

## The Photochemical Behavior of the Uranyl Ion ( $\text{UO}_2^{2+}$ ): a Dimer Perspective and Outlook

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Dedicated to Jean-Claude Bünzli on the occasion of his 65th birthday

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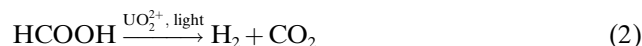
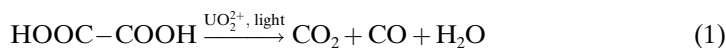
The complex formation of uranyl ( $\text{UO}_2^{2+}$ ) with oxalic acid ( $\text{HOOC-COOH}$ ) in acetone is studied by UV/VIS, absorption, luminescence, and excitation spectroscopy. Based on solid-state crystallographic data, we propose a dimer structure with  $D_{2h}$  symmetry for the complex in solution. This symmetry is vibrationally distorted to  $D_2$  by the out-of-plane equatorial-ligand vibration. From the spectroscopic point of view, this vibration induces intensity in the transitions  $\Pi_g \leftarrow \Sigma_g^+$  and one component of  $\Delta_g \leftarrow \Sigma_g^+$ . From the photochemical point of view, this vibration induces a twisting mechanism that destroys the complex. From the theoretical point of view, it is worthwhile to notice that the symmetry of the odd out-of-plane vibration is the same as the symmetry of the odd LUMO ( $f_{xyz}$ ). By vibrating accordingly to the LUMO symmetry, the complex is self-destroying by absorption of light, and the uranyl is regenerated. A small comment is devoted to a possible  $\delta-\delta$  interaction and the quintuple  $\text{U}_2$  bond distance proposed by Gagliardi and Ross [29].

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**Introduction.** – The photochemistry of actinide compounds is almost exclusively dominated by reactions involving the uranyl ion (=dioxouranium(2+);  $\text{UO}_2^{2+}$ ). This photochemical behavior of the uranyl ion is already known for two centuries. Consequently, uranyl has been extensively investigated in the 1970s and 1980s [1][2]. Many studies of the photo-oxidation of various substrates, particularly organic molecules (alcohols, oxalic and other carboxylic acids, aldehydes, *etc.*) have been summarized in books [3][4] and reviews [5–7]. Nevertheless, it is still one of the most confusing chapters of chemistry with many contradictions and unresolved problems. However, the study of the photochemistry of the uranyl ion has to be a challenge due to the presence of uranium(VI) as uranyl in our environment, like in various ores (autunite, carnotite, and torbernite). Even seawater contains  $3.3 \cdot 10^{-3}$  mg of uranium per liter.

For two centuries (since 1805), the photochemical behavior of uranyl oxalate is known. It was noticed that CO and  $\text{CO}_2$  gas bubbles evolve from an aqueous solution containing uranyl and oxalate ions ( $\text{C}_2\text{O}_4^{2-}$ ), when exposed to VIS light [3]. The yield of the decomposition of oxalic acid, induced by uranyl and UV/VIS light, is well reproducible. Therefore, this photochemical reaction was applied in chemical actinometry. In fact, uranyl oxalate was the first actinometer ever used. The produced CO concentration is related to the light intensity according to the reaction of *Eqn. 1*. Similar photochemical reactions have been observed for formic acid, acetic acid, and other monobasic and dibasic carboxylic acids (*Eqns. 2 and 3*) [3]. In all these reactions, the

uranyl ion serves, together with UV/VIS light, as a catalyst to induce the decomposition of the carboxylic acid, thereby forming CO<sub>2</sub> gas bubbles.



Although the phenomenon is well-known, the mechanism behind the photochemical reaction of oxalic acid has not yet been elucidated. *Balzani* and *Carassiti* wrote in 1970: ‘Spectrophotometric and potentiometric measurements show that various complex species (e.g., UO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>) and [UO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sup>2-</sup>]) are present in aqueous solutions containing UO<sub>2</sub><sup>2+</sup> and oxalic acid. However, the role played by these complexes in the photochemical behavior has not yet been clarified’ [4].

Recently, research on the uranyl ion gained a growing interest from a theoretical point of view due to the increase of computer power and the possibility of taking relativistic effects into account. The uranyl tetrachloro complex [UO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> has been successfully investigated by means of multiconfigurational perturbation theory (CASSCF/CASPT2) by the group of *Pierloot* [8]. This theoretical study exactly reproduced the excitation energies and the frequencies of the symmetric stretching vibration  $\nu_s$  determined in detail by *Denning et al.*, by measuring polarized absorption spectra of Cs<sub>2</sub>[UO<sub>2</sub>Cl<sub>4</sub>] single crystals at 4.2 K [9].

Studies of the uranyl oxalate system in solution have been carried out by means of NMR, UV/VIS absorption spectroscopy, uranium L<sub>III</sub>-edge EXAFS spectroscopy, and theoretical calculations [10–12]. When reproducing the solutions used by *Vallet* and co-workers for their EXAFS measurements, we noticed that the photocatalytic effect of the uranyl ion was completely overlooked [10]. Therefore, we doubt about the speciation proposed for the different test solutions. *Vallet* and co-workers assume that an aqueous solution of 0.0122M sodium oxalate and 0.0601M uranyl nitrate contains more than 99% of [UO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sup>2-</sup>, whereas 95% of the [UO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>4-</sup> complex is present in an aqueous solution containing 1.68M potassium oxalate and 0.0601M uranyl nitrate [10]. Moreover, the uranyl oxalato complexes are probably partly or even completely destroyed in these solutions by the photocatalytic effect. In his paper on the determination of the stability constants of uranyl oxalato complexes, *Havel* and co-workers [11] point to the photochemical behavior of the uranyl ion. Furthermore, he stated that the stability constant associated with the formation of a trioxalato complex has to be considered with caution because of the possible competing formation of polynuclear 2:3 and 2:5 species.

As a guideline for the type of bonding formed between the uranyl unit and oxalate ions, the crystal structures of solid uranyl oxalato complexes are a useful starting point. Crystal-structure determinations of uranyl oxalato complexes reveal different modes of coordination of the oxalato ligand. The oxalato ligand is chelated through one O-atom from each COO<sup>-</sup> group, coordinated through two O-atoms of the same COO<sup>-</sup> group or bound to a single COO<sup>-</sup> O-atom. In most of these crystal structures, the oxalato ligands are bridging different uranyl units [13–15]. These structures of solid-state complexes,

however, have to be considered with caution when applying them for the determination of the geometry of solution species.

In this paper, we present our point of view on the complex formation of the uranyl ion with oxalate ions, mainly based on spectroscopic measurements, *i.e.*, UV/VIS absorption spectroscopy, luminescence and excitation spectroscopy, as well as magnetic circular dichroism (MCD). The experiments were performed in nonaqueous solution because of the higher stability of the complexes. This is analogous to the observation of the complexes  $[\text{UO}_2\text{Cl}_4]^{2-}$  and  $[\text{UO}_2(\text{NO}_3)_3]^-$  in MeCN, whereas no significant complex formation with chloride and nitrate ions occurs in aqueous solution. In addition, we believe that the photochemical reaction is slower in nonaqueous solvents. But, we have also studied the complex formation with oxalate ions in aqueous solution. We were only able to record UV/VIS absorption spectra, since the luminescence of the uranyl ion is completely quenched, due to the photocatalytic effect, once a trace of oxalate ions is present. Indeed,  $\text{CO}_2$  and  $\text{CO}$  gas bubbles evolved from these aqueous solutions. This complete quenching of the uranyl luminescence in the presence of oxalate ions in aqueous solution has already been reported in [16].

**Results.** – The UV/VIS absorption spectra of uranyl complexes with oxalate ions in acetone exhibit spectral features which differ from the characteristic vibrational fine structure of the ‘free’ (hydrated) uranyl ion (*Fig. 1*). The uranyl-to-oxalic acid ratio was varied analytically from 1:0 to 1:6. This means that we mixed the uranyl perchlorate and oxalic acid in acetone in these ratios; however, this does not mean that we know the

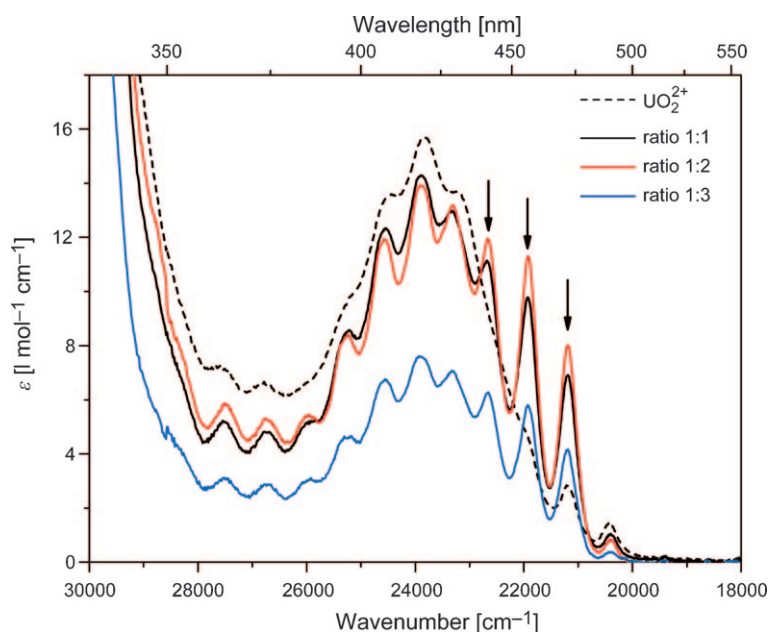


Fig. 1. UV/VIS Absorption spectra of uranyl complexes with oxalate ions in acetone at room temperature:  $[\text{UO}_2^{2+}]/[\text{oxalic acid}]$  1:0 ( $\text{UO}_2^{2+}$ ), 1:1, 1:2, and 1:3. The uranyl concentration is  $5 \cdot 10^{-3}$  M. The arrows indicate the absorption peaks belonging to the same progression.

equilibrium molar concentrations as the stability constants are not known. Upon addition of oxalate ions, an increase in intensity occurs in the first region of the spectrum (20500–23000  $\text{cm}^{-1}$ ) with respect to the spectrum of the ‘free’ uranyl ion. The energies of the involved peaks, indicated by an arrow in *Fig. 1*, are 21195, 21920, and 22675  $\text{cm}^{-1}$ . At a ratio metal/oxalic acid  $> ca.$  1:3, a yellow precipitate is formed that disturbs the spectroscopic measurement.

In analogy to the three high absorption bands in the UV/VIS absorption spectra, the same increase in intensity also appears in the excitation spectra (*Fig. 2*) with some more fine structure in the progression terms (see arrows).

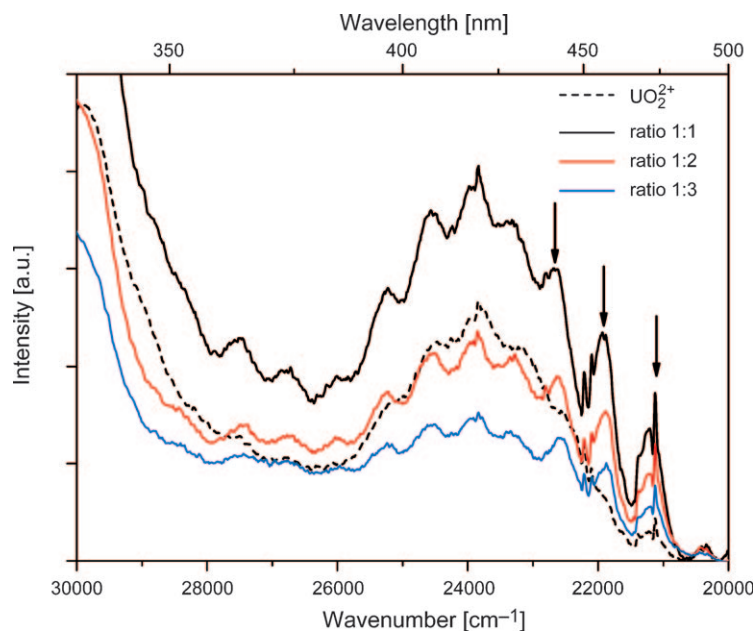


Fig. 2. Excitation spectra of uranyl complexes with oxalate ions in acetone at room temperature:  $[\text{UO}_2^{2+}]/[\text{oxalic acid}]$  1:0 ( $\text{UO}_2^{2+}$ ), 1:1, 1:2, and 1:3. The uranyl concentration is  $5 \cdot 10^{-3}$  M. The emission wavelength was set at 513.8 nm (19463  $\text{cm}^{-1}$ ). The arrows indicate the peaks belonging to the same progression.

In the emission spectra, we also observe remarkable changes in the intensity upon subsequent coordination of the uranyl ion with oxalate ions (*Fig. 3*).

We re-emphasize that neither luminescence nor excitation spectra of uranyl oxalato complexes could be measured in aqueous solution due to a complete quenching. The remarkable absorption features, *i.e.*, the enhancement in intensity at the low-energy side of the UV/VIS absorption spectra, are also visible in the spectra recorded in aqueous solution. However, they are less pronounced than in acetone. No precipitation is observed in aqueous solution.

**Discussion and Outlook.** – The below-developed hypothesis, is based on the assumption that the increase in intensity of the progression at the low-energy side of the UV/VIS absorption spectra is responsible for the decomposition of the oxalate ions. At

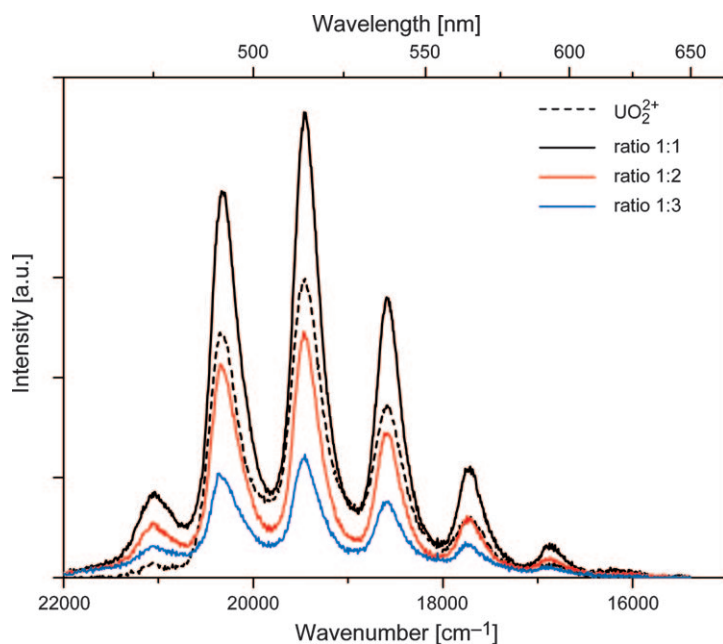


Fig. 3. Emission spectra of uranyl complexes with oxalate ions in acetone at room temperature:  $[UO_2^{2+}]/[oxalic\ acid]$  1:0 ( $UO_2^{2+}$ ), 1:1, 1:2, and 1:3. The uranyl concentration is  $5 \cdot 10^{-3}$  M. The excitation wavelength is 420.0 nm ( $23809\text{ cm}^{-1}$ ).

the moment, the most relevant question is to find the geometry of the species, which on one hand can explain the intensity enhancement in the transitions  $\Pi_g \leftarrow \Sigma_g^+$  and  $\Delta_g \leftarrow \Sigma_g^+$  [9][17][18] and which on the other hand points to a mechanism behind the photochemical reaction of oxalate ions.

From [9][17–22] and references therein, the optical properties of the uranyl oxalato complexes cannot be attributed to a  $D_{3h}$  coordination symmetry, since no intense negative A-terms are observed in the MCD spectra. Furthermore, the UV/VIS absorption spectra do not coincide with the vibronic spectrum of the uranyl tetrachloro complex  $[UO_2Cl_4]^{2-}$  either, thereby rejecting the possibility of monomeric oxalato complexes with  $D_{4h}$  symmetry. Vallet and co-workers proposed a monomeric fivefold coordination of the uranyl ion in oxalato complexes, where two oxalato ligands are bidentate and one oxalate ligand is coordinated through one single  $COO^-$  O-atom [10]. But, in case of a  $D_{5h}$  coordination symmetry,  $\Gamma_g$  states would be detected in the UV/VIS absorption spectra of uranyl oxalato complexes, as observed in the spectrum of  $[UO_2F_5]^{3-}$  ( $D_{5h}$ ) [23]. All the assignments mentioned above are only based on the formation of *monomeric species* [10].

At the moment, we tentatively propose a *dimeric structure* with  $D_{2h}$  coordination symmetry for the uranyl oxalato complexes formed in acetone. Each uranyl unit in this dimer is a pentagonal bipyramid (Fig. 4). The structure, depicted in Fig. 4, has been reported in the literature for solid uranyl oxalato complexes, where one oxalato group is 1,4-coordinated to two uranyl ions. The other oxalato ligand is bidentate to one

uranyl ion and monodentate to another. In the solid state, infinite double chains  $[\text{C}_2\text{O}_4(\text{UO}_2)\text{C}_2\text{O}_4(\text{UO}_2)\text{C}_2\text{O}_4]_n^{2n-}$  are produced in this way [15]. In solution, however, this chain could be limited to a dimeric species with a bridging oxalato ligand. Coordinated  $\text{H}_2\text{O}$  molecules instead of the monodentate carboxylato group have also been observed in crystal structures of oxalato complexes [15].

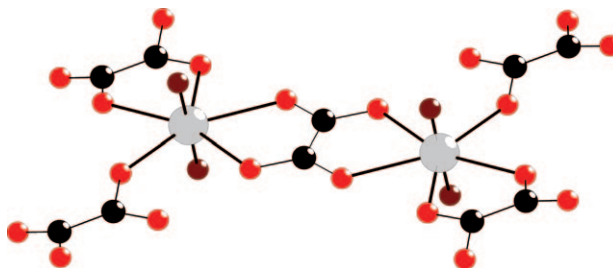


Fig. 4. Proposed dimeric structure of uranyl oxalato complexes in solution [15]

Analogous dimeric structures [24][25] have been published for solid uranyl sulfate compounds, which also, as we published in [19][26], exhibit sharp peaks in the low-energy part of their UV/VIS absorption spectra at room and low temperatures [24–26]. Recently, a crystal-structure determination revealed that the complex  $[(\text{UO}_2)_2(\text{bet})_6(\text{H}_2\text{O})_2](\text{Tf}_2\text{N})_4$  (bet = betaine =  $\text{Me}_3\text{N}^+\text{CH}_2\text{COO}^-$ ; Tf =  $\text{CF}_3\text{SO}_2$ ) is built up of two uranyl units bridged by two betaine ligands [27].

Based on [9][17][18], we believe that all the spectroscopic data from absorption, excitation, and luminescence spectra of uranyl oxalato complexes are consistent with the formation of a dimeric species with  $D_{2h}$  symmetry that is distorted to  $D_2$  by the dynamic ligand field or vibronic coupling (more details on vibronic coupling can be found in [28]) for the following reasons: 1. The transitions between the totally symmetric ground-state  $\Sigma_g^+$  (A in  $D_2$ ) and the  $B_3$  and  $B_2$  excited states, both arising from  $\Pi_g$ , are electric-dipole-allowed along the  $x$ - and  $y$ -axis, respectively. The transition to the  $B_1$  component of the  $\Delta_g$  state is electric-dipole-allowed along the  $z$ -axis. These electric-dipole transitions induce intensity between 20500 and 23000  $\text{cm}^{-1}$  in the UV/VIS absorption spectra of uranyl oxalato complexes.

2. The origins of the transitions to the  $B_3$ ,  $B_2$ , and  $B_1$  excited states cannot be distinguished. However, these transitions appear in the correct region, *i.e.*, between 20500 and 23000  $\text{cm}^{-1}$ , when compared with the assignment of the electronic transitions in the spectra of  $\text{Cs}_2[\text{UO}_2\text{Cl}_4]$  single crystals [9].

3. In the MCD spectra of uranyl oxalato complexes in acetone, only B-terms are observed, which is consistent with the absence of degenerate states in a  $D_2$  coordination symmetry. In addition, the MCD signals are very weak.

4. From [17] and therein page 1131, the only equatorial vibration that is efficiently active in the intensity process is the out-of-plane bending  $\nu_{10}$  ( $b_{1u}$  in  $D_{4h}$ ,  $a_u$  in  $D_{2h}$ , and  $a$  in  $D_2$ ). Two ligand atoms are vibrating upwards and two ligand atoms downwards out of the equatorial plane, as displayed in Fig. 5. This vibration becomes totally symmetric and transforms as  $a$  in  $D_2$  coordination symmetry with an order of magnitude of  $\pm 100 \text{ cm}^{-1}$  [9].

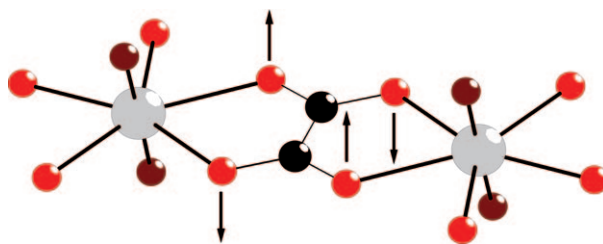


Fig. 5. Out-of-plane bending  $\nu_{10}$  (a in  $D_2$ ) inducing an intramolecular twisting mechanism

In favor of the dimer are: 1. From the photochemical point of view, the out-of-plane vibration in Fig. 5 induces an intramolecular twisting mechanism, thereby destroying the oxalate ions.

2. From a spectroscopic point of view, several quanta of the out-of-plane vibration correlate with the symmetric stretching vibration  $\nu_s$  of the uranyl ion, both vibrations transforming as the totally symmetric representation a in  $D_2$ . This out-of-plane bending induces intensity in the low-energy region of the UV/VIS absorption spectrum and could be in resonance with the symmetric stretching vibration  $\nu_s$ .

3. From the theoretical point of view, the vibration  $\nu_{10}$  has the same symmetry as the LUMO. Both transform as the tesseral harmonic  $[32 > _-]$  that describes the  $f_{xyz}$  orbital. Consequently, the otherwise parity-forbidden transition  $\delta_u (f_{xyz} \text{ component}) \leftarrow \sigma_u^+$  is allowed along the  $z$ -axis due to the simultaneous excitation of the  $b_{1u}$  vibration according to  $B_{1u} \times B_{1u} \leftarrow A_{2u}$  in  $D_{4h}$ . This becomes  $A_u \times A_u \leftarrow B_{1u}$  in  $D_{2h}$  and  $A \times A \leftarrow B_1$  in  $D_2$ .

**Conclusions.** – Based on spectroscopic measurements (absorption, excitation, and fluorescence spectra) in the UV/VIS region, we tentatively propose a structure of the uranyl oxalato complexes formed in acetone as well as a mechanism behind the photochemical reaction of oxalic acid. We suggest the existence of a dimeric compound with  $D_{2h}$  vibrationally distorted to  $D_2$  symmetry. This symmetries allow to explain how intensity is pumped in the progression between 20000 and 23000  $\text{cm}^{-1}$  and how the odd vibration of the equatorial ligands in the complex that has exactly the same symmetry as the odd LUMO  $f_{xyz}$  induces a twisting mechanism that is self-destroying for the oxalato ligand. This case is unique and could not be found in d-systems where only an odd vibration (u-type) can induce intensity and can obviously not have the same symmetry as the even d-orbitals (g-type). The case of uranyl is unique as the molecular orbitals have a quantization along the O-U-O axial axis ( $z$ ), but in that quantization, the lowest nonoccupied orbitals remain atomic ( $f_{xyz}$  and  $f_{(x^2-y^2)}$ ). The absorption of light in the UV/VIS occurs from the  $\sigma_u^+$  HOMO to the atomic  $\delta_u$  LUMO (or one of its components) that by ‘vibrating along its own symmetry’ destroys the complex and regenerates the uranyl. Unfortunately, this out-of-plane vibration is neither *Raman* nor IR active (silent vibration). Moreover, due to the limited spectral resolution that is obtained in solution, we could not confirm the presence of the vibration by absorption spectroscopy. A better resolution was obtained in the excitation spectrum (see Fig. 2). We can thus not claim definite evidence for the existence of this vibration and hope that this hypothesis can be confirmed in the future by the analyses of uranium  $\Lambda_{III}$ -edge

EXAFS spectra of uranyl oxalato complexes in acetone and by theoretical calculations on dimeric species, which so far were not performed.

From a completely other point of view, the intensity enhancement in the first progression could be due to  $\delta$ – $\delta$  interaction between two uranium atoms as proposed by theoretical calculations by *Gagliardi* and *Ross* [29]. In that case, the transition  $\delta \rightarrow \delta^*$  is allowed along  $z$  ( $x$  or  $y$  in our axis system) and could explain the intensity enhancement, following:  $\delta_u \rightarrow \delta_g$  or  $b_{1u} \rightarrow b_{2g}$  in  $D_{4h}$ ,  $a_u \rightarrow b_{1g}$  in  $D_{2h}$ , and  $a \rightarrow b_1$  in  $D_2$ . The transition is electric-dipole-allowed following  $z$  and coupled to the interatomic uranium-uranium symmetric vibration. Note that the  $f_{xyz}$  tesseral harmonic is invariant under a  $x \rightarrow y \rightarrow z$  axis rotation so that the same conclusion holds true for  $z$  replaced by  $x$  or  $y$  in the equatorial plane [30].

The U–U distance in the dimer is of the order of magnitude  $\pm 4 \text{ \AA}$  as the two U-atoms are bridged by the O-atoms of the oxalato ligand. This is obviously more than the quintuple  $U_2$  bond distance  $2.43 \text{ \AA}$  predicted in [29] but could explain a vibrational structure.

In the framework of a dimer hypothesis, we intend to revisit our results on complexation with chloride ligands published in [18][22] on the basis of crystallographic data (*e.g.*, [31] and therein footnote 8).

### Experimental Part

*Coordination of Uranyl with Oxalate*  $^{-}OOC-COO^{-}$ .  $UO_2(ClO_4)_2 \cdot x H_2O$  was mixed with oxalic acid ( $C_2H_2O_4$ ) in acetone in metal-to-oxalic acid ratios of 1:0 to 1:6, with steps of 1. The uranyl concentration was approximately  $5 \cdot 10^{-3} \text{ M}$ .

*Spectrophotometric measurements.* UV/VIS Absorption spectra were measured with *Varian-Cary-5000* spectrophotometer between 600 and 300 nm. Luminescence measurements were carried out with an *Edinburgh-Instruments-FS-900* spectrofluorimeter. The light source used was a 450 W Xe arc lamp. Emission spectra were recorded between 430 and 650 nm, whereas excitation spectra were measured between 300 and 530 nm ( $\lambda_{ex}$  420.0 nm,  $\lambda_{em}$  513.8 nm).

### REFERENCES

- [1] C. K. Jørgensen, R. Reisfeld, *J. Electrochem. Soc.* **1983**, *130*, 681.
- [2] C. K. Jørgensen, R. Reisfeld, *Struct. Bonding* **1982**, *50*, 121.
- [3] E. Rabinowitch, L. R. Belford, 'Spectroscopy and Photochemistry of Uranyl Compounds', Pergamon Press, Oxford, 1964.
- [4] V. Balzani, V. Carassiti, 'Photochemistry of Coordination Compounds', Academic Press Inc., London, 1970.
- [5] C. P. Baird, T. J. Kemp, *Prog. React. Kinet.* **1997**, *22*, 87, and ref. cit. therein.
- [6] H. Güsten, 'Gmelin Handbook of Inorganic Chemistry', 'Uranium', Suppl. Vol. A6, Springer-Verlag, Berlin–Heidelberg, 1983.
- [7] A. B. Yusov, V. P. Shilov, *Russ. Chem. Bull., Int. Ed.* **2000**, *49*, 1925.
- [8] K. Pierloot, E. van Besien, *J. Chem. Phys.* **2005**, *123*, 204309.
- [9] R. G. Denning, T. R. Snellgrove, D. R. Woodwark, *Mol. Phys.* **1976**, *32*, 419.
- [10] V. Vallet, H. Moll, U. Wahlgren, Z. Szabó, I. Grenthe, *Inorg. Chem.* **2003**, *42*, 1982.
- [11] J. Havel, *Coll. Czech. Chem. Commun.* **1969**, *34*, 3248; J. Havel, J. Soto-Guerrero, P. Lubal, *Polyhedron* **2002**, *21*, 1411.
- [12] D. Ferri, M. Iuliano, C. Manfredi, E. Vasca, T. Caruso, M. Clemente, C. Fontanella, *J. Chem. Soc., Dalton Trans.* **2000**, 3460.



- [13] Z. Szabó, A. Fischer, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2002**, 58, i56.
- [14] N. W. Alcock, *J. Chem. Soc., Dalton Trans.* **1973**, 1610; N. W. Alcock, *J. Chem. Soc., Dalton Trans.* **1973**, 1614; N. W. Alcock, *J. Chem. Soc., Dalton Trans.* **1973**, 1616.
- [15] J. Leciejewicz, N. W. Alcock, T. J. Kemp, *Struct. Bonding* **1995**, 82, 43.
- [16] T. M. McCleskey, T. M. Foreman, E. E. Hallman, C. J. Burns, N. N. Sauer, *Environ. Sci. Technol.* **2001**, 35, 547.
- [17] R. G. Denning, T. R. Snellgrove, D. R. Woodward, *Mol. Phys.* **1979**, 37, 1109.
- [18] S. De Houwer, PhD Thesis, Katholieke Universiteit Leuven, 2003.
- [19] C. Görller-Walrand, S. De Jaegere, *J. Chim. Phys.* **1972**, 69, 726.
- [20] C. Görller-Walrand, S. De Jaegere, *J. Chim. Phys.* **1973**, 70, 360.
- [21] C. Görller-Walrand, S. De Jaegere, *Spectrochim. Acta, Part A* **1972**, 28, 257.
- [22] C. Görller-Walrand, S. De Houwer, L. Fluyt, K. Binnemans, *Phys. Chem. Chem. Phys.* **2004**, 6, 3292.
- [23] C. Görller-Walrand, W. Colen, N. Q. Dao, *J. Chem. Phys.* **1982**, 76, 13.
- [24] L. Niinistö, J. Toivonen, J. Valkonen, *Acta Chem. Scand., Ser. A* **1979**, 33, 621.
- [25] A. Zalkin, H. Ruben, D. H. Templeton, *Inorg. Chem.* **1978**, 17, 3701.
- [26] M.-P. Gos, Master Thesis, Katholieke Universiteit Leuven, 1986.
- [27] P. Nockemann (Laboratorium Coordination Chemistry, K. U. Leuven, Belgium), personal communication.
- [28] C. Görller-Walrand, *Mol. Phys.* **2004**, 102, 1361.
- [29] L. Gagliardi, B. O. Ross, *Nature (London)* **2005**, 433, 848.
- [30] C. Görller-Walrand, *Mol. Phys.* **2003**, 101, 993.
- [31] H. G. Brittain, D. L. Perry, *J. Phys. Chem.* **1980**, 84, 2630.

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