposition error (BSSE) corrections were not considered. The former effect is negligible for the ground state of uranium(VI), but is very important for that of the excited state. The neglect of the spin-orbit effect, therefore, may be an oversimplification and may potentially be misleading. We will come back to this point later in the results and discussion. Non-equilibrium TD-DFT calculations[24] were performed in the gas phase producing both singlet and triplet excited states. Ten singlet and ten triplet excited states were determined using the ground states geometries of each uranyl(VI) halide.

Results and Discussion

The quenching of uranium(VI) luminescence by halide ions was studied by DFT calculations on monohalide 1:1 complexes with saturated first shell $(UO_2X(H_2O)_4)^+$, X = F, Cl, Br, I). The results of the DFT calculations of the methanol system were taken from reference [6]. The structures, energies, coordinates, and molecular orbitals of the halide complexes are given in Supporting Information.

In Table 1, geometries and vertical transition energies (de-excitation energies) of the first triplet states of four systems (F^-, Cl^-, Br^-, I^-) are given. Vertical transition energy from the $^3B_2$ state to the $^1A_1$ state in the F^- system correspond to 2.12 eV (584 nm), in agreement with the luminescence emission in the presence of F^-.[25] For Cl^- and Br^- systems, the calculated transition energies are redshifted (1.87 and 1.35 eV, respectively) and thus comply with the lack of visible luminescence in the presence of these halides.[12] In the case of I^-, the excited states most likely decays by nonradiative relaxation, because the transition energy is extremely low (0.02 eV). On the other hand, the lowest-lying triplet excited state $^3B_1$ of uranyl iodide has an equilibrium U–I distance of 3.78 Å, which is sufficiently long to consider this complex already dissociated. This may explain why uranyl(VI) iodide is unstable especially under the influence of light[12] although several U^{VI}–I compounds have been successfully isolated.[26]

Table 1. The structural parameters (uranium to halogen interatomic distance) in the ground state and the lowest-lying triplet state of uranyl(VI) monohalide $UO_2X(H_2O)_4^+$ for X = F, Cl, Br, and I. The forth column gives the vertical transition energy from the lowest-lying triplet state to the ground state.

	Electronic state and U–X distance [Å]		Transition energy [eV]
	Ground state	Triplet state	
$UO_2F(H_2O)_4^+$	$^1A_1$ 2.09	$^3B_2$ 2.08	2.12
$UO_2Cl(H_2O)_4^+$	$^1A'$ 2.62	$^3A'$ 2.73	1.87
$UO_2Br(H_2O)_4^+$	$^1A_1$ 2.77	$^3B_2$ 3.04	1.35
$UO_2I(H_2O)_4^+$	$^1A_1$ 3.00	$^3B_1$ 3.78	0.02

To further understand the nature of the triplet excited states, the Mulliken spin density $\alpha-\beta$ of these triplet states was calculated and is depicted in Figure 1. There is a clear distinction in the spin density between the system with quenching (I^- and methanol) and without quenching (F^-). In the former systems, the spin density is localized on uranyl and on the ligand (I^- and methanol) to roughly equal extent. For example, in the I^- system, the spin density is localized on UO_2 and on I by 0.98 and 1.00, respectively. This shows that in going from the ground state to the triplet excited state there is an electron transfer from iodine to the uranyl entity of nearly 1.0 e, and uranium in the $^3B_1$ state has uranium(V) character. In the F^- system (no quenching), spin density is localized almost exclusively on the uranyl unit (spin density 1.93 on UO_2), indicating that the singlet-to-triplet excitation occurs by excitation within the uranyl

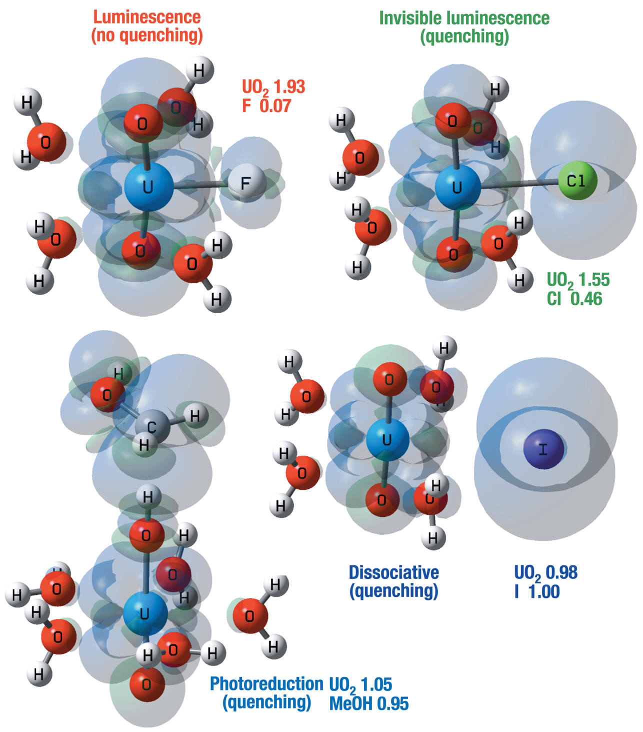

Figure 1. Geometries and Mulliken spin densities $\alpha-\beta$ of the lowest-lying triplet states of UO_2^{2+} aquo ion associated with F^-, Cl^-, I^-, and methanol obtained by DFT calculations. Spin densities are given in numbers and in contour plot (isovalue of the plot is 0.0004 a.u.).

unit and the oxidation state remains uranium(VI). The Cl^- and Br^- system stay in between I^- and F^- systems. The spin density in $UO_2Cl(H_2O)_4^+$ is 1.55 and 0.46 for UO_2 and Cl entities, respectively. The spin density in $UO_2Br(H_2O)_4^+$ is 1.27 and 0.74 for UO_2 and Br entities, respectively. This trend may be predictable from the electronegativity of the halide ions, but the extension to organic compounds, such as methanol, requires a more detailed quantum chemical description as performed here based on DFT. In the methanol system, uranium(VI) is reduced to uranium(V) in the triplet state, and the triplet state is energetically highly stabilized by hydrogen-atom abstraction and does not transfer back to the ground state. Therefore the oxidation state of uranium remains V in the methanol system, in agreement with experiments.[6] It is known that Mulliken population analysis generally tends to overestimate the charge separation within a molecule because of the equal division of the off-diagonal terms between the two basis functions. The charge separation is further exaggerated when larger basis functions are used as in the present investigation. Therefore, we emphasize that it is not the actual degree of spin localization on each system, but rather the trend of this quantity in the different halide systems that can be related reasonably well with experimental data and may thus indicate that the predictive power is mainly governed by the relative degree of spin localization.

The above described photochemical and radiative decay channels were determined from the analysis of the lowest-lying triplet states of the uranyl(VI) complexes and shown to be largely determined by the spin density $\alpha-\beta$ of the respective system. However, the primary photoexcitation is a singlet-to-singlet transition, after which the triplet states are reached only by internal conversion and intersystem crossing. We wondered whether the energetic ordering and the electronic configuration of the analyzed triplet states may be paralleled by features of the corresponding excited singlet states that precede the triplet state formation in each system. Because the higher excited states cannot be appropriately modelled by a single-determinant method, we tried to go beyond the single-determinant DFT. The best way to achieve this is to use multi-reference configuration interaction (MRCI) calculations. However, since such calculations are time consuming and allow only a few active space orbitals to be included, we used the less time-consuming approach of time-dependent DFT (TD-DFT) calculations to obtain vertical transition energies of the singlet-to-singlet excitations and their molecular orbital (MO) contributions. TD-DFT methods should be used with care, because their applicability to the systems containing uranyl(VI) is controversial. Pierloot et al.[27] reported that the TD-DFT tends to overestimate the covalency of the U−Cl bond in $UO_2Cl_4^{2-}$. Kozimor et al.[28] successfully reproduced chlorine K-edge X-ray absorption spectra of uranium–bis(pentamethylcyclopentadienyl)dichloride compounds with the use of TD-DFT. However, the approach used by Kozimor et al. does not account for the relaxation in occupied MOs associated with the core hole, and a systematic energy shift of 64.9 eV has, therefore, been employed to compensate for this effect. Réal et al.[9–10] studied the excitation and reactivity of uranyl(VI) complexes using TD-DFT and other sophisticated theories. They conclude that although the TD-DFT method does not provide accurate excitation energies, it leads in most cases to reasonable geometries, relaxation energies, and reactivity trends for uranyl(VI) complexes. Wiebke et al.[29] applied TD-DFT method to calculate the absorption spectra of uranyl(VI) complexes.

Here, TD-DFT is again used in a comparative manner, but is now applied to singlet-to-singlet transitions in UO_2F^+, UO_2Cl^+, and UO_2I^+. The five low-lying singlet excited states of UO_2F^+, UO_2Cl^+, and UO_2I^+ and their major MO contributions are given in Table 2. In all cases, MO 41 is the HOMO and MO 42 is the LUMO. So the singlet-to-singlet transitions occur mainly by HOMOs (HOMO−1 to HOMO) to LUMOs (LUMO to LUMO+3) transitions. In Figure 2, the HOMO−1 and HOMO of UO_2F^+, UO_2Cl^+

Table 2. Five low-lying singlet excited states of UO_2F^+, UO_2Cl^+, and UO_2I^+ aquo ions and their major MO contributions. From top to down, the lowest to higher excited states. In all cases, MO 41 is the HOMO and MO 42 is the LUMO.

$UO_2F(H_2O)_4^+$	$UO_2Cl(H_2O)_4^+$	$UO_2I(H_2O)_4^+$
${}^{1}B_1(41\rightarrow44)$	${}^{1}A'(41\rightarrow42)$	${}^{1}B_2(41\rightarrow43)$
${}^{1}A_2(41\rightarrow45)$	^{1}A“(41→45)	${}^{1}A_2(41\rightarrow45)$
${}^{1}B_2(41\rightarrow42)$	^{1}A“(41→44)	${}^{1}B_1(41\rightarrow44)$
${}^{1}A_1(41\rightarrow43)$	${}^{1}A'(41\rightarrow43)$	${}^{1}A_1(41\rightarrow42)$
${}^{1}A_2(40\rightarrow42)$	^{1}A“(40→42)	${}^{1}A_2(40\rightarrow42)$

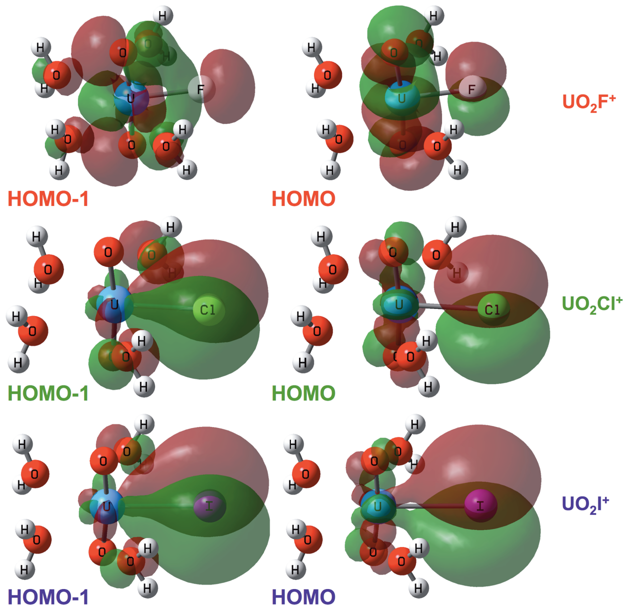

Figure 2. The highest occupied molecular orbital (HOMO) and HOMO−1 of UO_2F^+, UO_2Cl^+, and UO_2I^+ aquo ions obtained by DFT calculations. Both HOMO and HOMO−1 are centred mainly on UO_2^{2+} in UO_2F^+. In UO_2I^+, the HOMO and HOMO−1 are localized virtually only on the I atom. The isovalue of the surface is 0.02 a.u.

and UO_2I^+ are given. In UO_2F^+, both HOMO−1 and HOMO are centred mainly on the UO_2 entity. In UO_2I^+, the HOMO−1 and HOMO are localized almost exclusively on the I ion. In all of UO_2F^+, UO_2Cl^+ and UO_2I^+, the LUMOs mainly consist of non-bonding U $5f_\delta$ and $5f_\phi$ orbitals (see Supporting Information). The singlet-to-singlet transition occurs mainly within the uranyl unit in UO_2F^+ and the excited states are metal-centred charge-transfer (MCCT) states. In UO_2I^+, the transition occurs by an electron transfer from the I ion to the central uranium, and the excited states are ligand-to-metal charge transfer (LMCT) states. The photoexcited UO_2I^+ can be considered as a $U^VO_2^+$–$I^\bullet$ pair. UO_2Cl^+ stays in between UO_2F^+ and UO_2I^+, but has more LMCT character.

From the TD-DFT results, there is a clear distinction between the singlet excited states of UO_2F^+ and UO_2I^+. This difference is very similar to that observed in the lowest-lying triplet states of UO_2F^+ and UO_2I^+ as shown in Figure 1. The origin of these differences is ascribed to a larger contribution of the ligand MO to the HOMOs in UO_2I^+. As discussed earlier, we are aware of the fact that the application of TD-DFT to uranyl(VI) complexes may not provide precise excitation energies. Thus, the relative energetic ordering of the close-lying excited states obtained by TD-DFT are less reliable. However, all of the five low-lying singlet states have the character of HOMOs→LUMOs transitions and their relative ordering is not central to our reasoning. In addition, as shown earlier, the analysis of Mulliken spin density $\alpha-\beta$ of the lowest-lying triplet states also confirm MCCT and LMCT mechanisms in the excitations in UO_2F^+ and UO_2I^+, respectively.

Despite the use of a rather simplified method (B3LYP) that neglects both spin-orbit coupling and multireference effects, the vertical transition energies of the first triplet states of uranium(VI) in the presence of halide ions and methanol have been shown here to correlate surprisingly well with the experimentally observed luminescence and photochemistry of these complexes. The results show that luminescence features of uranium(VI) complexes can be derived from both the HOMOs of the target uranium(VI) complexes and from the spin density of the lowest-lying triplet states.

The presented data confirms the quenching mechanism proposed by Burrows involving the uranium(V) radical pair, $[UO_2^+X^\bullet]$.[13] An alternative mechanism proposed by Burrows employs a binuclear radical anion $X_2^{\bullet-}$, which may be a subject for future investigations. For the luminescence quenching in the presence of Cl^- or Br^- ion, the present DFT study illustrates a mechanism, in which the luminescence is not entirely quenched, but redshifted. However, a significant change in geometry upon a charge transfer transition in uranium chloride and bromide implies a large electron-phonon interaction in these systems. Hence luminescence may never be observed in practice and a thorough spectroscopic investigation in the infrared (IR) to near-IR region is required to clarify this point.

In combination with the previous DFT investigation on uranium(VI) photoreduction by alcohol,[6] our results underscore that the analysis of the lowest-lying triplet state obtained by the single-determinant DFT method leads to a realistic representation of the state of interest. Evidently, the DFT method appears promising for exploring the uranium(VI) photochemistry. However, great care should always be taken because of the implicit simplifications of DFT and TD-DFT methods. Importantly, the results should always be verified against experiments. One may argue that we may not have reached the correct electronic state with the use of simple DFT with the neglect of spin-orbit coupling. Rotzinger[30] studied uranyl(VI) monohalide system (UO_2Cl^+) using multireference configuration interaction theory, but his focus was on the ligand substitution process and no information about the lowest triplet state is provided. Previous studies on UO_2^{2+} by Réal et al.[9–11] suggest that the lowest-lying triplet state may differ with different levels of theory, preferring either $^3\Phi_g$ ($\sigma_u \rightarrow f_\phi$) or $^3\Delta_g$ ($\sigma_u \rightarrow f_\delta$) states. The work by Réal et al. is a good example to indicate that in order to get correct excited states for uranyl(VI) complexes it is mandatory to use sophisticated level of theory including spin-orbit effect. In the present case, within the framework of DFT, we may have reached the correct triplet states by pure chance. This, however, seems to be less likely to happen for all cases and most likely we have mixed the two different triplet states that involves excitations to the U $5f_\delta$ and $5f_\phi$ orbitals. However, due to the nonbonding nature of the $5f_\delta$ and $5f_\phi$ orbitals, de-excitation processes of the states involving these orbitals are expected to be very similar. Therefore, for the present systems it is not critical to distinguish between the two states as far as the luminescence properties are concerned. It is worthwhile studying the described systems and other related complexes by a more sophisticated quantum chemical approach that includes spin-orbit coupling and multireference configuration interaction to eventually identify the minimal degree of complexity required for the accurate prediction of experimental observations. This will be a subject of our future investigation.

Acknowledgements

We acknowledge generous allocation of CPU time on supercomputers at the Zentrum für Informationsdienste und Hochleistungsrechnen (ZIH), Technische Universität Dresden, Germany.

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Received: February 15, 2010