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### ► To cite this version:

Hanna Oher, Geoffroy Ferru, Laurent Couston, Laurence Berthon, Dominique Guillaumont, et al.. Influence of the first coordination of uranyl on its luminescence properties: study of uranyl binitrate with N,N-dialkyl amide DEHiBA and water. *Inorganic Chemistry*, 2022, 61 (2), pp.890-901. 10.1021/acs.inorgchem.1c02618 . hal-03325299

**HAL Id: hal-03325299**

<https://hal.science/hal-03325299v1>

Submitted on 31 Aug 2021

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# Influence of the first coordination of uranyl on its luminescence properties: study of uranyl binitrate with N,N-dialkyl amide DEHiBA and water

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## Abstract

Uranyl binitrate complexes have a particular interest in the nuclear industry, especially in the reprocessing of spent nuclear fuel. The modified PUREX extraction process is designed to extract U(VI) in the form of  $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  as it has been confirmed by EXAFS, XRD and TRIFS measurements. In this study, the L ligands are two molecules of N,N-di-(ethyl-2-hexyl)isobutyramide (DEHiBA) monoamide used to bind uranyl in its first coordination sphere. DEHiBA ligands can coordinate uranyl in either *trans*- or *cis*-positions with respect

to the nitrate ligands and these two conformers may co-exist in solution. In order to use luminescence spectroscopy as a speciation technique, it is important to determine whether or not these conformers can be discriminated by their spectroscopic properties. To answer this question, the spectra of *trans*- and *cis*- $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$  conformers were modeled with ab initio methods and compared to the experimental time-resolved luminescence spectra on the  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$  systems. Moreover, the hydrated uranyl binitrate  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  complexes in the same *trans* and *cis* configurations were modeled to quantify the impact of organic DEHiBA on the luminescence properties.

## Introduction

The production of electricity from nuclear energy has been developed in several countries. Some countries among which the U.S.A., France, the United Kingdom, chose to reprocess the spent nuclear fuel for an economic reuse of the uranium and plutonium, and a reduction of the radioactivity and volume of the wastes.<sup>1</sup> The recovery of uranium and plutonium, and effective separation from fission products and minor actinides has been achieved at both laboratory and industrial scales by solvent extraction techniques using an aqueous phase and an immiscible organic phase. The transfer of actinide metal cations occurs from an acidic aqueous phase resulting from the dissolution of the fuel in nitric acid into an organic phase by complexation with liposoluble extracting molecules.<sup>2</sup> Nowadays, the main industrial solvent extraction process is Plutonium Uranium Refining by Extraction (PUREX) in which the tri-*n*-butyl phosphate (TBP) extracting agent is used to separate U(VI) and Pu(IV) from minor actinides and fission products in highly concentrated nitric acid solution.<sup>3</sup> Though efficient the PUREX process requires a reduction of plutonium for the U/Pu partitioning by addition of U(IV) and anti-nitrous reagents. Moreover, the washing and recycling of the solvent has to account for the degradation of TBP by radiolysis.<sup>4</sup> Thus, several processes have been developed to modify or replace the PUREX process, and meet new requirements such as

the development of a one-cycle process without redox chemistry. Following the principle of interaction of O- or N-donor organic molecules with uranium or plutonium,<sup>5,6</sup> new types of complexing agents have been studied.

In France, the Group ActiNide EXtraction (GANEX) process has been developed for the industrial reprocessing of spent nuclear fuel and the homogeneous recycling of actinides.<sup>7,8</sup> In this process, the selective separation is operated by solvent extraction using a new group of the N,N-dialkyl amides (further monoamides) first appeared in the 1960s.<sup>9-11</sup> It has been demonstrated that monoamides have a strong affinity with both the uranyl or plutonium cations.<sup>12-15</sup> Their selectivity can be adjusted by varying either the length or the ramification of monoamide alkyl chain.<sup>9,16,17</sup> The use of N,N-di-(ethyl-2-hexyl)isobutyramide (DEHiBA) has been proposed for U(VI) recovery and U(VI)/Pu(IV) or U(VI)/Th(IV). The knowledge of the stoichiometries and coordination of the actinide cations in aqueous and organic media are of high importance not only to better understand the extraction mechanism but also to optimize the extraction efficiency and selectivity. In the case of uranyl extraction, it has been shown that the neutral complex  $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  forms in the organic phase.<sup>18-20</sup> It has a hexagonal bipyramidal geometry corresponding to the uranyl center to which two nitrates and two amide groups are linked as it has been confirmed by X-ray Diffraction (XRD), Raman, and IR spectroscopies.<sup>12,21</sup> One should point out that the nitrates can be located either in *cis*- or *trans*-positions. Although they are cases reported in the literature involving a *cis*-conformation around the uranyl moiety,<sup>12,13,22</sup> it is far less common than the *trans* conformation. As the two conformations exist in crystals, they might both be present in nitric acid solution and in organic phases.

The existence of different species could induce a change in the electronic structure of uranyl binitrate complexes. In order to reveal a difference in the coordination sphere of uranyl in terms of position of the nitrates and monoamides, the organic phase after extraction can be characterized by UV-Vis or time-resolved laser-induced fluorescence spectroscopy (TRLFS). The latter method has some advantageous features allowing to measure luminescence spectra

at low total uranium concentration and discriminate side emitting compounds by temporal resolution. Moreover, the positions of the luminescence bands, band spacings, bandwidths, and intensities are features that can be interpreted to determine the nature and the number of ligands in the first coordination layer of  $\text{UO}_2^{2+}$ , as well as the local symmetry of the complex. For this, the spectroscopic characteristics should be well analyzed and interpreted. However, the determination of an electronic structure information from the luminescence spectra is either still unresolved or it requires additional experimental data. For instance, to study an electronic structure of  $\text{UO}_2\text{Cl}_4^{2-}$  complex, Görller-Warland et al.<sup>23</sup> used UV-Vis and magnetic circular dichroism spectroscopies. Another way is based on the Franck-Condon principle, where the overlapped region between the absorption and luminescence spectra gives an idea about the position of the electronic transitions on the energy scale, but not the exact value, since several transitions may appear in that region.

As it has already been described previously,<sup>24,25</sup> to study the uranium-based complexes and interpret the experimental spectra, the quantum chemical modeling is an insightful tool as it provides an accurate description of the electronic structure. Using the methodology described in our recent publications,<sup>24,25</sup> the luminescence spectra, as well as spectroscopic characteristics can be computed and used for the assignment of the experimental spectra. In our previous studies, the methodology has been proven to give an accurate description of the uranyl complexes electronic structures allowing to elucidate and quantify the influence of the first and second coordination spheres on the luminescence features. The structural parameters, emission energies and simulated luminescence spectra were found to be in good accordance with experimental data giving a significant level of confidence in the chosen theoretical methodology.

Here, we aim at studying the uranyl binitrate complexes and the influence of water and monoamide molecules in the first coordination sphere using quantum chemical simulations and the comparison to available and newly acquired experimental data. Theoretical models were created based on previous studies on the uranyl binitrate compounds<sup>26,27</sup> and will be

described in details further. The structural parameters of uranyl binitrate models will be discussed at the relativistic PBE0 level of theory in their *cis* and *trans* configurations. In the sake of guiding future experimental studies on uranyl binitrate compounds, the conformers stabilities and probabilities have been computed. As the spin-orbit CAM-B3LYP method has been found to accurately place electron transition energies of actinide complexes,<sup>28</sup> it is used to determine the “hot band” position in experimental luminescence spectra, since it is not easily identified experimentally. Moreover, we expect that this study is not only useful in illustrating the broad applicability of quantum modeling, but may also guide scientists in spectral data processing, *i.e.*, identification of the bands and importance of their intensities.

## Experimental details

### Materials

DEHiBA was purchased from Pharmasynthese (purity  $\geq 99\%$ ) and used as received. Hydrogenated tetrapropylene (TPH) used as a diluent was purchased from Novasep. The organic phases were prepared by dissolving weighed amounts of monoamide in TPH.

The U(VI) aqueous phase was prepared by dissolution of solid uranium (VI) nitrate hexahydrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) obtained from Prolabo (purity  $\geq 99\%$ ) into a solution of  $2\text{ mol L}^{-1}$  lithium nitrate (reagent grade) with deionized water produced by the Milli-Q Plus apparatus (Millipore). The pH was adjusted to pH=2 by adding a suitable volume of  $1\text{ mol L}^{-1}$  nitric acid.

### Liquid-liquid extraction

Suitable volumes of DEHiBA at a concentration of  $1.5\text{ mol L}^{-1}$  in n-TPH were contacted with aqueous phases ( $V_{\text{org}}/V_{\text{aq}}$ ). Extraction was performed at room temperature ( $\approx 25\text{ }^\circ\text{C}$ ) with 30 min stirring. Then, the solution was centrifugated and separated for titration and analytical procedures.

Uranyl concentrations were determined using X-ray fluorescence technique (Thermo Scientific - ARL QUANT'X - EDRXRF Analyser). Samples were diluted in  $1 \text{ mol L}^{-1}$  DEHiBA in TPH. The calibration range, performed with references solutions of uranyl nitrate in the same matrix is  $100\text{--}2000 \text{ mg L}^{-1}$ .

**UV-Vis absorption spectroscopy** UV-Vis measurements were performed on a Varian Cary 50 Scan spectrophotometer between 350 and 500 nm in quartz cells.

### **TRLFS analysis**

A narrow-band Nd-YAG/OPO/Fx1 laser line (tripled Surelite 8010 and doubled sunlite EX from Continuum) was used as the excitation source. This solid-state laser is ideal for selecting any wavelength between 220 and 1800 nm (energies from 1 to 20 mJ). Fluorescence was observed at right angle to the excitation by an alignment of 8 Si/Si optical fibers illuminating the entrance slit of a flat-field spectrometer (300i from Princeton Instrument) equipped with a pulsed intensified CCD camera (IMAX,  $1024 \times 256$  pixels, Princeton Instrument, USA) synchronized on the laser shot. The multichannel detection of eight local fluorescence channels along the laser beam in the quartz cell enables real-time correction in case of prefilter effect.

In this work, the excitation source was tuned 420 nm to avoid the decomposition of the organic ligand by UV radiation. The laser pulse energy was decreased until the intensity of the fluorescence remained stable with excitation times, i.e. 0.6 mJ and the laser beam was defocused into the cell by a quartz lens. A double chamber cell was used to attenuate the energy. The first chamber contained a reference aqueous solution of uranyl nitrate  $0.1 \text{ mol L}^{-1}$  in  $2 \text{ mol L}^{-1}$   $\text{LiNO}_3$  pH=2 used for normalization of the spectra while the sample was in the second chamber.

The samples were excited with a 10 Hz repetition rate. The recording of spectra was performed by integration of the pulse light signal given by the intensifier with a time delay of 150 ns and during a determined aperture time of 1  $\mu\text{s}$ . Accumulation of 5 laser shots were

averaged for each spectrum.

## Computational Details

The choice of the used QM methods is justified in previous works.<sup>24,25,29</sup> The ground and excited-state molecular geometries were optimized with Gaussian 16<sup>30</sup> software including scalar relativistic effects and using the PBE0 functional of the density.<sup>31</sup> For the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis-/trans-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>* complexes, the water solvent was accounted for using the continuum polarizable conductor model (CPCM)<sup>32</sup> ( $\epsilon_r = 78.36$ ). The experimentally studied N,N-di(2-ethylhexyl)-*iso*-butanamide (DEHiBA) molecule was transformed to the N,N-diethyl-*iso*-butanamide (DEiBA) molecule with a shorter alkyl chain, to keep the computational costs reasonable, as the original alkyl chain is located beyond the first coordination sphere of U(VI) and is expected not to affect the uranyl-core electronic structure.<sup>24</sup> The experimental luminescence spectrum of the  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$  complex was recorded in hydrogenated tetrapropylene (TPH), which is an industrial solvent that is often described as a branched dodecane; thus one can assume that it has similar properties to that of *n*-dodecane, namely a low polarity. Therefore, the structures of *cis-/trans-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub>* complexes were optimized in the gas phase, as the solvent is expected not to induce sizable changes of the complex geometries because of its low permittivity value ( $\epsilon_r = 2.00$  taken for *n*-dodecane).<sup>24</sup> The geometries of the luminescent states (first triplet excited states) were optimized using the time-dependent (TD)-DFT/PBE0 approach as implemented in Gaussian 16 code<sup>30</sup> with equilibrium solvation where it was necessary. The vibrational harmonic frequencies of the ground and luminescent states were computed analytically. All optimized geometries considered for the vibronic spectra calculations represent real minima as they have no imaginary frequencies. In these calculations, the def2-TZVP basis sets<sup>33,34</sup> were used for the H, C, N and O elements. A small-core Relativistic Effective Core Potential (RECP), that accounts for scalar relativistic effects of the 60 core electrons<sup>35,36</sup> was used for



the uranium atom, while the valence electrons were described by the def-TZVP basis set.<sup>37</sup> To speed up the TD-DFT calculations within the Gaussian 16 package, the inner U(5*s*, 5*p*, 5*d*), O(1*s*), C(1*s*), N(1*s*) orbitals were frozen.

In order to compute accurate absolute energies of the electronic transitions involved in the luminescence spectra of uranyl nitrate complexes, we have performed CAM-B3LYP<sup>38</sup> TD-DFT single-point calculations, at the spin-free excited-state structures, including spin-orbit coupling effects with the ZORA Hamiltonian,<sup>39</sup> and modeling the environment effect (water solvent for *cis*- and *trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>*n*</sub> (*n*=1,2) and *n*-dodecane for UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub>) with the conductor-like screening model COSMO.<sup>40-42</sup> These calculations were carried out with the Amsterdam Density Functional package (ADF 2018.01).<sup>43</sup> All atoms were described by TZ2P Slater-type basis sets<sup>44</sup> without freezing the atomic cores.

The theoretical luminescence spectra of uranium (VI) complexes have been computed with the `ezSpectrum 3.0`<sup>45</sup> software. The Franck-Condon factors (FCFs) were computed analytically including Duschinsky transformations of the normal modes between the ground and excited states. The number of vibrational quanta in the luminescent and ground state were selected to be one and five, respectively, to match the recorded experimental vibronic transitions. All the vibronic progressions were computed at 300 K to include contributions from the thermally active vibrational modes. As the proposed quantum chemical methods cannot compute absolute intensities, the intensity of the “hot band” peak was manually adjusted to match the experimental intensity distributions. The spectral shapes were estimated by convoluting the discrete stick spectra with Lorentzian broadening functions adjusting the width to match the experimental one.

The free energy calculations were performed using a composite method. While all the entropic and vibrational contributions are obtained from the DFT calculations, the electronic energies are estimated either at DFT/PBE0 or at the MP2 levels of theory using the Turbomole 7.3<sup>46</sup> and the Gaussian 16.<sup>30</sup>

## Choice of the model systems

In general, the coordination number of the uranyl unit varies from four to six depending on the ligands nature and media.<sup>47</sup> In nitric acid solutions the uranium(VI) speciation may be composed of several species like uranyl  $\text{UO}_2^{2+}$  and uranyl nitrate complexes  $(\text{UO}_2(\text{NO}_3)_n)^{(2-n)}$ ,  $n = 1, 2$ ) that can be detected by TRLFS.<sup>48</sup> In organic media the uranyl nitrate complex is soluble as a neutral compound  $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$ .<sup>27</sup> As one of the main goals of this study is to elucidate the influence of organic ligands present in the first coordination sphere, the chemical model systems should have the same coordination number and molecular charge. In the present work, the majority of the model systems are sixfold coordinated and are neutral. The structures are shown in Figure 1. In the crystal phase, the uranyl nitrate complex hydration shell contains six water molecules, but there are at most two water molecules in the first coordination sphere,  $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ .<sup>49</sup> As the  $\text{UO}_2(\text{NO}_3)_2$  molecule has a coordination of four, with the two bidentate nitrate groups coordinated to uranyl, we have added one or two water molecules in the uranyl equatorial plane 1 to check the influence of the amount of water molecules on the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_n$  ( $n = 1, 2$ ) complexes spectra and emission energies, and 2) to quantify the relative stability of *cis-/trans*- $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  conformers (see Table S1 of the ESI). Hereafter, the two water molecules were substituted by two N,N-dialkyl amides. As already mentioned, in order to keep reasonable computational costs, the N,N-di(2-ethylhexyl)-*iso*-butanamide (DEHiBA) ligand was substituted with the N,N-diethyl-*iso*-butanamide (DEiBA), which has shorter alkyl chains.

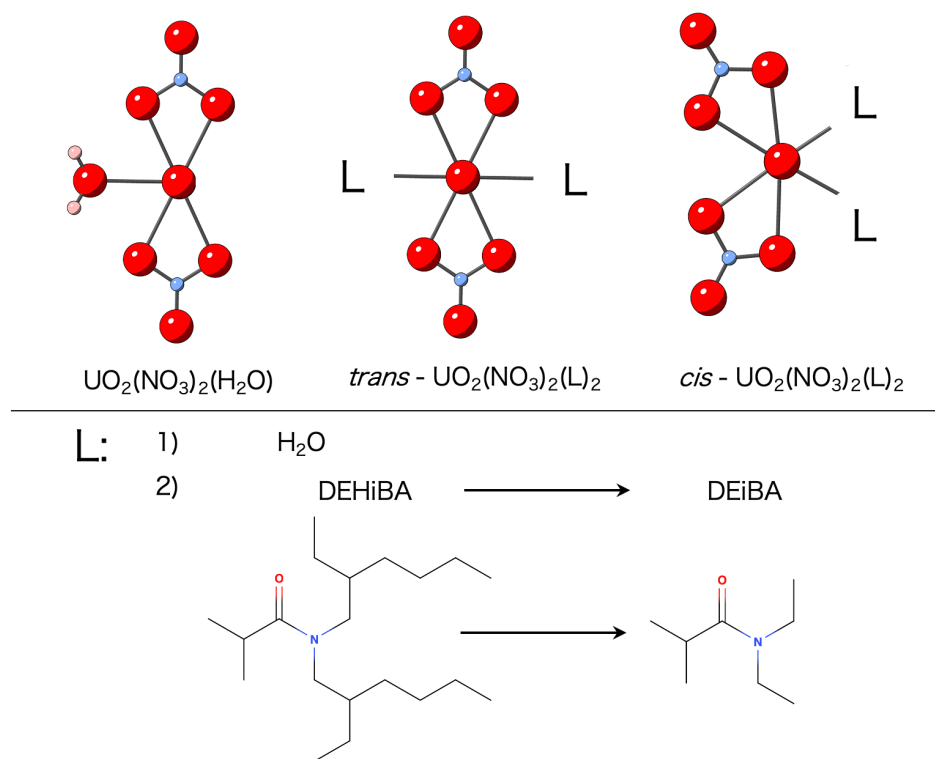


Figure 1: The structures of  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and  $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  ( $\text{L}=\text{H}_2\text{O}$ , DEiBA) model systems in their *trans*- and *cis*-configurations. The view is made along the z axis defined by the uranyl unit.

# Results

## Theoretical ground and excited-state structures

### *cis-/trans-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>n</sub> (n=1, 2)*

Uranyl nitrate is a water-soluble uranium salt. It exists in the form of the crystal uranyl binitrate hexahydrate  $[\text{UO}_2(\text{NO}_3)_2] \cdot 6 \text{H}_2\text{O}$ . The structural studies performed on a crystal compound showed that there are two bidentate nitrates and two water molecules bounded to uranyl unit in a *trans*-configuration.<sup>50-52</sup> Unluckily, the speciation of uranyl nitrate compounds in aqueous phase is less documented as there are other solvated and nitrate species present.<sup>48,53</sup> The dissolution of crystallohydrates in water may be accompanied by the destruction of the crystal lattice, as well as (de-)hydration process. Thus, we have made an assumption that either one or two water molecules may fill the  $\text{UO}_2(\text{NO}_3)_2$  first coordination sphere.

All the distances for the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis-/trans-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>* complexes are reported in Table 1 along with experimental data available in the literature. The ground-state structures of these two complexes are found to be almost identical with a maximum deviation of 0.003 Å for  $\text{U}-\text{O}_{\text{ax}}$ ,  $\text{U}-\text{O}_{\text{NO}_3}$  and  $\text{U}-\text{N}_{\text{NO}_3}$  bond lengths. The  $\text{U}-\text{O}_{\text{H}_2\text{O}}$  bond is 0.024 Å longer in the *trans-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>* complex than in the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  complex, as there are more electrostatic repulsions in the former than in the latter. One interesting observation is that Taylor et al.<sup>51</sup> obtained non-equivalent  $\text{U}-\text{O}_{\text{ax}}$  bond distances (1.770(7) and 1.749(7) Å), while in our calculations these distances are strictly equal (1.749 Å). We suspect the experimental bond length difference to be related to the fit uncertainty, because most of the uranyl complexes have almost equivalent  $\text{U}-\text{O}_{\text{ax}}$  bond lengths.<sup>54,55</sup> The *trans-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>* complex structure has been studied previously by theoretical DFT/SVWN<sup>56</sup> and Car-Parrinello (CP/BLYP) calculations.<sup>57</sup> The results obtained by these two methods overestimate the bond lengths found in the crystal structures by neutron diffraction measurements,<sup>51</sup> whereas our DFT/PBE0 ground-state structures are

in better agreement with the experimental structural data. These compiled results indicate that the choices of both the functional and the basis sets have a significant impact on the accuracy of the computed U(VI)-based complexes structures, and since we are aiming at capturing the changes between the ground and luminescent-state geometries, we can postulate that any functional should be benchmarked to be able to provide a reasonable picture. Comparing the computed geometries of *cis*- and *trans*- $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  conformers, we did not observe any change in the structures except for the U–O<sub>H<sub>2</sub>O</sub> bond which was found to be 0.014 Å longer in the *cis* conformer than in the *trans*. This is probably related to the greater energetic stability of the *trans* complex as shown in Table S1 of the ESI.

The geometrical parameters of the lowest triplet excited states are also reported in Table 1. As a result of the electronic excitation, we observe an elongation of the U–O<sub>ax</sub> bond length by 0.038 Å for the uranyl binitrate complex with one water molecule and 0.037 Å for both *cis*- and *trans*- $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  conformers. For the equatorial ligands, the structural changes are found to be very minor; the greatest bond-length change is 0.006 Å, suggesting that there are no significant contributions of the water ligands to the orbitals participating to the excitation.

Insofar as vibrational frequencies contribute to the luminescence spectra to some extent, it is of high importance to characterize them. There are three main vibrational modes that may appear in the vibronic progressions: uranyl bending  $\nu_b$ , symmetrical stretching  $\nu_s$  and asymmetrical stretching  $\nu_a$  modes. The values of these frequencies are reported in Table 2 together with the experimental IR and Raman data obtained for solid<sup>58</sup> and liquid<sup>26</sup> uranyl binitrate. The experimental  $\nu_s$  and  $\nu_a$  are found to be almost identical for  $\text{UO}_2(\text{NO}_3)_2$  in solid and in solution, the largest difference being 16 cm<sup>-1</sup> for the uranyl asymmetrical stretching mode. The analysis of the theoretical harmonic frequencies of  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis*-/*trans*- $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  complexes shows that they are nearly the same, but they are found to be overestimated by at most 62 cm<sup>-1</sup> for the uranyl symmetrical stretching mode as compared to experimental data. In the series of the chemical models, the largest

Table 1: Ground and excited state geometries (in Å) of  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis-/trans-* $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  (L= $\text{H}_2\text{O}$ , DEiBA) compared to selected results from the literature (dam - N',N-diethylacetamide; eam - N-ethylacetamide).

	U-O <sub>ax</sub>	U-O <sub>NO3</sub>	U-N <sub>NO3</sub>	U-O <sub>L</sub>	Method	Ref.
	Ground State					
$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$	1.746	2.473	2.917	2.474	PBE0/CPCM	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	1.749	2.470	2.914	2.498	PBE0/CPCM	this study
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	1.749	2.469	2.914	2.512	PBE0/CPCM	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	1.756	2.496	2.945	2.390	PBE0/GP	this study
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	1.755	2.480	2.929	2.441	PBE0/GP	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	1.749(7)	2.504(5)		2.397(3)	neutrons	51
	1.770(7)	2.547(7)			diffraction	
	1.820	2.530		2.550	CP/ZORA(aq)	57
	1.800	2.490		2.590	CP/BLYP/ECP60	57
$\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$	1.77(1)	2.53(1)	2.97(3)	2.38(2)	EXAFS	27
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{dam})_2$	1.760(3)	2.533(3)	-	2.362(3)	X-ray	12
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{eam})_2$	1.747(3)	2.526(4)	-	2.363(3)	X-Ray	12
	Excited state					
$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$	1.784	2.479	2.921	2.479	PBE0/CPCM	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	1.786	2.476	2.918	2.500	PBE0/CPCM	this study
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	1.786	2.473	2.918	2.515	PBE0/CPCM	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	1.792	2.515	2.963	2.375	PBE0/GP	this study
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	1.791	2.495	2.943	2.428	PBE0/GP	this study

changes of the theoretical frequency values are found to be  $9\text{ cm}^{-1}$  and  $11\text{ cm}^{-1}$  for  $\nu_s$  and  $\nu_a$  modes, respectively, values that are in line with the magnitudes of the structural changes. Moreover, our calculations showed that the  $\nu_b$  mode is coupled with the motions of ligands, an information that cannot be deduced from the IR spectra of  $\text{UO}_2(\text{NO}_3)_2$  in solution.<sup>26</sup> It is thus inappropriate to describe this vibrational frequency as a pure uranyl bending mode. Experimentally, it was measured at  $254\text{ cm}^{-1}$ , matching the range of our computed values  $217\text{--}276\text{ cm}^{-1}$ .

Table 2: Ground and excited state vibrational frequencies (in  $\text{cm}^{-1}$ ) of the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis-/trans-* $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  (L= $\text{H}_2\text{O}$ , DEiBA) compared to selected results from the literature (dam - N',N-diethylacetamide; eam - N-ethylacetamide).

	$\nu_b$	$\nu_s$	$\nu_a$	Method	Ref.
Ground state					
$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$	217-276	934	989	PBE0/CPCM	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	230-264	925	978	PBE0/CPCM	this study
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	217-265	928	980	PBE0/CPCM	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	280	911	987	PBE0/GP	this study
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	278	913	989	PBE0/GP	this study
$\text{UO}_2(\text{NO}_3)_2$	254	872	961	IR/Raman	<sup>26</sup>
$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$		875	945	IR/Raman	58
$\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$			935	IR	14
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{dam})_2$			923	IR	12
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{eam})_2$			932	IR	12
Excited state					
$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$	210-267	833	856	PBE0/CPCM	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	220-257	833	857	PBE0/CPCM	this study
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	223-261	834	857	PBE0/CPCM	this study
<i>trans-</i> $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	275	822	850	PBE0/GP	this study
<i>cis-</i> $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	270	823	850	PBE0/GP	this study

As a result of the U–O<sub>ax</sub> bond elongation from the ground to the luminescence state, the  $\nu_s$  and  $\nu_a$  vibrational frequencies are lowered by  $101\text{ cm}^{-1}$  and  $133\text{ cm}^{-1}$ , respectively in the *trans-* $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  complex. A similar behavior, within  $12\text{ cm}^{-1}$  difference, is observed for *cis-/trans-* $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  complexes. One can, however, note that the coupled  $\nu_b$  frequency range is not significantly affected by the excitation process.

### *cis-/trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub>

To probe the electronic structure of U(VI) surrounded by inorganic and organic ligands, two molecules of the DEiBA monoamide were placed in the first coordination sphere instead of the water molecules forming UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> *cis*- and *trans*-conformers (Fig. 2). The optimized bond distances are shown in Table 1. The substitution of water molecules by the DEiBA monoamide ligands induces a lengthening of the U–O<sub>ax</sub>, U–O<sub>NO<sub>3</sub></sub> and U–N<sub>NO<sub>3</sub></sub> bonds in the range of 0.007–0.031 Å for *trans*- and 0.006–0.015 Å for *cis*-conformer, while the distance between uranium and the oxygen atom of the monoamide is shorter than that with the oxygens of the water molecules, by 0.108 Å and 0.071 Å for the *trans* and *cis* configurations, respectively. This is simply a result of the larger electron donation to uranium by the DEiBA monoamide as compared to water.<sup>27</sup>

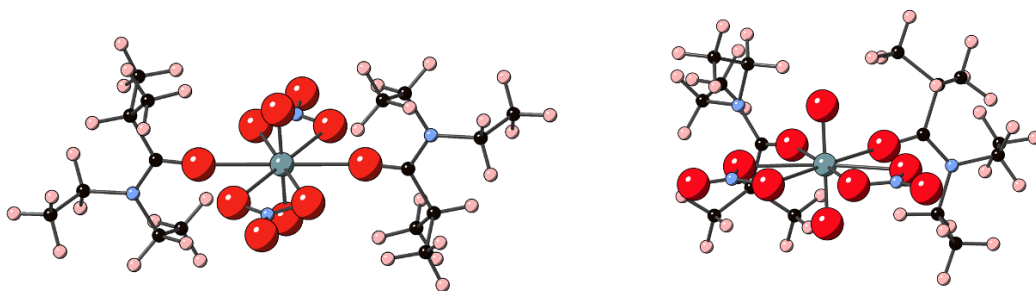


Figure 2: The optimized at R-ECP DFT/PBE0 ground state geometries of the *cis*- and *trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> conformers.

The ground-state geometries of the *cis*- and *trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> complexes have very similar distances in the equatorial plane, and the free energy difference of two conformers is small. Nevertheless, the *trans* conformer is found to be more stable as compared to *cis*, by about 23 kJ mol<sup>-1</sup> and 15 kJ mol<sup>-1</sup> at the DFT/PBE0 and MP2 levels of theory, respectively (see Table S1 of the ESI). The computed geometry of the *trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> complex agrees well with the experimental EXAFS results obtained by Acher et al.<sup>27</sup> In the same way, the computed bond lengths within UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> conformers also agree with the



single-crystal X-ray structures of similar amide compounds like *cis*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(dam)<sub>2</sub> (dam - N',N-diethylacetamide) and *trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(eam)<sub>2</sub> (eam - N-ethylacetamide).<sup>12</sup>

The changes in the geometries when switching from the ground to the luminescent state in *cis*-/*trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> complexes is of the same order as that reported for the *cis*-/*trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> complexes. The minor differences are the variations of U-O<sub>NO<sub>3</sub></sub> and U-N<sub>NO<sub>3</sub></sub> bonds of monoamide complexes upon excitation which is a little larger than in complexes with water molecules, and the U-O<sub>L</sub> bonds are shortened by about 0.014 Å, while in case of the complexes with water, they remained almost unchanged. These structural changes will be reflected in the theoretical luminescence intensities distribution as discussed further.

The theoretical vibrational frequencies of *cis*- and *trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> complexes are listed in the Table 2. As in UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> complexes, there is almost no difference for the  $\nu_b$ ,  $\nu_s$  and  $\nu_a$  frequencies values between the *cis* and *trans* conformers. Moreover, the  $\nu_b$  frequency corresponds to a pure uranyl bending motion, uncoupled from the equatorial ligands,  $\nu_s$  is smaller and  $\nu_a$  remains almost unchanged. The changes are most probably related to the weakening of the U-O<sub>ax</sub> bond paired with the decrease in uranyl stretching force constant. The calculated  $\nu_a$  frequency can be compared with experimental data measured by IR spectroscopy for various crystals and liquid samples of *cis*-/*trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub> complexes.<sup>12,27</sup> As observed for the UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> complexes, our theoretical vibrational frequencies for the UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> complexes are overall larger than the experimental values by 65 cm<sup>-1</sup>. Thus this systematic difference might be related to choice of the computational methodology (DFT functional, basis sets, and/or solvation model).

The changes between the ground and the luminescent states vibrational frequencies in the *cis*-/*trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub> complexes are equal in average to 90 cm<sup>-1</sup> and 138 cm<sup>-1</sup> for the symmetrical and asymmetrical uranyl stretching modes, respectively, while the  $\nu_b$  frequency is similar to that in the ground state.

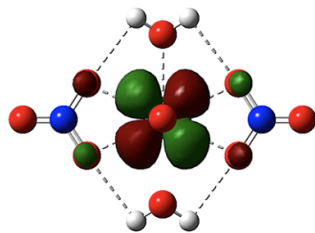
## Emission energies

For the uranyl-based complexes, the nature of the luminescent emission was previously discussed in several experimental<sup>59-61</sup> and theoretical<sup>62-64</sup> studies. It was deduced from the examples of uranyl tetrachloride  $\text{UO}_2\text{Cl}_4^{2-}$ <sup>24</sup> and uranyl triscarbonate  $\text{UO}_2(\text{CO}_3)_3^{4-}$ <sup>25</sup> complexes that the luminescence state has a triplet character and that the emission occurs as a result of an electron transition from one of the four non-bonding  $5f$  orbitals of uranium(VI) to an orbital that has a uranyl  $\sigma$  character possibly mixed with orbitals of the equatorial ligands. In the present  $\text{UO}_2(\text{NO}_3)_3(\text{L})_2$  complexes, the plots of the molecular orbitals involved in the luminescent process shown in Figure 3 reveal that the emission corresponds to a metal-to-ligand charge transfer de-excitation from non-bonding uranium(VI) orbitals to orbitals delocalized over the uranyl unit, the nitrate ligands and the monoamide linking groups.

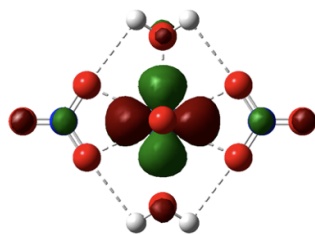
Since the luminescence spectra of uranyl-based complexes have similar shapes (with some exceptions like  $\text{UO}_2\text{Cl}_4^{2-}$ ), the nature of the equatorial ligands can be deduced from the position of the spectral envelope in the energy scale. In the luminescence spectra, the origin is usually defined by the position of the “hot band.” For instance, luminescence blue shifts of the uranyl triscarbonate complexes are observed as compared to most other uranyl species, while hydrated uranyl exhibits a red shift.<sup>65-67</sup> It has been proposed by Wang et al.<sup>65</sup> that the position of the “hot band” in uranyl minerals depends on the basicity of the equatorial ligand. The ionic interactions between uranyl ion and ligands with higher pKa lead to a larger decrease of the  $\nu_s$  frequency, and a larger red shift of the luminescence spectra.

Here, we have used the SOC CAM-B3LYP calculations to predict the “hot band” positions by the averaging of first four vertical emission energies computed out of the first low-lying excited state geometry and corrected by the zero-point energies of the ground and luminescent states of the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis-/trans-* $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  ( $\text{L}=\text{H}_2\text{O}$ , DEiBA). The computed “hot band” energies  $E$  are listed in Table 3. The comparison of theoretical data with experimental results is not relevant at this stage, because to our knowledge,

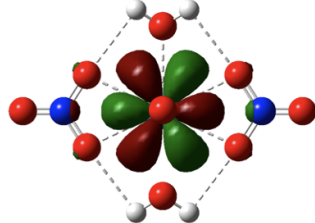
*trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>



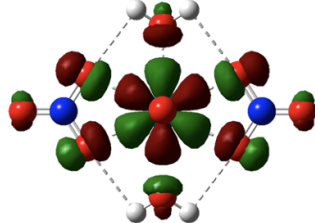
U 5f<sub>-δ</sub>



U 5f<sub>+δ</sub>

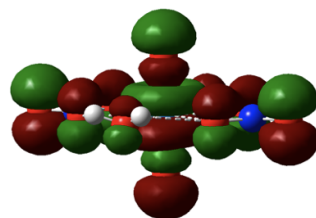


U 5f<sub>-φ</sub>

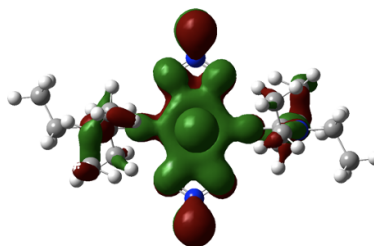
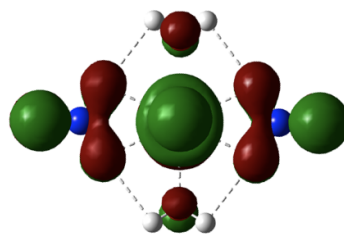


U 5f<sub>+φ</sub>

U 5f,6d + O 2p



*trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>



*trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(DEiBA)<sub>2</sub>

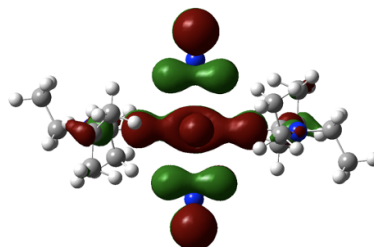


Figure 3: The highest occupied (right panel) and lowest unoccupied (left panel) molecular orbitals of *trans*-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub> (L = H<sub>2</sub>O, DEiBA) involved in the triplet-singlet electronic transitions, responsible of uranyl luminescence. The molecular orbitals were obtained at the RECP DFT/PBE0 level of theory.

the position of the “hot band” was never discussed before for the uranyl binitrate complexes.

Table 3: The “hot band” energies  $E$  of uranyl binitrate complexes (in  $\text{cm}^{-1}$  and nm) compared to  $\text{Na}_3\text{UO}_2(\text{CO}_3)_3^-$  and  $[\text{A336}]_2[\text{UO}_2\text{Cl}_4]$  results. The computed values are obtained at the all-electron SOC CAM-B3LYP level of theory, and corrected with the spin-free Zero-Point Energy correction of the ground and luminescent states.

	$E$ [ $\text{cm}^{-1}$ ]	$E$ [nm]
Water COSMO		
$\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$	20204	495
<i>trans</i> - $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	20456	489
<i>cis</i> - $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$	20616	485
$\text{Na}_3\text{UO}_2(\text{CO}_3)_3^-$	20978	477
<i>n</i> -dodecane COSMO		
<i>trans</i> - $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	20116	497
<i>cis</i> - $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$	20171	496
$[\text{A336}]_2[\text{UO}_2\text{Cl}_4]$	20001	500

The theoretical “hot band” energies of the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis*-/*trans*- $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  complexes in water come out close, within  $413 \text{ cm}^{-1}$  (10 nm). These differences are within the expected accuracy of our quantum chemical methodology. Notwithstanding, we restrict ourselves to making a comparison with the results obtained for compounds with different basicity of equatorial ligands. Within the uranyl binitrate water complexes with one or two coordinated water molecules, since the equatorial plane does not differ by the nature of the ligands (it means that basicity remains unchanged), we can take an average “hot band” value of  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$ , *cis*-/*trans*- $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  and compare it to the  $\text{Na}_3\text{UO}_2(\text{CO}_3)_3^-$  complex value. It is known from the study by Parr and Pearson et al.<sup>68</sup> that nitrates and water molecules are less basic than the carbonate anions. From our calculations, the “hot band” of  $\text{Na}_3\text{UO}_2(\text{CO}_3)_3^-$  is placed at  $20\,978 \text{ cm}^{-1}$  (477 nm), while the averaged value of the uranyl binitrate “hot band” is  $20\,425 \text{ cm}^{-1}$  (490 nm), showing  $553 \text{ cm}^{-1}$  (13 nm) red shift which is in consistency with Wang’s assumption. et al.<sup>65</sup>

For the *cis*- and *trans*- $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$  (for which the basicity is not known yet) in *n*-dodecane, we have computed the “hot band” energies at  $20\,116 \text{ cm}^{-1}$  (497 nm) and  $20\,171 \text{ cm}^{-1}$  (496 nm), respectively. They are somewhat red shifted with respect to that

of the water complexes of uranyl binitrate. As compared to the “hot band” value of the  $[A336]_2[UO_2Cl_4]$  complex,  $20\,001\text{ cm}^{-1}$  (500 nm), the uranyl binitrates with monoamides “hot band” energy exhibit a blue shift.

One can notice that the *cis*- and *trans*-conformers of uranyl binitrate complexes may hardly be discriminated solely by the “hot band” energy.

## Vibronic progressions

In the luminescent emission of U(VI) complexes, the principal vibronic progression is a result of an electronic transition coupled to the symmetrical stretching mode of the uranyl unit. Secondary progressions may also appear to some extent because of the coupling to other symmetrical motions of the molecular complex. The quantum chemical simulations of the vibronic spectra allow to quantify the contributions of the vibronic modes. To guide the discussion and the comparison to experimental data, the computed stick spectra of all binitrate uranyl complexes are convoluted and drawn on Figure 4.

The structural and vibrational parameters directly reflect in the shape of the luminescence spectra. The most evident and easily detectable fingerprint is the ground state symmetrical stretching mode of the uranyl moiety, as it is equal to the spacing between the main peaks of the vibronically resolved envelope. Some other vibrational frequencies (symmetrical mostly) appear in the vibronic progression to a smaller extent and might hardly be detectable in the broad spectral envelope. The vibrational frequencies contributions, their natures and intensities are listed in Table 4 for the  $UO_2(NO_3)_2(H_2O)$  and *cis*-/ *trans*- $UO_2(NO_3)_2(L)_2$  (L =  $H_2O$ , DEiBA) complexes. One can note that the excited state uranyl symmetrical stretching mode can be detected in these luminescence spectra as discussed further.

The ground-state symmetrical stretching uranyl frequency has been discussed previously. From the comparison of the spectra displayed in Figure 4 and the symmetric stretching frequencies listed in Table 4, we can infer that the vibronic band spacings are very similar, thus the spectra of aqueous and organic uranyl binitrate complexes are difficult to separate

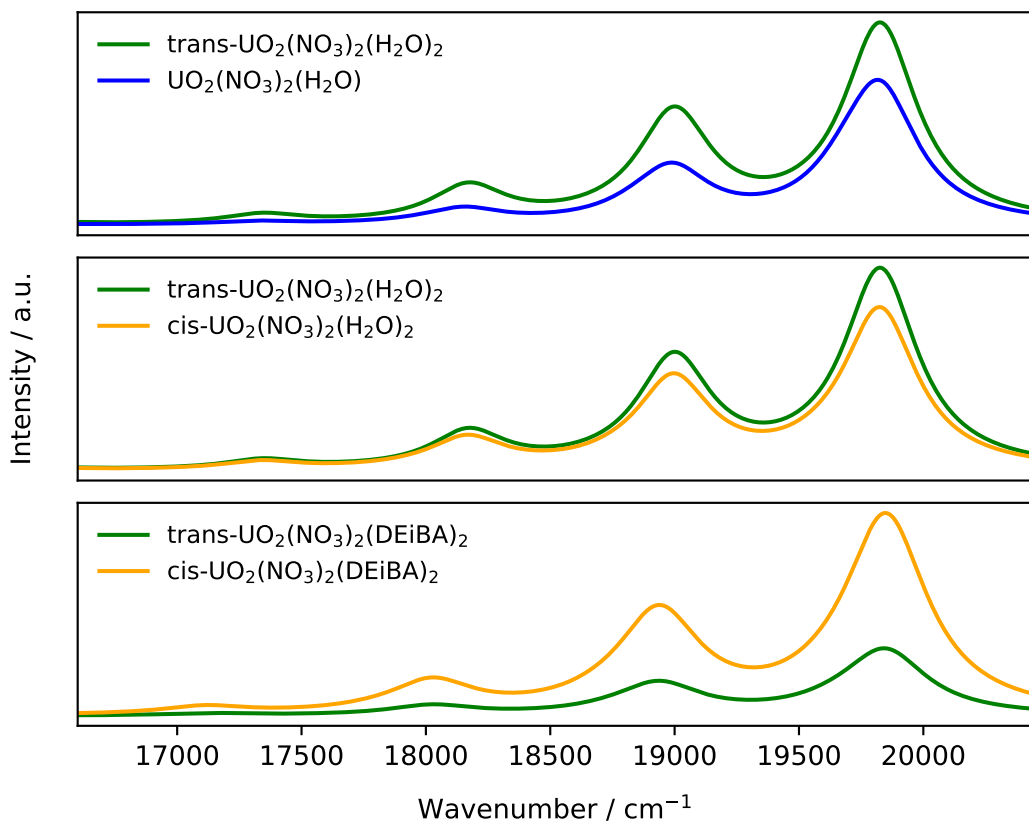


Figure 4: Theoretical vibronic progressions of the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis-/trans*- $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  ( $\text{L} = \text{H}_2\text{O}$ , DEiBA) complexes. The position of the first peak is adjusted to the computed “hot band” value of the *trans*-complexes and corrected by the  $\nu_s$  of the excited state. The spectral shapes were estimated by convoluting the stick spectra with Lorentzian functions with a FWHM of  $400 \text{ cm}^{-1}$ .

solely by the main vibronic band spacings. The detailed analysis of the vibronic bands (See Table 4) reveals that some other modes build up a secondary vibronic progression. In the case of the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  complex, the uranyl rocking appears at  $156\text{ cm}^{-1}$  after the  $0 \rightarrow 0$  band. In the *cis*- and *trans*- $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  spectra, we observe contributions from the  $\text{U}-\text{H}_2\text{O}$  stretching mode coupled to uranyl bending motions at  $249\text{ cm}^{-1}$  and  $315\text{ cm}^{-1}$  for the *cis*- and *trans*-conformers, respectively. A symmetrical  $\text{U}-\text{NO}_3$  stretching mode coupled with the weak uranyl bending motion contributes to the spectra of the *cis*- and *trans*- $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$  complexes at  $234\text{ cm}^{-1}$  and  $212\text{ cm}^{-1}$ , respectively.

The theoretical luminescence intensities distributions are mainly linked to the  $\text{U}-\text{O}_{\text{ax}}$  bond elongations between the ground to the luminescent state,<sup>69</sup> but this relationship is not defined yet. We have performed a comparison of the vibronic progressions to elucidate the influence of the nature of the ligands and of their orientations on theoretical intensities. On the top panel of Figure 4 we observe that the absolute intensity of the *trans*- $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  complex is higher than that of  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  by 0.184 au for the  $0 \rightarrow 0$  band. The middle panel of Figure 4 reveals that the *trans*-conformer of uranyl binitrate with two water molecules exhibits higher intensities than the *cis* conformer by 0.107 au. In the bottom panel of Figure 4, the spectra of *cis*- and *trans*- $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$  have been compared and, unlike in the uranyl binitrate water complexes, the spectrum of the *cis* conformer is more intense by 0.216 au than the *trans*-one. From the analysis of the geometries and the shifts from the ground to the luminescent state, we did not find any significant difference, especially in the  $\text{U}-\text{O}_{\text{ax}}$  bond. It means that intensities change is not related here to the geometrical changes discussed earlier, but rather to some other factors. As the vibronic intensities arise from the Franck-Condon overlaps between the ground and excited-state normal modes, if they are not parallel, Duschinsky rotations need to be accounted for, and may contribute to the intensity changes.

Table 4: Assignments of the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis-/trans*- $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  (L =  $\text{H}_2\text{O}$ , DEiBA) theoretical luminescence spectra computed in the gas phase and in the CPCM water solvent for complexes with organic and inorganic ligands respectively. The energy of the spectrum was adjusted to the theoretical “hot band” value and corrected by  $\nu_s$  of the excited state.

E [ $\text{cm}^{-1}$ ]	$\Delta E$ [ $\text{cm}^{-1}$ ]	I [au]	E [ $\text{cm}^{-1}$ ]	$\Delta E$ [ $\text{cm}^{-1}$ ]	I [au]	Identification
<b><math>\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})</math></b>						
19831		0.347				0(0)→1(0)
19675	156	0.061				0(0)→1( $1\nu_1$ )
18897	934	0.138				0(0)→1( $1\nu_s$ )
18741	156	0.018				0(0)→1( $1\nu_1, 1\nu_s$ )
17963	934	0.037				0(0)→1( $2\nu_s$ )
17807	156	0.004				0(0)→1( $1\nu_1, 2\nu_s$ )
17028	935	0.008				0(0)→1( $3\nu_s$ )
16094	934	0.001				0(0)→1( $4\nu_s$ )
<i>trans</i> - $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$			<i>cis</i> - $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$			
20104		0.531	20344		0.424	0(0)→1(0)
19789	315	0.005	20095	249	0.014	0(0)→1( $1\nu_2$ )
19179	925	0.291	19417	927	0.236	0(0)→1( $1\nu_s$ )
18864	315	0.003	19167	249	0.008	0(0)→1( $1\nu_2, 1\nu_s$ )
18255	924	0.096	18489	927	0.080	0(0)→1( $2\nu_s$ )
17645	315	0.000	18240	249	0.003	0(0)→1( $1\nu_2, 2\nu_s$ )
17330	925	0.024	17562	927	0.021	0(0)→1( $3\nu_s$ )
16405	925	0.005	16634	927	0.005	0(0)→1( $4\nu_s$ )
<i>trans</i> - $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$			<i>cis</i> - $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$			
19674		0.097	19850		0.313	0(0)→1(0)
19462	212	0.007	19616	234	0.011	0(0)→1( $1\nu_3$ )
18763	911	0.047	18937	913	0.158	0(0)→1( $1\nu_s$ )
18551	212	0.003	18703	234	0.007	0(0)→1( $1\nu_3, 1\nu_s$ )
17852	911	0.014	18024	913	0.049	0(0)→1( $2\nu_s$ )
17640	212	0.000	17790	234	0.002	0(0)→1( $1\nu_3, 2\nu_s$ )
16942	911	0.003	17111	913	0.012	0(0)→1( $3\nu_s$ )

$\nu_1$  is uranyl rocking,  $\nu_2$  is U- $\text{H}_2\text{O}$  stretching + weak  $\nu_b$ ,  
 $\nu_3$  is U- $\text{NO}_3$  stretching + weak  $\nu_b$



# Discussions

As for most of the U(VI) compounds, the luminescence spectra of the uranyl nitrate complexes show well-resolved vibronic progressions that overlap with the pure electronic transition from the luminescent state to the ground state. We have collected TRLFs experimental data for  $\text{UO}_2(\text{NO}_3)_2$  in nitric acid (plain line),<sup>48</sup>  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$  in TPH solvent (dotted line) and  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  in supercritical  $\text{CO}_2$  (dashed line).<sup>70</sup> The normalized experimental time-resolved luminescence spectra are shown in Figure 5.

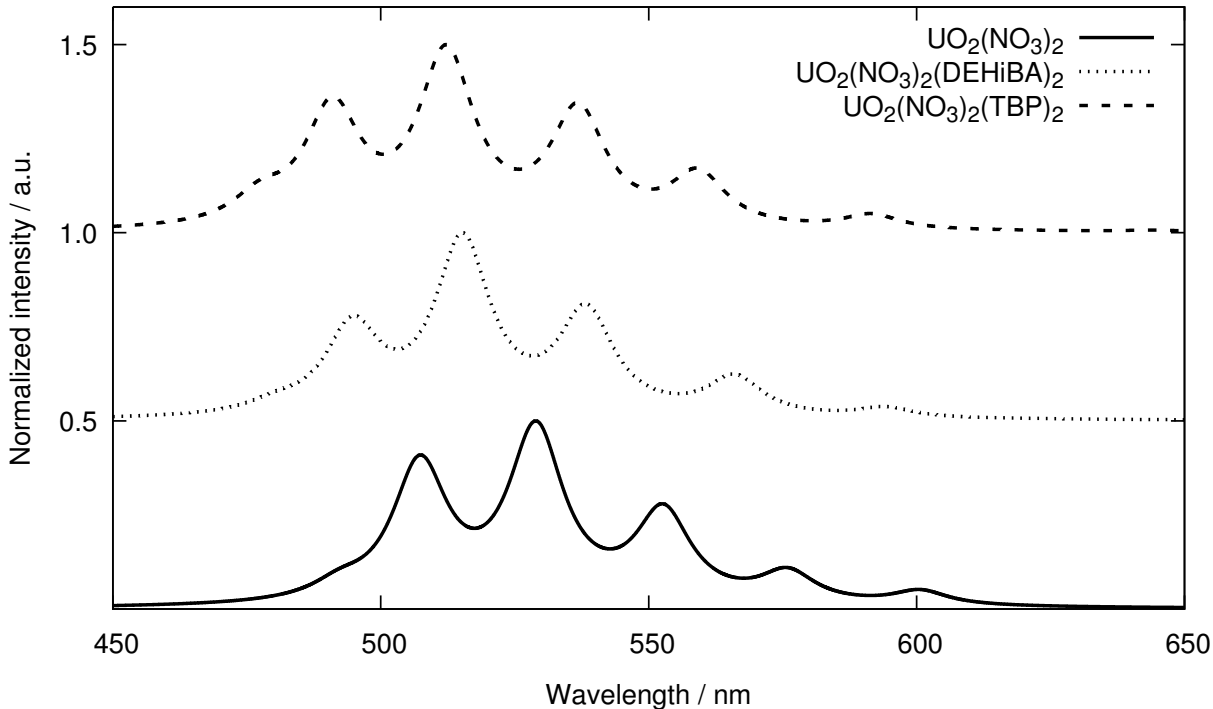


Figure 5: Experimental time-resolved luminescence spectra of  $\text{UO}_2(\text{NO}_3)_2$  in nitric acid<sup>48</sup> (plain lines),  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$  in TPH solvent,  $\epsilon=2.0$  (dotted line) and  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  in a supercritical  $\text{CO}_2$ ,  $\epsilon=1.6$ <sup>70</sup> (dashed line). The spectra were rebuilt from the data of the quoted references.

The different complexes of uranium(VI) in nitric acid aqueous solution induce several luminescence components with similar monoexponential luminescent decay. The individual components are thus difficult to separate by using the time resolution of the detection. It has been assumed that in uranium(VI) sample with 0.2–4.0 M nitric acid concentration,

three species are present:  $\text{UO}_2^{2+}(\text{aq})$ ,  $\text{UO}_2(\text{NO}_3)^+(\text{aq})$  and  $\text{UO}_2(\text{NO}_3)_2(\text{aq})$ .<sup>48</sup> First, the  $\text{UO}_2^{2+}(\text{aq})$  species was measured in highly acidic conditions. Then, using the assumption of a bathochromic shift upon nitrate complexation, stepwise least square fittings were applied iteratively to a set of experimental and numerical data gathered over the nitric acid concentration range. Accordingly, the spectrum of  $\text{UO}_2(\text{NO}_3)_2$  in nitric acid was extracted by the deconvolution procedure detailed by Couston et al.<sup>53</sup> The spectral shape and characteristics compare well with the ones measured earlier in similar conditions<sup>71</sup> and in the solid state.<sup>72</sup> The picture becomes less complicated in the presence of organic extracting agent (like TBP or monoamides), when the uranyl binitrate complexes can be present as a single species, and only potentially conformers.

To the best of our knowledge, there is no information in the literature about the nature of observed transitions in the uranyl binitrate complexes. The general observation that the vibronic progression overlaps with the electronic transition can be interpreted in different ways. In the example of the emission spectrum of the  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$  complex (Fig. 5 and Fig. 6) we observe two peaks in the low energy region at 480–495 nm with different intensities. It is known that the intensity of luminescence depends on the quantum yield - the ratio of the rate of de-excitation by photons emission and the rate of de-excitation by both radiative and non-radiative processes.<sup>69</sup> For this particular case, it is difficult not only to determine the origin of the relaxation but also to predict the temporal evolution of the electronic intensity; thus both transitions could correspond to the electronic one. From another viewpoint, in most of the uranium(VI)-based complexes the absorption spectrum is a mirror image of the emission spectrum.<sup>23</sup> This phenomenon is known as the mirror image rule and is related to the Franck–Condon principle which states that electronic transitions are vertical, that is the energy changes without any geometry change. This means that the vibration levels of the excited state resemble that of the ground state. Usually, when the absorption and emission spectra are built on the same energy scale, they overlap at the electronic transition region as shown on Figure 6. Here we notice the overlay of the same two

peaks around 480 and 495 nm. Using the analogy adverted by Görller-Warland et al.<sup>23</sup> on the example of uranyl chloride complexes, the first small peak at 480 nm could be assigned to a “hot band,” while the second at 495 nm should correspond to the  $0 \rightarrow 0$  band (dashed line on Figure 6).

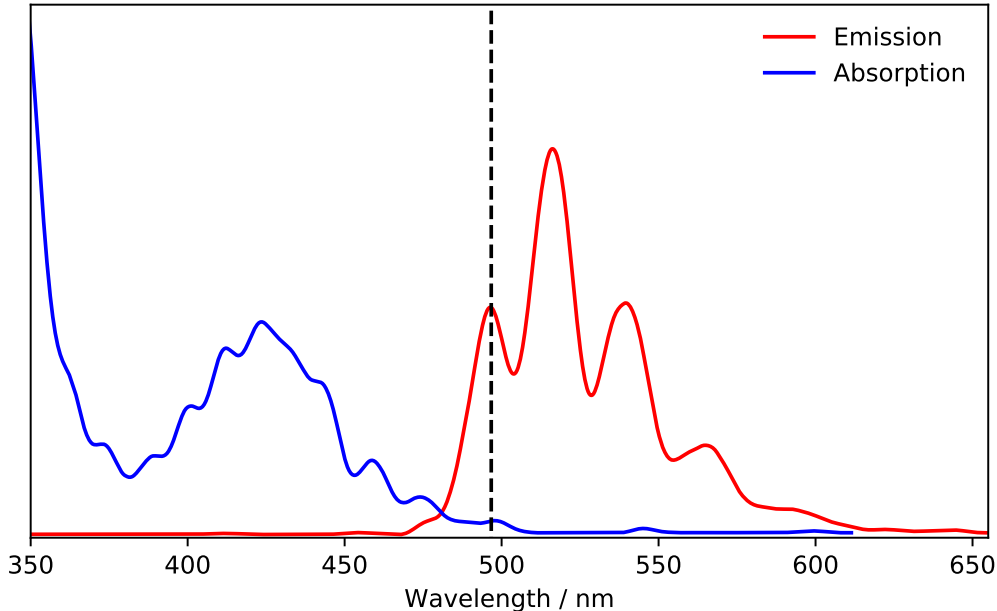


Figure 6: Superposition of the emission (TRLFS) and absorption (UV-vis) spectra of  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$  in TPH solvent of the same sample.

Another way to attribute the position of the “hot band” in  $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  is to use the band spacing value and results obtained by the *ab initio* calculations. In the luminescence spectrum, the vibronic progression starts at the  $0 \rightarrow 0$  transition with a spacing equal to the ground state uranyl stretching frequency  $\nu_s^{gs}$ . The “hot band” appears at an energy shifted by the excited state uranyl stretching frequency  $\nu_s^{es}$  above the  $0 \rightarrow 0$  transition. A multi-peaks Lorentzian fitting was applied to the experimental spectra to determine the band spacing values. The results of this fitting and the  $\nu_s^{gs}$ ,  $\nu_s^{es}$  frequencies computed by (TD)-DFT/PBE0 methods are shown in Table 5.

It has been observed that for  $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  complexes, the experimental ground and excited-state symmetrical stretching frequencies of the uranyl reproduced the theoretical

trend that the  $\nu_s^{gs}$  frequency is larger than the  $\nu_s^{es}$ . Moreover, the  $\nu_s^{gs}$  extracted from the luminescence spectra agreed within  $11 \text{ cm}^{-1}$  with Raman data for  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  in liquid.<sup>26</sup> The shifts between the ground and excited state stretching frequencies  $\Delta\nu_s$  are 65 and  $49 \text{ cm}^{-1}$  for the  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$ , respectively, while the theoretical shifts equal to  $90 \text{ cm}^{-1}$  in average. As it has been explained in previous works,<sup>24,25</sup> our theoretical methodology tends to overestimate the vibrational frequencies values; thus we can consider that the agreement between theoretical and experimental data is satisfactory. Moreover, it is difficult to estimate the degree of anharmonicity effects in experimental spectra, which might obviously decrease the band spacings in the higher energy region.

Table 5: Experimental and theoretical spectral characteristics of uranyl binitrate complexes. The peak maxima are reported in nm. Experimental  $\nu_s^{gs}$  and  $\nu_s^{es}$  values were obtained by a Lorentzian fitting procedure. The  $\nu_s^{gs}$  corresponds to the averaged band-spacing values between the vibronic transitions, the  $\nu_s^{es}$  corresponds to spacing between the  $1 \rightarrow 0$  and  $0 \rightarrow 0$  transitions.  $\nu_s^{gs}$  and  $\nu_s^{es}$  are given in  $\text{cm}^{-1}$ .

$\text{UO}_2(\text{NO}_3)_2(\text{L})_2$ L	Spectral maxima (nm)					$\nu_s^{gs}$ [ $\text{cm}^{-1}$ ]	$\nu_s^{es}$ [ $\text{cm}^{-1}$ ]
	$1 \rightarrow 0$	$0 \rightarrow 0$	$0 \rightarrow 1$	$0 \rightarrow 2$	$0 \rightarrow 3$		
Experimental							
$\text{H}_2\text{O}^{48}$	507	529	554			864	799
DEHiBA	495	516	540	566	593	844	795
Theoretical							
<i>trans</i> - $\text{H}_2\text{O}^a$	507	529	557	587	621	925	833
<i>cis</i> - $\text{H}_2\text{O}^a$	507	529	557	587	621	928	834
<i>trans</i> -DEiBA <sup>b</sup>	495	516	542	570	601	911	822
<i>cis</i> -DEiBA <sup>b</sup>	495	516	542	570	601	913	823

<sup>a, b</sup> the  $1 \rightarrow 0$  was taken from experimental  $\text{UO}_2(\text{NO}_3)_2(\text{L})_2$  (L =  $\text{H}_2\text{O}$ , DEHiBA) emission spectra to match position of theoretical peaks with experimental ones

Based on the discussions above we have tried to attribute the electronic and vibronic transitions of experimental spectra being guided by the theoretical results. The direct comparisons of our theoretical spectra with the experimental ones can be visualized on Figure 7, the spectral characteristics and attribution of bands are listed in Table 5. To simplify the discussion, we have shifted the theoretical spectra to match the experimental energy range and normalized the intensities of both sets to the maximum value. First of all, the differ-

ence between the  $\nu_s^{gs}$  and  $\nu_s^{es}$  experimental values lead us to propose that the  $1 \rightarrow 0$  band pops up at 507 and 495 nm for  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  and  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$ , respectively. Another remarkable result is that the theoretical vibronic progression intensities distributions beautifully match the experimental ones when placing them next to the proposed “hot band.” Moreover, it has been confirmed previously that the  $0 \rightarrow 0$  bands in uranium(VI)-based complexes are usually more intense compared to the “hot band” intensity at room temperature.<sup>24,65,69</sup> The nature of the bands at 495 and 480 nm in  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  and  $\text{UO}_2(\text{NO}_3)_2(\text{DEHiBA})_2$ , respectively, remains an open question. Thus we can just suggest that these bands are related to the sample reabsorption, since the luminescence intensity of the band at 480 nm changes depending on the uranium(VI) concentration. Also this band could correspond to an emission from another excited state.

One last point that was not yet discussed in details is the detection probability of the *cis*- and *trans*-conformers of uranyl binitrate complexes to confirm it from the experimental luminescence data. When we discussed the differences in the structures (Table 1) and harmonic frequencies (Table 2) of both conformers, the same as predicted luminescence spectra (Table 5), it was difficult to distinguish the more probable configuration of the  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  and  $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$ . Furthermore, the relative free energies between the two conformers (see Table S1 of ESI) are found to be very small to give an exact picture. Nevertheless, the *cis-trans* energetic difference data predicted the *cis*- and *trans*-isomers to be probable by about 30 % and 70% respectively for the uranyl binitrate complexes with water, and *trans*- $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$  complex to be 100% probable. This kind of analysis represents a static picture only, while in the experimental conditions, the systems are dynamics, with possible rapid exchanges between conformers.

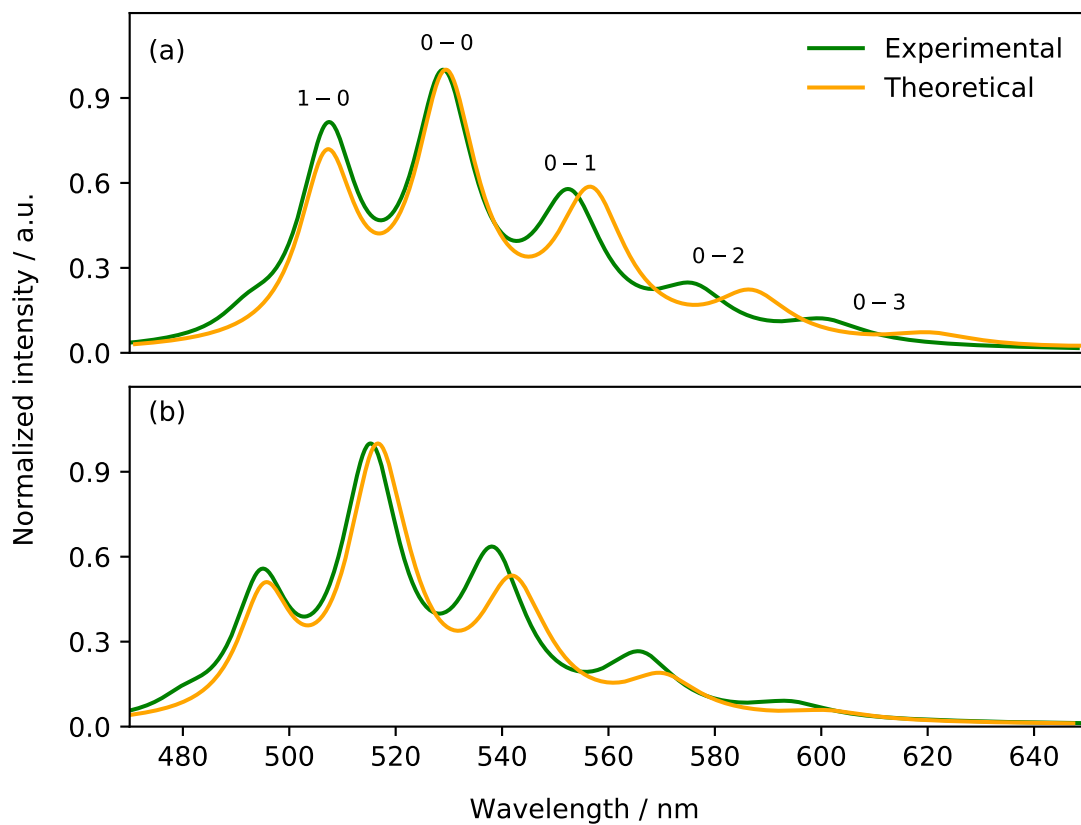


Figure 7: Comparison of experimental emission spectra (TRLFS) with theoretical spectra of (a)  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2$  and (b)  $\text{UO}_2(\text{NO}_3)_2(\text{DEiBA})_2$ .

## Conclusions

The speciation of uranyl in solution can be investigated by TRLFS to determine the species that may dominate or coexist. This requires an accurate decomposition scheme and experimental data of high quality. In the context of spent fuel reprocessing, monoamide molecules are developed to selectively extract uranium(VI) from the aqueous to the organic phase. The present work by TRLFS and *ab initio* based methodology shows that no significant change is to be expected in the electronic structure of the uranium binitrate moiety. PBE0 (TD)-DFT approach accurately captured the ground and excited state structures with minor discrepancies which can probably be attributed to the choice of the functional of the density, the basis set and the solvation model. The proposed theoretical methodology allowed to calculate the main vibronic progression of the complexes with the corresponding assignment of the electronic transitions and vibrational modes involved, showing that PBE0 (TD)-DFT is an effective tool for prediction and assignment of luminescent spectra of U(VI)-based complexes.

In this work, we have used a stepwise growth of the chemical models to assess the sensitivity to the amount of water molecules in the coordination sphere of uranyl, and by substituting the water molecules with monoamide DEiBA. Using the chemical models in a form of  $\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})$  and *cis-/trans-UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(L)<sub>2</sub>* ( $L = \text{H}_2\text{O}, \text{DEiBA}$ ) it has been confirmed that the structural and spectroscopic parameters exhibit similar and hardly distinguishable features. Structural isomers for a given stoichiometry are indeed energetically very close and have almost identical TRLFS spectra. Calculations of luminescence bands intensities were found to be in excellent agreement with experimental TRLFS spectra, giving confidence in the validity of our methodology. This approach could be emphasized for a deeper interpretation of the data from time-resolved laser-induced fluorescent spectroscopy which is often efficiently used to track changes in the first coordination sphere of uranyl unit.

## Acknowledgements

We acknowledge support by the French government through the Program "Investissement d'avenir" (LABEX CaPPA / ANR-11-LABX-0005-01 and I-SITE ULNE / ANR-16-IDEX-0004 ULNE), as well as by the Ministry of Higher Education and Research, Hauts de France council and European Regional Development Fund (ERDF) through the Contrat de Projets État-Région (CPER CLIMIBIO). Furthermore, this work was granted access to the HPC resources of [CINES/IDRIS/TGCC] under the allocation 2020–2021 [A0090801859] made by GENCI. We also acknowledge the CEA for the PhD grant attributed to H.O.



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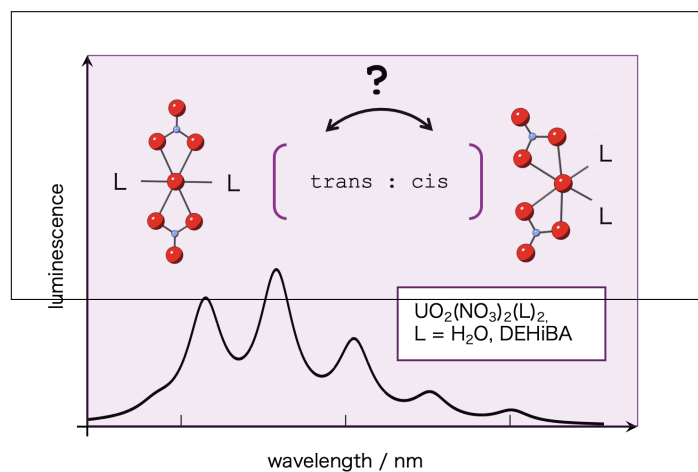
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## Graphical TOC Entry



By comparing available experimental spectra of uranyl complexes and a newly recorded one, in which the latter is in interaction with large organic ligands, with extensive *ab initio* simulations, we rationalize to which extent the inorganic and organic uranyl coordination spheres, as well as the solvent polarity, influence the spectral shapes and vibrational progressions. Relativistic DFT calculations of the luminescence spectra based on the Franck-Condon principle allow us to reproduce and assign the peak positions.