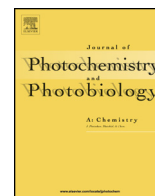




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## Deactivation of lowest excited state of uranyl in the presence of acetate: A DFT exploration

Vladimir Sladkov<sup>a,b,\*</sup>, Jérôme Roques<sup>a,b</sup><sup>a</sup> CNRS, Institut de Physique Nucléaire (IPN), UMR 8608, Orsay F-91406, France<sup>b</sup> Univ Paris-Sud, Orsay F-91405 France

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## ABSTRACT

Interaction of uranyl with acetate is studied by density functional theory (DFT) calculations. Particular attention is given to the interaction of excited uranyl with acetate to explain the quenching in aqueous solution and the photodecomposition of acetate in the presence of uranyl. The structures of uranyl with the acetate ion in monodentate and bidentate coordinations are calculated in the ground and in the lowest lying excited triplet state. Uranyl-acetate is found to be stable in both coordinations in the lowest lying triplet state. Uranyl can also form a number of stable structures with acetate involving apical oxygen in the triplet state. The photoreduction of U(VI) associated with hydrogen abstraction from ligand is observed in the case of uranyl coordinated by two molecules of acetic acid in monodentate and apical modes. The stability of the  $[\text{UO}(\text{OH})(\text{H}_2\text{O})_4]^{2+}$  species is also examined in the ground state. It is found that this structure is stable. These species may play a key role in the dynamic quenching of uranyl. The structures of  $[\text{UO}(\text{OH})(\text{H}_2\text{O})_4]^{2+}$  coordinated with acetate in monodentate and bidentate modes are also investigated. The nonradiative deactivation of the uranyl excited state in the presence of acetate with photodecomposition of acetate could not be demonstrated, taking into account the lowest lying triplet state of excited uranyl.

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### 1. Introduction

The interaction of uranyl with acetate has attracted a lot of attention in the past few years [1–7]. Due to the combination of a methyl group and a carboxylic acid group, acetic acid/acetate is a primordial of complex organic molecules. It can represent the most simple substance model for humic acids, it can occur as humic acid building block and can simulate their structure and functionality [1,8,9]. Acetic acid can also be the product of the chemical industry and may be produced during some technological processes [10,11].

The luminescence properties of actinide ions allow us to obtain rich information about their speciation in solutions [12–20]. Recently, the luminescence properties of uranyl have been used to study the interaction of uranyl with acetate [7]. It has been demonstrated, that uranyl exhibits dynamic and static quenching in the presence of acetate. Dynamic quenching occurs in the range of acetate concentrations from  $\sim 5 \times 10^{-4}$  M to  $\sim 1 \times 10^{-4}$  M ( $C(\text{U}(\text{VI})) = 1 \times 10^{-4}$  M), when mutual approach of excited uranyl

( $^*\text{UO}_2^{2+}$ ) and acetate is possible during the excited-state lifetime [21]. It is demonstrated, that this process is diffusion-limited; the observed rate constant for quenching is equal to the diffusional rate constant [7]. In these conditions U(VI) presents mainly as an aqua complex of uranyl  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$  in aqueous solution. The concentration of acetate-uranyl complex ( $[\text{UO}_2\text{CH}_3\text{COO}]^+$ ) is negligible. An intermediate complex of uranyl with acetate forms only in an excited state of uranyl. Most probably, the reason for nonradiative deactivation of the uranyl excited state (dynamic quenching) is the bimolecular reaction of an intermediate uranium (V)/radical pair with acetate, which precedes the oxidation and decomposition of acetate. By the excitation of the uranyl ion, the electron from the higher bonding molecular orbital  $3\sigma_u$  located mainly on the oxygen atom, passes to the uranium 5f orbitals ( $5\sigma_u$  and  $5\phi_u$ ) [22,23]. The uranyl in this state can be considered “partly reduced” as U(V). In the ground state, the uranyl ion has only slight electron-acceptor capacity ( $E^\circ = 0.06$  V). However, on excitation, it becomes a strong oxidant. Its standard redox potential is estimated to be 2.6–2.7 V [22,24]. At a higher concentration of acetate (from  $1 \times 10^{-4}$  M), static quenching occurs in addition to dynamic quenching. The reason for the static quenching is, most probably, the formation of non-luminescent uranyl acetate ( $[\text{UO}_2\text{CH}_3\text{COO}]^+$ ) complex species in aqueous solution.

\* Corresponding author at: CNRS, Institut de Physique Nucléaire (IPN), UMR 8608, Orsay F-91406, France.

E-mail address: [sladkov@ipno.in2p3.fr](mailto:sladkov@ipno.in2p3.fr) (V. Sladkov).

The excited uranyl can oxidize organic acids, alcohols etc [12,22]. Reactions generally involving photooxidation of substrate occur either by excitation of complexes or bimolecular reactions between excited uranyl ion and substrates. If UV irradiation of the solution, containing uranyl ions (up to 0.05 M) and the acetic acid (up to 0.5 M) (pH 0.5–3.0), is used for the periods ranging from 3 to 16 hours, the gaseous products (CO<sub>2</sub> and CH<sub>4</sub>) of photodecomposition of acetic acid can be detected (anaerobic photolysis) [25]. The photochemical reduction of U(VI) is also observed in the presence of acetic acid, using a commercial quartz photoreactor [26].

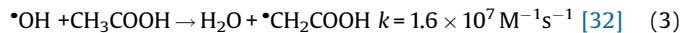
The quenching of uranyl luminescence by alcohol, by oxalic and by formic acids has been recently interpreted with more details as an electron-transfer process involving a uranium(V) radical pair. The calculated spin density of the lowest-lying triplet state of uranyl complexes is found to be the key parameter from which experimentally observed luminescence and photochemical properties can be predicted [27–29]. In the case of oxalic [28] and formic [29] acids it is shown that photoreactivities of uranyl(VI) complexes are largely associated with ligand coordination arrangement.

Another possibility of dynamic quenching of excited uranyl in the presence of acetate may involve a deactivation mechanism through hydrogen atom abstraction involving water from the first shell of uranyl:



The strong evidence, that the decay of the lowest excited state of the complex ion  $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$  in aqueous solutions involves hydrogen abstraction from water shell to produce U(V) and hydroxyl radicals, has been presented in a paper [30]. The formation of  $\cdot\text{OH}$  is also confirmed by electron spin resonance

spectra in a UV-irradiated aqueous solution of uranyl acetate [30,31]. The generation of hydroxyl radicals plays a major role in the luminescence decay of  ${}^*\text{UO}_2^{2+}$  [31].  $\cdot\text{OH}$  can react with acetate/ acetic acid to produce the  $\cdot\text{CH}_2\text{COOH}$  and  $\cdot\text{CH}_2\text{COO}^-$  according to

$$\cdot\text{OH} + \text{CH}_3\text{COO}^- \rightarrow \text{H}_2\text{O} + \cdot\text{CH}_2\text{COO}^- \quad k = 8.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \quad [32] \quad (2)$$


The formation of the  $\cdot\text{CH}_2\text{COOH}$  radical has also been observed under the irradiation of solutions U(VI) in neat acetic acid by electron spin resonance [12,33].

We suggest that one of the possible pathways of dynamic quenching of uranyl by acetate may be the formation of an intermediate complex of  $\text{UO}_2\text{H}^{2+}$  with acetate.

The aim of this study is to investigate the structures of uranyl with acetate in its lowest triplet state by DFT calculations to explain luminescence quenching of uranyl in the presence of acetate. The possibility of the formation of  $\text{UO}_2\text{H}^{2+}$  species and their intermediate complexes with acetate is also investigated in this paper by DFT calculations.

## 2. Computational approach

All structures are optimized using the density functional theory (DFT) approach as implemented in the Gaussian09 package [34]. Calculations are performed using the hybrid B3LYP [35] functional. The MWB60 Stuttgart relativistic effective core potentials [36] are used to describe uranium atoms and the 6-311++G\*\* basis set for others. To take into account part of the solvent effect, the solvation is introduced using a dielectric continuum model of

**Table 1**

Structural parameters (in Å) of uranyl-acetate in monodentate (A) and bidentate (B) coordinations in ground and triplet states calculated by DFT and compared with other theoretical data from literature.

	A.		B.	
	Monodentate		Bidentate	
	Ground	Triplet	Ground	Triplet
U-O <sub>1</sub>	<b>2.26</b> 2.213 [38] 2.201 [39] 2.24 [40] 2.253 [1]	<b>2.25</b>	<b>2.42</b> 2.371 [39] 2.470–2.500 [40] 2.427, 2.421 [1]	<b>2.42</b>
U-O <sub>axial</sub>	<b>1.77</b> 1.749 [38] 1.790 [39] 1.766 [1]	<b>1.83</b>	<b>1.78</b> 1.787 [39] 1.781 [40] 1.763, 1.764 [1]	<b>1.83</b>
U-O <sub>w</sub> <sup>a</sup>	<b>2.52</b> 2.42 [39] 2.48 [1]	<b>2.56</b>	<b>2.48</b> 2.36 [39] 2.44 [1]	<b>2.49</b>
C-C	<b>1.50</b> 1.453 [38]	<b>1.50</b>	<b>1.50</b>	<b>1.50</b>
C-O <sub>1</sub>	<b>1.30</b>	<b>1.31</b>	<b>1.27</b>	<b>1.27</b>
C-O <sub>2</sub>	<b>1.24</b>	<b>1.24</b>	<b>1.27</b>	<b>1.27</b>

<sup>a</sup> Average value.

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