Multilinear analysis of Time-Resolved Laser-Induced Fluorescence Spectra of U(VI) containing natural water samples

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Abstract. Natural waters’ uranium level monitoring is of great importance for health and environmental protection. One possible detection method is the Time-Resolved Laser-Induced Fluorescence Spectroscopy (TRLFS), which offers the possibility to distinguish different uranium species. The analytical identification of aqueous uranium species in natural water samples is of distinct importance since individual species differ significantly in sorption properties and mobility in the environment. Samples originate from former uranium mine sites and have been provided by Wismut GmbH, Germany. They have been characterized by total elemental concentrations and TRLFS spectra. Uranium in the samples is supposed to be in form of uranyl(VI) complexes mostly with carbonate (CO$_3^{2-}$) and bicarbonate (HCO$_3^{-}$) and to lesser extend with sulphate (SO$_4^{2-}$), arsenate (AsO$_4^{3-}$), hydroxo (OH$^{-}$), nitrate (NO$_3^{-}$) and other ligands. Presence of alkaline earth metal dications (M = Ca$^{2+}$, Mg$^{2+}$, Sr$^{2+}$) will cause most of uranyl to prefer ternary complex species, e.g. M$_n$(UO$_2$)(CO$_3$)$_{3-4n}$ ($n \in \{1; 2\}$). From species quenching the luminescence, Cl$^{-}$ and Fe$^{2+}$ should be mentioned. Measurement has been done under cryogenic conditions to increase the luminescence signal. Data analysis has been based on Singular Value Decomposition and monoexponential fit of corresponding loadings (for separate TRLFS spectra, the “Factor analysis of Time Series” (FATS) method) and Parallel Factor Analysis (PARAFAC, all data analysed simultaneously). From individual component spectra, excitation energies $T_{00}$, uranyl symmetric mode vibrational frequencies $\omega_{0s}$ and excitation driven U-O$_{yl}$ bond elongation $\Delta R$ have been determined and compared with quasirelativistic (TD)DFT/B3LYP theoretical predictions to cross-check experimental data interpretation.

1 Motivation

This contribution presents a first step in a longer run of both experimental and theoretical chemical (quantum chemistry and molecular dynamics) studies of uranium speciation in natural water samples and subsequent studies of possible chemical/physical remediation meeting criteria for health and environment protection.

A preliminary analysis of six samples TRLFS [1-6] spectra (S1-S5,S9) by FATS method [7] and of seven samples (the previously mentioned and S10) together by PARAFAC [8-12] will be presented.

The speciation, i.e. the information on how is given total analytical concentration of uranium partitioned into different chemical forms (coexisting in the same sample in chemical equilibrium), is of environmental importance because different chemical species will have different physical, chemical and biological properties such as mobility, toxicity and will require different measures for remediation. For example, studied samples are aerobic ($E_{H}$ range from 130-450 mV), in pH range 5.5-9.3 and are supposed (based on analysis presented further) to consist dominantly of the neutral ternary complex Ca$_2$UO$_2$(CO$_3$)$_5^{2-}$, the two-fold negatively charged Ca$_2$UO$_2$(CO$_3$)$_7^{2-}$; Mg$_2$UO$_2$(CO$_3$)$_7^{2-}$ (and to a lesser extent UO$_2$(CO$_3$)$_7^{2-}$, UO$_2$(SO$_4$)$_2^{2-}$) and the highly negatively charged UO$_2$(CO$_3$)$_{10}^{3-}$. One of the remediation possibilities for uranium contaminated waters refers to the interaction of the water with anion-exchange resins, but the stable and by concentration dominating Ca$_2$UO$_2$(CO$_3$)$_5^{2-}$
complex poses a problem, due to its electrical neutrality (and chemical equilibration changed by resin might not be fast enough in given experimental setup). But not all physical-chemical properties should be reduced to electric charge only, of course.

2 Theoretical background

2.1 Uranyl compounds spectra and optimal spectroscopic parameter choice

The aqueous uranyl complex compound luminescence theoretical background is briefly discussed in [1]. To shortcut the basis of it into two sentences – the luminescence corresponds to (by a good working hypothesis) a single electronic transition on frontier molecular orbitals of central uranyl group (chromophore), and is resolved by a symmetric stretching vibrational mode of UO$_2^{2+}$ group. The ligands coordinated to uranyl group can be seen as merely changing the excitation energy $T_{00}$ of the transition, the vibrational frequencies $\omega_{g}, \omega_{e}$ and $\Delta R$ parameter mentioned later in text.

For a practical reasons, it should be stressed that while standard literature information on luminescence spectra (of individual chemical species in aqueous samples) consists of mere three to six luminescence band positions in nm (given usually with 1 nm precision), this might be a bit unfortunate format.

The reason is that since uranyl compounds luminescence spectra are very similar to each other, there is a need for a very careful spectroscopic parameter set choice. It is easy to observe that band positions, however in-energy-proportional unit (e.g. cm$^{-1}$), form by (two) parts linear function of their ordinary number (please see Fig. 1,2 and Fig. 5 in [1])$^b$. That is, both cold- and hot-bands are equidistant in cm$^{-1}$ scale. The respective slopes in linear dependence on ordinary peak number $n$,

$$ \frac{1}{\lambda_{a,n}} = v_{a,n} = T_{00,n} - \omega_{a,n}, $$

or “peak maxima spread”s correspond to “effective symmetric stretching mode vibration frequency of uranyl, UO$_2^{2+}$ (central group)” for electronic ground (cold-bands, $\omega_{g}$ [cm$^{-1}$]) and luminescence-active excited state (hot-bands, $\omega_{e}$ [cm$^{-1}$]). The most energetic (highest in cm$^{-1}$) cold-band, ($0'\rightarrow0$), peak energy complete the three parameter set ($T_{00}$ [cm$^{-1}$], $\omega_{g}, \omega_{e}$) describing all peak positions (no matter if they are three as well, or up to seven). While the linearity (or equidistances) of peak cm$^{-1}$ position is usually very strong (uranyl group anharmonicity $\omega_{a,n}$ is below 15 cm$^{-1}$ [19-23] as compared to $\omega_{g} = 870$ cm$^{-1}$ [1,23-25] for pentaqua complex in water under ambient conditions) it is still better to obtain $T_{00}$ as an intercept in linear regression of peak cm$^{-1}$ positions instead of just $0'\rightarrow0$ peak position only. But storing seven peak positions seems to be rather redundant.

On the other side, the luminescence spectra shouldn’t be reduced to band position information only – the way the signal is partitioned between different peaks (i.e. ratio of peak heights / areas under the peaks) provides important independent information. And since all spectroscopic parameters of individual uranyl chemical species coexisting in the same aqueous sample usually differ by quantity on an edge of experimental uncertainty (or even below) every piece of non-redundant spectral information matters greatly. Peak ratios information can be characterized by a property with a direct quantum chemical meaning (and therefore accessible by theoretical modelling) – the „excitational elongation” $\Delta R_{pm} = R_{ex} - R_{gs}$, meaning an absolute value of difference between U-Oyl equilibrium bond length in electronic excited state ($R_{ex}$) and in electronic ground state ($R_{gs}$, for further information, please see [1], the one-parameter fit with linear harmonic oscillator Franck-Condon factors for pentaqua uranyl is given in Fig. 6 [1]).

Another independent information might be provided by individual peak FWHMs and their shapes (possible asymmetry or deviation from gaussian/voigt shape), but since this information is much more measurement-setup-dependent (e.g. the aperture slit widening will cause peak widening) and much less easy to interpret, it makes less sense to collect it.

For consistency check it is also important that certain independent spectroscopical measurements (different from TRLFS) can be used to determine the above mentioned parameters – UV-VIS ($T_{00}$ and $\omega_{g,d}$ spectrophotometric measurements are possible even for sub miliolm to micromolar total uranium concentration range when light absorbance is measured in a very long capillary (as is practiced at Helmholtz-Zentrum Dresden-Rossendorf (HZDR) [27]) and Raman ($\omega_{gs}$), Excited state EXAFS ($\Delta R$ – from $R_{ex}$ if $R_{gs}$ is measured by normal EXAFS). The IR spectroscopy would provide information on anti-symmetric stretching mode of the uranyl central group$^c$ (IR is possible only under special circumstances for aqueous samples, of course).

$^a$ $\omega_{g}$ corresponds to the distance between peaks (assigned to the same initial and same final (excited) electronic state, but different vibrational substates of the electronic states in question). The value fitted from absorption spectrum (e.g. $\omega_{g} = 708$ cm$^{-1}$ for [UO$_2$(H$_2$O)$_3$]$^{2+}$ from [26]), however, might be different from the value determined through TRLFS (or fluorimetric) hot-band maxima fit since the initial state in luminescence might be different from the final state active in UV-VIS absorption spectrum.

$^b$ For a bare UO$_2^{2+}$ in vacuum the symmetric and anti-symmetric vibrational mode frequencies have fixed ratio (for derivation, see [28] (just change $^{54}$Ca $\rightarrow ^{238}$U)).
Spectroscopic property derived from temporal domain is the luminescence lifetime, \( \tau_n \) [ms] (under cryogenic conditions is in the ns range, unlike the \( \mu s \) range corresponding to the ambient conditions). Each species is characterized by a single \( \tau_n \) value \((m\) is the index of chemical species) parametrizing the simplest monoexponential luminescence decay model. However, the \( \tau_n \) value even for a fixed species may vary from sample to sample because of different concentrations of quenchers (Cl \([13]\), Fe\(^{2+}\), Mn\(^{2+}\) \([14]\) and organic compounds \([2,15-17]\)) and/or different major species chemical composition (see eq. (21) and (22) in [1]). This is addressed as “matrix effect” and can, to some extend, affect spectroscopic parameters derived from (emission) wave-length/wave-number domain \((T_{00}, \omega_{00}, \omega_{k0}, \Delta R, \mathrm{FWHM})\) as well. The luminescence life-times are also dependent on temperature (approximately by an Arrhenius Law for \(k_q\) parameters in eq. (22) of [1]) and matter phase (different in amorphous ice and liquid water even for the same temperature).

Interestingly, measurable changes in \(T_{00}\) and \(\omega_{00}\) of the same individual chemical compounds (UO\(_2^{2+}\), UO\(_2\mathrm{SO}_4\), UO\(_2(\mathrm{SO}_4)_2^{2-}\) and UO\(_2(\mathrm{SO}_4)_3^{4-}\)) have been detected between ambient and cryogenic conditions for uranyl – sulfate system (which has been measured under both conditions in one experimental campaign by author recently (the results will be published in near future) at HZDR). This phenomenon has been well known to other experimentalists at HZDR as well \([29]\). Unfortunately, such a comparison, is not possible for uranyl – carbonate system since uranyl carbonates yield insufficient luminescence under ambient conditions. However, some of the experience learned on the uranyl – sulfate system “ambient vs. cryo” comparison will help to answer questions such as “Is the speciation (un)changed in the process of cryogenic cooling of the sample?”. The general hope is that change is either small or predictable (and therefore, by thermodynamics based calculation correctable) and I will address this topic in my future contributions.

### 2.2 Multilinear experimental data analysis methods used – FATS and PARAFAC

#### 2.2.1 Problem formulation

Since uranium total concentration in all studied samples is well below 0.003 mol.dm\(^{-3}\) (more concentrated solutions may exhibit self-absorption and luminescence signal might not be linear with respect to individual component concentrations), laser pulse energy has been around 1000 \(\mu\)J only and MCP chosen so measurement has been done inside the linear part of dynamic range of ICCD detector, we can write measured luminescence signal in \(i\)-th spectrum, \(Y(\lambda)\) as a linear combination of (yet unknown) TRLFS spectra from individual chemical species,

\[
Y(\lambda) = \sum_{n=1}^{m} C_{in} Z_n(\lambda) + n(\lambda),
\]

where \(\lambda\) is wavelength, \(C_{in}\) luminescence amount in \(i\)-th spectrum corresponding to \(m\)-th species (individual component) and \(Z_n\) spectrum of the individual chemical species \((\mathrm{e.g. } \text{UO}_2^{2+}, \text{UO}_2\mathrm{SO}_4, \text{UO}_2\mathrm{CO}_3, \text{Ca}_2\text{UO}_2(\mathrm{CO}_3)_3^{6-}, \text{Ca}_2\text{UO}_3(\mathrm{CO}_3)_2^{2-}, \text{Mg}_2\text{UO}_2(\mathrm{CO}_3)_2^{2-}, ...\), \(m\) is a positive integer corresponding to some of the above written species). The total number of distinguishable components is denoted as \(b\), \(n_i(\lambda)\) is the noise function. The spectrum index \(i\) can either represent given \(i\)-th delay \(t_i\) between laser excitation of a sample and ICCD camera luminescence signal collection (case of kinetic/time series \((\mathrm{TS})\) as in FATS) or given \(i\)-th sample (when delay is kept constant for all samples), or in the most robust procedure, there can be mapping between index \(i\) values and doubles \((t, k), k\) where \(t\) represents delay and \(k\) sample number (all kinetic series analyzed together).

The most general multilinear fitting procedure based on Singular Value Decomposition (SVD) \([30-36,43,5,50,51]\) can be formulated as follows:

- let us assume that from SVD decomposition of measurement data matrix \(Y\) (spectral index \(i \in \{1, 2, ...\}, \) wave-length index \(f \in \{1, 2, ..., N\}\))

\[
Y_i = \sum_j U_{ij} W_{ij} V_{ij},
\]

or in matrix form

\[
Y = UVV^T,
\]

we take first \(f\) components \((j \in \{1, 2, ..., f\})\) as representing signal and filter out the remaining components \((j > f)\).

Matrix \(U\) in (5) has orthonormal columns (and same dimensions as the original data matrix \(Y\), the columns of \(U\) are called “subspectra”, the first \(f\) of them represent orthonormal basis of subspace of \(R^N\) corresponding to signal spectra), matrix \(W\) is diagonal positive semi-definite with diagonal elements (“singular values”) sorted from the greatest to the smallest and \(V\) columns are called “loadings”, they form an orthonormal set and \(j\)-th loading elements \(V_{ij}\) represent relative amount of \(j\)-th subspectrum in \(i\)-th original spectrum. Again we can think about columns of \(V\) (loadings) as basis vectors (in \(R^N\), space of different concentration/amount profiles of individual chemical species). Filtering out noise-like small components mentioned in previous paragraph means that in later derivation only first \(f\) columns are considered for matrices \(U\) and \(V\) and that only first \(fxf\) diagonal block of \(W\) is considered as well.
Setting (5) equal to matrix variant of (3), which reads

\[ Y = Z C^T + E, \tag{6} \]

and using Ansatz

\[ Z = U R^T, \tag{7} \]

will lead to matrix equation

\[ V = CRW^{-1}, \tag{8} \]

entering fitting procedure described in detail later. The \( f \times f \) square matrix \( R \) has yet unknown elements (which will be retrieved by the fit of (8)) and represent transition matrix between orthonormal basis of subspectra and nonorthogonal set of (yet unknown) individual component spectra.

In general, we can consider gaussian likelihood functions \([37-42] \) for loadings \( V_{ij} \) (assumed to be statistically independent and random gaussian distributed around modelled average) variables (8), leading to problem of minimization of the objective function

\[ \chi^2_{\text{MLM}}(R, \beta, \gamma) = \sum_{i,j} \left( \frac{V_{ij} - C_{\text{model}}^{(i,j)}(\beta) R_{ij}}{\sigma_{ij}(\gamma)} \right)^2 + \sum_{i,j} \ln(\sigma_{ij}(\gamma)) \tag{9} \]

where summation is over \( i \in \{1,2,\ldots,s\} \) and \( j \in \{1,2,\ldots,f\} \), \( \sigma_{ij}^2 \) stands for variance of \( V_{ij} \) and \( \gamma \) for a set of parameters of dependence \( \sigma^{ij} \) on \( V_{ij} \), for Poisson-like distribution model, we can consider

\[ \sigma_{ij}^2(\gamma^{ij}) = \gamma^{ij} \cdot \text{mean}[Y_{ij}], \tag{10} \]

and \( C_{\text{model}}^{(i,j)} \) stands for model of luminescence amount „profile“ in studied spectra.

2.2.2 SVD-based methods and models

Three different cases should be considered:

1) FATS (Factor Analysis of Time Series, \([3,5,7,30,33]\) analysis (The \( s \) spectra represent one TRLFS kinetic series measurement of one separate sample, to each \( i \) correspond given delay \( t_i \), then \( C_{\text{model}}^{(i,j)} \) corresponds to the model of luminescence decay and for the most simple one, monoexponential, the parameters \( \beta \) are labeled \( \tau_m \) and correspond to

\[ C_{\text{model}}^{(i,j)} = \Omega_m \exp(-\tau_m / t_i), \tag{11} \]

where \( \Omega_m \) is a prefactor corresponding to non-zero width of ICCD detector integration window (\( \Delta t \), integration time). For single FATS analysis, \( \Omega_m(12) \) can be omitted.

\[ \Omega_m = \tau_m \left( 1 - \exp\left( -\tau_m / t_i \right) \right). \tag{12} \]

2) FACSC (Factor analysis connected to speciation computation, \([5,7,43,50,51]\) – in this case the \( s \) spectra correspond to \( s \) different samples measured within one fixed delay and \( C_{\text{model}}^{(i,j)} \) represent speciation model (i.e. (implicit) formula for \( m \)-th species molar concentration in \( i \)-th sample (\( i \) can be linked to \( i \)-th total ligand concentration \( c_{L,i} \) or similar variable)). The parameters in this model can be, e.g., speciation/chemical equilibrium constants characterizing stability of individual components.

\[ C_{\text{model}}^{(i,j)} = C_{\text{speciation}}^{(i,j)}(\beta_{m,i}^{\text{spec}}; c_{L,i}), \tag{13} \]

3) FATSCSC (Robust method extracting simultaneously information from temporal and concentrational domains, i.e. taking all kinetic series from all samples together, \([5,7,43]\)). This method is more general and theoretically more powerful than PARAFAC as it allows for both „matrix effect“ incorporation via having whole matrix of time-time parameters \( \tau_{m,k} \), where \( m \) stands for species and \( k \) for sample. Index \( i \) here corresponds to doubles (\( t_i, k \)). Expression for modelled luminescence amount is product of (11) and (13). The factor \( \Omega_m (12) \), unlike for FATS, shouldn’t be omitted here (as it depends on life-time \( \tau_{m,k} \) which change with \( k \) and therefore with \( i \)).

\[ C_{\text{model}}^{(i,j)} = C_{\text{speciation}}^{(i,j)}(\beta_{m,i}^{\text{spec}}; c_{L,i}) \cdot \Omega_m \exp\left( -\tau_{m,k} / t_i \right). \tag{14} \]

2.2.3 \( \chi^2 \) minimization procedure \([3,7]\)

The objective function \( \chi^2_{\text{MLM}} \) can be minimized with constrains when necessary (e.g. in case of multicomponent analysis of noisy spectra), the constrains can be put on \([3,50]\)

i) Individual component spectra (usual constrain should be positivity evaluated in small set of spectral points – this leads to linear inequality conditions on rows of variable matrix \( R \))

ii) C-model parameters (usual constrain should be for life-times \( \tau_m \), or speciation constants \( \beta_m \) to be positive or from given interval).

iii) Variance model parameters \( \gamma \) (positivity)
2.2.2 SVD

amount distribution model, we can consider parameters of dependence where sum spectra.

non-orthogonal set of (yet unknown) individual components entering fitting procedure described in detail later. The multicomponent constrains when necessary (e.g. in case of the species would be analyzed and least-square fitting of series of equations (for different $k$ and $m$) would be done (based on assumption that molar luminescence for the same species $m$ is independent on solution index $k$), but author has rather negative experience with such a fit, except $s >> b$ [3,5].

b) FACSC and FATSCSC: norm of $Z$ columns corresponds to molar luminescence directly. These methods provide direct access to molar concentrations of chemical species in question.

The choice of norm is discussed in 2.2 section of [1]. The raw spectra $Z_m(\lambda)$ (or $Z_m(\nu)$ when considering the wave-number, $\nu$, scale cm$^{-1}$) are divided by their norms to provide normalized individual component spectra $Z_m(\nu)^6$. Their further processing will be discussed in later section 2.2.6.

The data preprocessing preceding the SVD and question of factor dimension, $f$, choice will be briefly addressed inside the experimental data analysis section.

2.2.4 Individual component spectra normalization

Pre-last note on the three (1), 2), 3)) SVD-based methods should be made on normalization of individual component spectra obtained from $R$ matrix elements (7).

a) FATS and PARAFAC: norm of $Z$ columns ($Z_m(\lambda)$, $m$ fixed) corresponds to „luminescence amount” emitted by $m$-th component and will be denoted $\xi_m$ (in case prefactor $\Omega_m$ is considered in the model (11), $\xi_m$ has dimension s$^{-1}$ (counts per second)). The $\xi_m$ is a product of molar concentration $C_{k,m}$ [mol·dm$^{-3}$] and „molar luminescence” $\mu_m$ [s$^{-1}$·mol$^{-1}·$dm$^3$] of a given species,

$$\xi_m = \mu_m \cdot C_{k,m} \cdot$$  

(16)

It is not possible to conclude the two factors on left side of (16) separately. It might be possible if $s > b$ samples with the same $b$ species would be analyzed and least-square fitting of series of (16) equations (for different $k$ and $m$) would be done (based on assumption that molar luminescence for the same species $m$ is independent on solution index $k$), but author has rather negative experience with such a fit, except $s >> b$ [3,5].

And that some additional information is known, here it could be a total uranium concentration. Then,

$$c_k^{(U)} = \sum_m \xi_m \cdot \varphi_m$$  

(17)

for $k \in \{1, 2, \ldots, s\}$ and that some additional information is known, here it could be a total uranium concentration. Then,

$$c_k^{(U)} = \sum_m \xi_m \cdot \varphi_m$$  

for $k \in \{1, 2, \ldots, s\}$ for $s > b$ is, in principle, ready for $\Sigma$ (LHS-RHS)$^2$ fit with variables $\mu_m$ to be determined (and subsequent use in (16) to determine $C_{k,m}$ from $\xi_m$).

$\varphi_m$ (and $\mu_m$) contains device-dependent prefactor (independent on $m$ and $k$) and only their ratios are comparable across literature.

The primes are later dropped and „normalized” is omitted in naming as long as it is not important in particular.

The terms 3-way data or 3-mode data is also widely used in chemometrics. The PARAFAC method can be formulated also for $M$-way data when $M > 3$. 

5 And that some additional information is known, here it could be a total uranium concentration. Then,
In contrast to SVD-based methods listed in 2.2.2, PARAFAC need neither model of luminescence decay nor speciation model as an input. It is widely known and well utilized method available in several different software implementations and could be therefore used almost as a black-box. This makes it method of the first choice for several preliminary data analysis.

However, aside of the „matrix effect” neglection drawback discussed already in 2.2.2 (point 3)), there is another one – PARAFAC, in its original formulation, needs kinetic series of all samples to be measured with exactly the same temporal point choice (even if some samples exhibit only short-lived luminescence and some long-lived only). This is not case of FATSCSC. For a deeper analysis of complicated systems, PARAFAC results should be taken with caution and rather as second to FATSCSC or FATS results.

2.2.6 Individual component spectra fitting and further analysis

The (normalized) individual component spectra has been fitted to linear combination of seven gaussian peaks (indexed by index n, which can be interpreted as difference between vibrational quantum numbers of \( p' \rightarrow p, n = p - p' \) in the simplest model either \( p' = 0 \) or \( p = 0 \) and \( n \geq 0 \)) correspond to cold bands and \( n < 0 \) to hot bands),

\[
Z'_n(v) = \sum_{n=-N_k}^{N_k} c_{n,m}^2 \exp \left( -\frac{(v-v_{n,m})^2}{2\sigma_{n,m}^2} \right)
\]  \hspace{1cm} (19)

where \( v = 1/\lambda \) (connecting \( Z'_n(v) \) and \( Z'_{in} \) notation) is wave-number, summation limits are \(-N_k\) (\( N_k \) being number of cold bands) and \( N_k \) (number of cold bands), \( c_{n,m}^2, v_{n,m} \) and \( \sigma_{n,m} \) are \( n \)-th peak height, maximum and variance parameter respectively. Gaussian fits has been done via routine in Wolfram Mathematica [100].

Subsequently, peak maxima are correlated with their number \( n \) according to formulae

\[
v_{n,m} = T_{0,m} - \omega_{gs,m} \cdot n,
\]  \hspace{1cm} (20)

\[
v_{n,m} = T_{0,m} - \omega_{es,m} \cdot n.
\]  \hspace{1cm} (21)

Area under \( n \)-th peak according to (19)

\[
S(n) = \sqrt{2\pi} \sigma_{n,m} c_{n,m}^2 \]

could be used to determine \( \Delta \omega_m \) through fitting to linear harmonic oscillator Franck-Condon factor [52-55] ratio as suggested in [1] (page 5).

For single mode linear harmonic oscillator Franck-Condon factor explicit formula (23) from [56] has been used. In following formula (23) in this study, simplified version for vibrational quantum number \( v = 0 \) has been used (with \( v' \) any natural number), i.e.

\[
2^n n! \cdot \left| \{0;\omega,R\mid n,\omega',R'\} \right|^2 = \sum_{c=0}^{\left[ \frac{n}{2} \right]} \binom{n}{c} \frac{4\omega}{\omega + \omega'} (2k - 1)!! H_{n-2k} \left(-\Omega \omega' \cdot \frac{d}{\omega} \right)^2 \]

with

\[
\Omega = \frac{\omega + \omega'}{\omega' \omega} \]

(24)

where \( \left| \{0;\omega,R\mid n,\omega',R'\} \right|^2 \) is the Franck-Condon factor \((\Delta R = |R-R'|, \omega \) and \( R \) are shown to stress that bra and ket vectors from this expression are not dual to each other except for \( R=R' \) and \( \omega=\omega' \) case). For setting \( \alpha = \omega_k, \alpha' = \omega_k \) (or in reverse order for hot bands) in (23) [56], the variable \( d = C \cdot \Delta R \), where

\[
C^2 = \frac{\mu m_c}{\hbar}
\]  \hspace{1cm} (25)

where \( c \) is speed of light in vacuum, \( m_c \) atomic mass unit (Dalton) and \( \mu \) reduced mass of vibrational mode in question (here the symmetric stretching mode of uranyl group, i.e., \( \mu = m(U^{16}O) \) for the most common isotopologue \( 238U^{16}O_2^{2+} \)).

2.2.7 Two or one hot band? Interpretation questions

Since the differences between wgs and wes are even smaller than the \( \sim 160 \) cm\(^{-1}\) for \([UO_2(H_2O)_5]^{2+} \) [1] (for \(M=UO_2(CO_3)_{2n-4} \) (\( M = Ca, Mg \)), the difference \( \Delta \omega \) can be less than 50 cm\(^{-1}\)). It is hard to determine the crossing point of the two linear branches on peak maximum (peak number) curve and therefore decide whether studied luminescence spectra exhibit one hot band (and \( T_{000} \approx 20 000 \) cm\(^{-1}\)) or two hot bands (and \( T_{000} \approx 20 800 \) cm\(^{-1}\)) differ by one vibrational quantum \( \omega_k \sim \omega_k \approx 800 \) cm\(^{-1}\)). The impact to goodness of fit according to Franck-Condon factor formula (23) is greater and the two hot bands model have been found as better consistent with experimental data.

For comparison, the uranyl – sulfate system TRLFS spectra measured under ambient conditions exhibits one hot-band only [6]. Why would cryogenic conditions lead to greater number of hot bands (and much greater portion of luminescence emitted in the hot band peaks)? The possible answer might be that deexcitation in solid phase sample doesn’t enter \( \text{thex}^{*k} \) [62] stage as in liquid case and vibrationally excited substrates of electronic excited state are therefore stabilized. To assure both two hot band interpretation and theoretical explanation of its origin, series of TRLFS measurements on uranyl – sulfate

\footnote{This formula can be further generalized for the case of general 3N-5 or 3N-6 mode harmonic oscillator systems \([57,58] \) under the Duschinsky mixing effect \([59-61] \) (\( N \) is number of atoms in studied molecule).}

\footnote{Thermally Equilibrated Excited (electronic) State.}
system in both aqueous solutions and ice under several different temperatures should be done.

2.2.8 Identification of given chemical species – individual component assignment problem

Neither FATS nor PARAFAC could provide us with definite answer on chemical composition of samples in question alone. After the data analysis, we are left with a list with rows \( \xi_n, \zeta_n, \theta_{00, n}, \theta_{01, n}, \ldots \) for \( m \in \{1, 2, \ldots, f\} \). The interpretation to which chemical species \( m = 1, m = 2, \ldots, m = f \) components correspond is yet to be done. There are several possibilities for the above mentioned assignment:

a) Literature search for experimental spectra
b) Experimental speciation study (cryo-TRLFS measurement on series of artificial samples (solutions made from pure chemicals as \( \text{UO}_2, \text{Na}_2\text{CO}_3, \text{Na}_2\text{SO}_4, \text{CaSO}_4, \ldots \))

c) Quantum-chemical modelling (self-made or literature search).

d) By comparison of PARAFAC obtained luminescence-speciation and geochemical modelling (provided, e.g. by ThreeQ-methodology based on existing thermodynamic properties database).

3 Experiments

3.1 Sample characterization

Samples originated from a flooded uranium mine prior (S1) and after water treatment (S2) and from seepage water of uranium processing tailings management facilities (TMF’s; S3 – S5, S9).

Samples S5 and S4 have been created by hydrochloric acidification of sample S3 to pH = 6 and 5.5, respectively to investigate acidification driven speciation change.

Table 1 gives total elemental concentrations in mg/l, \( pH \) and \( E_h \) in mV, sample number is written in the first row. S(VI) stands for sulfate \( \text{SO}_4^{2-} \), C(IV) for hydrogenocarbonates (bicarbonates) \( \text{HCO}_3^- \) and carbonates \( \text{CO}_3^{2-} \), except for S9 almost all C(IV) is in the form of \( \text{HCO}_3^- \), N(V) for \( \text{NO}_3^- \).

Table 1: Total elemental conc. (mg/l, adopted from [66])

<table>
<thead>
<tr>
<th>E</th>
<th>S</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>121</td>
<td>122</td>
<td>1350</td>
<td>1550</td>
<td>1580</td>
<td>2520</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>12.8</td>
<td>12.8</td>
<td>27.4</td>
<td></td>
<td></td>
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<td>Mg</td>
<td>104</td>
<td>100</td>
<td>301</td>
<td>333</td>
<td>340</td>
<td>61.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>158</td>
<td>191</td>
<td>292</td>
<td>296</td>
<td>302</td>
<td>86.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>5.09</td>
<td>0.18</td>
<td>0.28</td>
<td>0.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>2.17</td>
<td>1.4</td>
<td>0.482</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>1.68</td>
<td>0.02</td>
<td>3.1</td>
<td>3.38</td>
<td>3.53</td>
<td>10.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>54.3</td>
<td>452</td>
<td>496</td>
<td>908</td>
<td>815</td>
<td>1170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(VI)</td>
<td>576</td>
<td>546</td>
<td>3620</td>
<td>4030</td>
<td>4100</td>
<td>3150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(IV)</td>
<td>574</td>
<td>14</td>
<td>657</td>
<td>113</td>
<td>300</td>
<td>2244</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(V)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>3.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.1</td>
<td>7.4</td>
<td>7.3</td>
<td>5.5</td>
<td>6</td>
<td>9.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E_h</td>
<td>130</td>
<td>450</td>
<td>310</td>
<td>310</td>
<td>310</td>
<td>400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 Measurement

The measurements have been done by HZDR collective [66]. Briefly, samples have been cooled by liquid nitrogen into solid-ice-blocks inside plastic cuvette and then placed into cryostat set to (-120±2)°C (Cool gas system TG-KKK produced by KGW). After 15 minutes for temperature equilibration, Time-Resolved Laser-Induced Fluorescence Spectra (TRLFS) has been recorded with pulse energy 1 mJ, excitation wave-length 266 nm and pulse duration 2 ns. Emission wave-length measurement range has been set to 450-650 nm Milinile Laser System (produced by Continuum) with Spectrograph and ICCD-camera iHR 550 (HORIBA Jobin) has been used. For the spectra recording, software LabSpec has been used [65].

Emission wave-length sampling corresponded to average step of \( \Delta \lambda \) = 0.463 nm (i.e. \( d\nu = 18.5 \text{ cm}^{-1} \) for \( \nu = 1/\lambda = 20000 \text{ cm}^{-1} \)). Time series (series of spectra differing by time interval \( t_i \) between laser excitation and start of emission spectra recording) consist of three types – short \( (\Delta t^2 , s = 41 \text{ points}, dt = 0.05 \text{ ms}, \text{i.e. } t_{14} = 2.001 \text{ ms}) \), long \( (\Delta t^3 , s = 51 \text{ points}, dt = 0.1 \text{ ms}, \text{i.e. } t_{51} = 5.001 \text{ ms}) \), very long \( (\Delta t^4 , s = 100 \text{ points}, dt = 0.101 \text{ ms}, \text{i.e. } t_{100} = 10 \text{ ms}) \). Sample S1 has been measured with D3 temporal sampling, samples S2, S3, S5 and S9 with D2+D3 sampling, sample S4 with D3+D4 sampling.

For PARAFAC data analysis D3 sampled kinetic series from samples S1-S5 and S9 have been the input.

4 Data analysis of Experimental results

4.1 FATS computations

The SVD decomposition as described in 2.2.1-2.2.3 has been applied with weighting-preprocessing\(^1\) [3,5,7,50,51] such that original measurement data matrix elements \( Y_{li} \) has been transformed onto \( Y_{li}' \) normalized data matrix via

\[
Y_{li}' = \frac{Y_{li}}{P_i Q_i}
\]

where \( P_i Q_i \) represent separable form of variable of \( Y_{li} \), so \( Y_{li}' \) are now closer to case of independent and identically distributed random variables. Since greater variance lies along temporal domain, \( P_i \) can be set as \( P_i = 1 \) and \( Q_i \) has, in software MyExpFit V4 [98] (used for all FATS computations, written in Matlab [99]), general form

\[
Q_i = \text{mean}[Y_{li}]^\phi
\]

where \( \phi \in (0; 1) \). For purely poisson noise, \( \phi = 0.5 \), this choice has been applied here. After SVD procedure (4), (5), \( Y'' = U' W' V'' \), the subspectra and loadings should be „denormalized“ back according to formulae below,

\(^1\) The term NmSVD is used then (Nm = Normalized).
The factor dimension $f$ can be, in general case, determined according to three different diagnostics [3,5,7,50,51]:

i) SCREE-plot diagnostics [63,64] focus on crossing of linear branches in log $W_j = f(j)$ plot (Fig. 1). On example for sample S3, $f = 3$ or $f = 4$ since the last branch with smallest slope corresponds to noise, but from SCREE-plot alone it is hard to recognize whether still to include $j = 4$ component or not.

ii) Loadings-based V-diagnostics focus on number of first, signal-like, loadings. For S3 sample, Fig. 2 and Fig. 3 show three signal-like loadings. Since fourth, loadings are much more noise-like (Fig. 4).

iii) Subspectra-based U-diagnostics works as previous, except for subspectra. Fig. 5 presents first three signal-like subspectra, Fig. 6 subspectrum $U_4$ already noise-like.

While ii) and iii) diagnostics for the chosen example (Sample S3 TRLFS kinetic series analysis) suggest to accept $f = 3$ components for further analysis, it is better just to conclude that it is possible to statistically distinguish $N = 3$ independent luminescence active species (according to the geochemical modelling it should be $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{30}$, $\text{CuUO}_2(\text{CO}_3)_{32}^-$ and most probably $\text{MgUO}_2(\text{CO}_3)_{32}^-$), but set $f = N + 1 = 4$.

Because the software based background correction/subtraction [65] is rather approximate, irrespective to method free parameter choice, FATS for $f > 2$ provide one individual component with several orders of magnitude larger life-time (and smaller luminescence amount) and bandless continuum-like luminescence spectrum. This component corresponds to background artifact and is ignored in further analysis. Therefore, for $N$ chemical component model, $f = N + 1$ has to be chosen. By preliminary analysis of randomness of residuals, case $N = 1$ has been found as insufficient for any sample investigated below, $N = 2$ as a slight under-fit and $N = 4$ as a slight over-fit.
signal (in $R^2$, where $N = 419$ is number of spectral points selected).

![Graph](image)

**Fig. 6.** First, NmSVD subspectrum $U'$ corresponding to noise has been added to further analysis for the need to represent background subtraction artifact, but subspectra for $f > 4$ are omitted from further analysis.

**4.2 Sample S1 (mine water)**

NmSVD for this sample suggest $N = 3$ (or 2) and therefore $f = 4$ (or 3) (Fig. 7). Denormalized $f$ loadings from NmSVD has been fitted to linear combination of $f$ exponential decays, resulting luminescence amounts $\zeta_n$ [$10^5$ ms$^{-1}$] and life-times $\tau_n$ [ms] are presented in Tab. 2.

![Graph](image)

**Fig. 7:** NmSVD SCREE-plot and U-diagnostics done by MyExpFit V4 program [98].

FATS $f = 3$ and $f = 4$ analysis has been done. Resulting individual component spectra (Fig. 8, Fig. 9) in the former case contained “structure” inside the background component (dotted in Fig. 8) which favoured latter $f$ parameter choice. Please note the peak maxima (e.g. for the highest peak) of the component differs by a tiny portion of 0.86 nm (less than twice of wave-length sampling period!) for $f = 3$ and ~ 1 nm (~ 50 cm$^{-1}$ in this region) for the two charged complex species for $f = 4$ as well.

![Graph](image)

**Fig. 8.** FATS, $f = 3$ analysis of sample S1 results for individual component spectra (nm scale).

![Graph](image)

**Fig. 9.** FATS, $f = 4$ analysis of sample S1 results for individual component spectra (nm scale, for better visibility of peak position differences, only three largest peak detail is shown).

Spectroscopic parameters – $T_{00}$ [$10^3$ cm$^{-1}$] (excitation energy) and $a_{gs}$ [cm$^{-1}$] (ground state vibrational frequency) have been calculated from gaussian fits of FATS $f = 4$ individual component spectra (Tab. 2, Fig. 10, 11 as an example for $m = 1$ component).

![Graph](image)

**Fig. 10.** $m = 1$, $\tau = 0.87$ ms component (assigned to MgUO$_2$(CO$_3$)$_2^2$) of $f = 4$ FATS decomposed according to (19) (cm$^{-1}$ scale).
Fig. 11. $m = 1$ component ($f = 4$), intensity plotted in logarithmic scale to show approximate gaussian character for red-most and blue-most tiny peaks too.

For this sample, an example of $\Delta R$ estimation from experimental data is shown in Fig. 12 and Fig. 13, where one and two hot band models, respectively, have been used. In their comparison, two hot band model seems to be more realistic with $\Delta R = (7.3 \pm 1.0)$ pm.

![Diagram](image1.png)

**Fig. 12.** FATS $f = 4$, $m = 0$ ($\tau_0 = 0.36$ ms, assigned to \(\text{CaUO}_2(\text{CO}_3)_3\)) Franck-Condon fit (23) within „one hot-band” model. Fitted $\Delta R = (10.4 \pm 1.0)$ pm. On vertical axis, $n'\rightarrow 0$ peak area (22) relative to $0'\rightarrow 0$ peak is plotted. Horizontal axis represents vibrational number $n'$.

**Fig. 13.** FATS $f = 4$, $m = 0$ as in previous Fig. 11, but within „two hot bands” model. $\Delta R = (7.3 \pm 1.0)$ pm. The dashed lines corresponds to $\Delta R = (\Delta R_{\text{min}} \pm 0.7$ pm, the dotted lines to $\Delta R = (\Delta R_{\text{min}} \pm 1.3$ pm, where $(\Delta R)_{\text{min}}$ is the $\chi^2$ fit optimum value.

**Table 2:** FATS $f = 4$ results for sample S1.

<table>
<thead>
<tr>
<th>$m$</th>
<th>$\tau_0$</th>
<th>$\omega_g$</th>
<th>$T_{00,m}$</th>
<th>$\omega_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.36</td>
<td>8.1</td>
<td>20.01</td>
<td>0.01</td>
</tr>
<tr>
<td>1</td>
<td>0.87</td>
<td>30.1</td>
<td>19.97</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>1.52</td>
<td>4.51</td>
<td>19.92</td>
<td>0.03</td>
</tr>
<tr>
<td>3</td>
<td>9.52</td>
<td>0.09</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

4.3 Sample S2 (treated mine water)

Same procedure as for S1 has been repeated, results are presented in Table 3 below (since now, background component is not listed). The uncertainties are $\delta(\omega_g) \sim 10\text{cm}^{-1}$, $\delta(\tau_0) \sim 0.1\text{ ms}$ and $\delta(\omega_g) \sim 0.2\text{ ms}^{-1}$.

**Table 3:** FATS analysis results, sample S2 (treated mine water)

<table>
<thead>
<tr>
<th>$f$</th>
<th>$m$</th>
<th>$\tau_0$</th>
<th>$\omega_g$</th>
<th>$T_{00,m}$</th>
<th>$\omega_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>0.45</td>
<td>2.57</td>
<td>19.98</td>
<td>0.01</td>
</tr>
<tr>
<td>1</td>
<td>1.15</td>
<td>2.53</td>
<td>19.94</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.21</td>
<td>1.83</td>
<td>20.97</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.76</td>
<td>2.38</td>
<td>19.97</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.26</td>
<td>1.55</td>
<td>19.92</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

4.4 Sample S3 (TMF seepage water)

NnSVD and FATS as done for previous samples revealed following parameters (Tab. 4). Due to the higher uranium content, signal/noise ratio has been higher and smoother individual component spectra resulted (Fig. 14). An example of fitting procedure for $T_{00}$, and $\omega_g$, determination is presented in Fig. 15, the uncertainties are lower than in S1 by roughly factor of 2.

**Table 4:** FATS analysis results, sample S3 (TMF seepage water)

<table>
<thead>
<tr>
<th>$f$</th>
<th>$m$</th>
<th>$\tau_0$</th>
<th>$\omega_g$</th>
<th>$T_{00,m}$</th>
<th>$\omega_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>0.81</td>
<td>93.2</td>
<td>19.98</td>
<td>0.01</td>
</tr>
<tr>
<td>1</td>
<td>1.39</td>
<td>36.9</td>
<td>19.93</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.75</td>
<td>39.6</td>
<td>19.99</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.88</td>
<td>59.5</td>
<td>19.96</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1.44</td>
<td>31.0</td>
<td>19.93</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 14:** FATS ($f = 4$), $m = 2$ individual component spectrum (later assigned to \(\text{Ca}_2\text{UO}_2(\text{CO}_3)_3\)) fitted to linear combination of gaussian profiles. Peak maxima has been fitted as a function of peak number $n$ in follow Fig. 15.

However after not one but two redmost peaks are excluded from the fit, $\omega_g = 833\text{ cm}^{-1}$ value results.
Fig. 15: Upper part: Peak maxima as peak number function (vertical principal axis in $10^3$ cm$^{-1}$) divides the two linear branches with almost identical slopes, the uncertainty of fit underestimates total experimental uncertainties, lower part: residuals of the fit (right axis in cm$^{-1}$).

4.5 Sample S4 (acidified TMF seepage water)

FATS analysis for $f = 4$ of the sample created by acidification of S3 by HCl (to pH = 5.5) possibly revealed in previous samples not present component with both high $T_{00}$ and $\omega_{gs}$ ($m = 1, \tau = 1.15$ ms), which might be either UO$_2$CO$_3$ or UO$_2$SO$_4$, but its small luminescence amount ($\mathcal{Q} \sim 0.07 \cdot 10^3$ ms$^{-1}$, Table 5) is in contrast with high relative content predicted by geochemical modelling for this acidified sample. Similarly, the component associated with $\tau = 0.84$ ms ($f = 3$) or $\tau = 0.88$ ($f = 4$) could be assigned to UO$_2$CO$_3$ ($\omega_{gs} = 815$ cm$^{-1}$, $T_{00} = 20080$ cm$^{-1}$) fitted from deep cryogenic measurements done in [67], $\tau = 0.47$ ms) or UO$_2$SO$_4$ due to the previously reported luminescence life-time of UO$_2$SO$_4$ under cryogenic conditions of 0.4 ms.

Table 5: FATS analysis results, sample S4 (acidified TMF seepage water)

<table>
<thead>
<tr>
<th>$f$</th>
<th>$m$</th>
<th>$\tau_m$</th>
<th>$\omega_{gs}$</th>
<th>$T_{100,m}$</th>
<th>$\omega_{gs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>0.83</td>
<td>36.9</td>
<td>19.99 ± 0.01</td>
<td>816</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.34</td>
<td>24.3</td>
<td>19.92 ± 0.01</td>
<td>819</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.83</td>
<td>36.6</td>
<td>19.99 ± 0.01</td>
<td>815</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.15</td>
<td>0.07</td>
<td>20.02 ± 0.02</td>
<td>827</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.34</td>
<td>24.4</td>
<td>19.92 ± 0.01</td>
<td>819</td>
</tr>
</tbody>
</table>

4.6 Sample S5 (acidified TMF seepage water)

Following table 6 presents FATS results for the sample S5 created by acidification of S3 by HCl to pH = 6.0.

Table 6: FATS analysis results, sample S5 (acidified TMF seepage water)

<table>
<thead>
<tr>
<th>$f$</th>
<th>$m$</th>
<th>$\tau_m$</th>
<th>$\omega_{gs}$</th>
<th>$T_{100,m}$</th>
<th>$\omega_{gs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0</td>
<td>0.84</td>
<td>97.4</td>
<td>19.96 ± 0.02</td>
<td>816</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.44</td>
<td>34.4</td>
<td>19.92 ± 0.02</td>
<td>820</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.59</td>
<td>6.81</td>
<td>20.06 ± 0.02</td>
<td>800?</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.88</td>
<td>98.5</td>
<td>19.95 ± 0.02</td>
<td>816</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.51</td>
<td>26.9</td>
<td>19.91 ± 0.02</td>
<td>830</td>
</tr>
</tbody>
</table>

Uncertainties of spect. param. are at least 20 cm$^{-1}$ here.

4.7 Sample S9

Since Sample 9 had the highest total uranium concentration among all studied samples, individual component spectra from FATS analysis have been smoother than in previous samples (Fig. 16, 17) and excitation energy parameter $T_{00}$ experimental uncertainties have been the lowest (Tab. 7).

Table 7: FATS analysis results, sample S9

<table>
<thead>
<tr>
<th>$f$</th>
<th>$m$</th>
<th>$\tau_m$</th>
<th>$\omega_{gs}$</th>
<th>$T_{100,m}$</th>
<th>$\omega_{gs}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0</td>
<td>0.48</td>
<td>87.7</td>
<td>19.99 ± 0.01</td>
<td>799</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.91</td>
<td>225.3</td>
<td>19.97 ± 0.01</td>
<td>806</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.50</td>
<td>134.4</td>
<td>19.93 ± 0.01</td>
<td>807</td>
</tr>
</tbody>
</table>

4.8 PARAFAC analysis of all samples together

PARAFAC decomposition according to (18) led to luminescence amount profiles (Fig. 18), by maximizing objective function

$$f(\pi) = \sum_{m=1}^{N} \left( \sum_{k=1}^{K} \Gamma_{k,m} M_{k,\pi(m)} \right) W_{\pi}, \quad (30)$$

where $F_{k,m} = C_{k}(m)/\Sigma C_{k}(n)$ is relative luminescence amount of $m$-th component (18) in $k$-th sample, $M_{k,\pi(m)}$ is $\pi(m)$-th species concentration in $k$-th sample according to...
geochemical modelling calculation [66] (Fig. 19, done in EQ3/6 [68] (default thermodynamic database data0.R2.com) in [66] and independently reproduced by PhreeqC [69] with a database input from NEA thermodynamic database [70] supplemented with parameters for Ca\textsubscript{2}UO\textsubscript{2}(CO\textsubscript{3})\textsubscript{3}0 \textsuperscript{2-} [71] and Ca\textsubscript{2}UO\textsubscript{2}(CO\textsubscript{3})\textsubscript{3}2- [72]), \(W_m\) is weight, \(N = 7\) (the background component is excluded) and maximization is done with respect to permutation \(\pi\). Resulting optimal assignment is presented in Table 8 and parameters \(\tau\), \(T_{\text{00}}\), and \(\omega\) (from monoexponential fits of \(D_m(t)\) and gaussian fits of \(Z_m(v)\)) (18) should be compared to found literature experimental data (Table 9) and quantum chemical calculations (section 6).

Table 8: Optimal component assignment

<table>
<thead>
<tr>
<th>(m)</th>
<th>Species</th>
<th>(\tau)</th>
<th>(T_{\text{00}})</th>
<th>(\omega)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ca\textsubscript{2}UO\textsubscript{2}(CO\textsubscript{3})\textsubscript{3}\textsuperscript{2-}</td>
<td>0.551</td>
<td>20051</td>
<td>806.0</td>
</tr>
<tr>
<td>2</td>
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Table 9: Comparison with literature

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<th>(\omega_{\text{gs,REF}})</th>
<th>(\tau_{\text{REF}})</th>
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<td>[74]</td>
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<td>7</td>
<td>0.400</td>
<td></td>
<td></td>
<td>[75]</td>
</tr>
</tbody>
</table>

\(a\) Average from all life-times assigned to this species in Tab. 4 of [66].

\(b\) The higher reference value for luminescence life-time of 1.282 ms from [67] is even closer, but corresponds to much lower temperature of 6K.

\(c\) Here and in first line of Table 9, the comparison of life-time is made with respect to different analysis of the same data.

\(d\) This \(\tau_{\text{m}}\) value correspond to a lower temperature of 6K. However, luminescence life-time should decrease with increasing temperature.
5 Computations for quantum chemical calculations

Similarly to [1] calculations were done in Turbomole V6.5 program [78,94] on MetaCentrum computational grid system [98]. Scalar relativistic effects were approximately included via 60 electron Effective Core Potential (ECP) for uranium atom [79,80], all other electrons were, at this level of approximation treated as non-relativistic. Hydration has been described by explicit inclusion of small number (denoted \( n \) in chemical formulae like \([\text{UO}_2(\kappa^2-\text{CO}_3)(\text{H}_2\text{O})_n] \cdot n \text{H}_2\text{O}\) of water molecules into investigated system. The atomic basis sets used were def-SVP (denoted \( \text{S} \)) in all tables in the section 6 below, [78,79,81-82]), def-TZVPP (denoted \( \text{Tc} \)), for solvated models, solvent water molecules only def-SVP atomic basis set was used to reduce the computational demands, denoted \( \text{Tc} \) [1] or \( \text{def-TZVPPc}^+ \) and def-QZVPP (denoted \( \text{Q}^+ \)) [95], for uranium at most def-TZVPP has been used).

For the ground state properties DFT/B3-LYP [84-86,93] has been used. For DFT calculations the D3 dispersion correction has been applied [91]. All figures have been exported from Molden [92] screenshots.

6 Quantum chemical calculation results

6.1 Uranyl Monocarbonate, \( \text{UO}_2\text{CO}_3 \)

Similarly as for the uranyl monosulfate, \( \text{UO}_2\text{SO}_4 \), four different configurations should be investigated, differing by dentacy of \( \text{CO}_3^{2-} \) ligand (\( \kappa^2 \) for bidentate, coordinated by two donor oxygen atoms, \( \kappa^- \) for monodentate, coordinated by one donor oxygen atom) and coordination number of central uranyl group \( \text{UO}_2^{2+} \) (i.e. number of water molecules coordinated to \( \text{U} \) along carbonate ligand), labeling from [1] will be adopted leading to \( \kappa^2\text{co}5 \) (for \([\text{UO}_2(\kappa^2-\text{CO}_3)(\text{H}_2\text{O})_5] \cdot n \text{H}_2\text{O}\)), \( \kappa^2\text{co}6 \) (\([\text{UO}_2(\kappa^2-\text{CO}_3)(\text{H}_2\text{O})_6] \cdot n \text{H}_2\text{O}\)), \( \kappa^-\text{co}5 \) (for \([\text{UO}_2(\kappa^2-\text{CO}_3)(\text{H}_2\text{O})_5] \cdot n \text{H}_2\text{O}\)) and \( \kappa^-\text{co}6 \) (for \([\text{UO}_2(\kappa^2-\text{CO}_3)(\text{H}_2\text{O})_6] \cdot n \text{H}_2\text{O}\)). In vacuum, only \( \kappa^2\text{co}5 \) has been found stable, explicit inclusion of water molecules allowed stabilization slightly less stable \( \kappa^2\text{co}6 \) and when at least 18 water molecules has been added around studied complex also \( \kappa^-\text{co}5 \). Ground state symmetric stretching mode frequency of uranyl group \( \omega_{\text{bey}} \) and vertical \( (T_v, \text{not } T_{0v}) \) excitation energies are reported in Table 10 below, where \( b \) stands for atomic basis set, \( n \) for number of explicit water molecules (not coordinated to uranyl, but as solvent), \( E \) for relative energy (in m\( \text{H} \) for different \( b \), in cm\(^{-1} \) if bold - for different local PES minima \( b, \text{form and } n \) identical), relative to closest most \( T_{0v} \) upside in the table), \( R \) for \( \text{UO}_3^{2+} \) bond distance in pm.

![Fig. 20. At def-TZVPP/B3LYP/DFT-D3 level optimized geometry of [UO\(_2\)(\(\kappa^2\)-CO\(_3\))\(_2\)(H\(_2\)O\(_3\))]\(_\cdot\)25 H\(_2\)O (solvent water molecules are represented by lines and def-SVP basis set used for their description). Please note the planarity of CO\(_3^{2-}\) ligand situated in equatorial plane (approximately perpendicular to uranyl axis)](image)

### Table 10: \( \text{UO}_2\text{CO}_3 \) prop. quant. chemical estimate.

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<th>( T_v )</th>
<th>( \omega_{\text{bey}} )</th>
<th>( R )</th>
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<td>179</td>
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<tr>
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<td></td>
<td>861</td>
<td>178</td>
</tr>
</tbody>
</table>

6.2 Uranyl bis(carbonate), \( \text{UO}_2(\text{CO}_3)^2^- \)

Among all six possibilities only \( \kappa^2\text{co}5 \) isomer (supposed to be most stable) has been investigated. Results are presented in table below.

### Table 11: Ground electronic state properties of \([\text{UO}_2(\kappa^2-\text{CO}_3)(\text{H}_2\text{O})_6] \cdot 25 \text{H}_2\text{O}\) (solvant water molecules are represented by lines and def-SVP basis set used for their description). Please note the planarity of \( \text{CO}_3^{2-} \) ligand situated in equatorial plane (approximately perpendicular to uranyl axis).

<table>
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<tr>
<th>ref</th>
<th>b</th>
<th>( n )</th>
<th>( E )</th>
<th>( T_v )</th>
<th>( \omega_{\text{bey}} )</th>
<th>( R )</th>
</tr>
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<td>181</td>
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<tr>
<td>2</td>
<td>T</td>
<td>-905</td>
<td>20349</td>
<td>808</td>
<td>181</td>
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<td>0</td>
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<td>-893</td>
<td>20507</td>
<td>827</td>
<td>179</td>
<td></td>
</tr>
</tbody>
</table>
Aside of the vibrational frequencies in Tab. 11, there is also another mode with smaller contribution to uranyl symmetric stretching with \( \omega \) of 723, 710 and 710 cm\(^{-1}\) for ref. 1, 2 and 3 respectively.

For this molecule, electronic excited state PES local minima solution has been done and adiabatic energies \( T_d \) and \( T_{de} \) are presented together with deexcitation energy \( T_{de} \) [all in cm\(^{-1}\)] in the following table (\( \omega_{ks} \) is the symmetric stretching mode vibrational frequency of uranyl group in the excited electronic state in cm\(^{-1}\) and \( \Delta R \) excitational elongation in pm).

### Table 12: Excited electronic state properties of \([\text{UO}_2(\text{c}^2-\text{CO}_3)\text{H}_2\text{O}])^2^+\)

<table>
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<tr>
<th>ref b. n</th>
<th>( T_d )</th>
<th>( T_{de} )</th>
<th>( \omega_{ks} )</th>
<th>( \Delta R )</th>
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<td>713</td>
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<tr>
<td>2 T 0</td>
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<td>669</td>
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<td>19312</td>
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<tr>
<td>4 S 12</td>
<td>20089</td>
<td>19442</td>
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</table>

Fig. 21: Left: \([\text{UO}_2(\text{c}^2-\text{CO}_3)\text{H}_2\text{O}])^2^+\) in vacuum at def-QZVPP atomic basis set level, \( \text{CO}_3^2^- \) ligands both planar and in equatorial plane, intramolecular H-bond, right: with 12 water solvent molecules around, carbonate ligands slightly out of equatorial plane.

### 6.3 Uranyl tris(carbonate), \( \text{UO}_2(\text{CO}_3)^3^- \)

Uranyl tris(carbonate) molecule has \( D_{3h} \) point group symmetry. For some explicit solvated models the symmetry has been broken due to asymmetric surrounding by water molecules. Though no water is directly coordinted to the uranyl group, the explicit inclusion of some water molecules significantly change uranyl bond (U-Oyl) length \( R \) (the bond is shortened), frequencies of vibrational modes with symmetric U-Oyl stretching (\( \omega_{ks,1} \) and \( \omega_{ks,2} \) – by increasing them – as opposed to \( \text{UO}_2^{2+} \) hydration effect) and to a lesser extend (e.g. when compared to \( \text{UO}_2\text{CO}_3 \) or \( \text{UO}_2(\text{CO}_3)^2^- \)) also vertical excitation energy \( T_e \) (Tab. 13).

Differences can be identified between “sandwich-like” supramolecular complex containing 12 water molecules (six from each side in planes parallel to the coordination plane, Fig. 22) and 24 water molecular explicit hydrated structure (Fig. 23), where also all three non-coordinated (“terminal”) oxygens of \( \text{CO}_3^2^- \) ligands have been surrounded by three water molecules (allowing for partial stabilization of negative charge, Tab. 13) each.

Predicted adiabatic \( (T_a \sim 20 \text{ 800 cm}^{-1}) – the value mentioned in theoretical background, Tab. 14) excitation energies for 12 water molecule solvated models would imply two-hot-bands interpretation of luminescence spectra. This is in contrast to uranyl bis(carbonate) model \([\text{UO}_2(\text{c}^2-\text{CO}_3)\text{H}_2\text{O}])^2^+ \cdot 12\text{H}_2\text{O} \) (with a similar “sandwich-like” explicit water molecules surrounding), where \( T_a \sim 20\text{ 089 cm}^{-1} \sim 20\text{ 000 cm}^{-1} \) – the value mentioned in the theoretical background for one-hot-band interpretation. It would be interesting to see two luminescence spectra with similar band positions but “shifted” peak assignment to vibronic transitions'. Predicted vertical excitation energies, however, decrease with number of explicitly included solvent molecules and in inifinity limit would drop to value closer to one-hot-band interpretation.

### Table 13: Ground electronic state properties of \([\text{UO}_2(\text{CO}_3)^3^- \) \( \text{(U-O}_1 \text{ bond length} R \text{ in pm, vibrational frequency of} \text{UO}_2^{2+} \text{symmetric mode} \omega_{ks} \text{cm}^{-1} \text{) and vertical excitation energies} T_e \text{ cm}^{-1} \text{].}

<table>
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<td>2 T 0</td>
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</table>

### Table 14: Excited electronic state properties of \([\text{UO}_2(\text{CO}_3)^3^- \) \( \text{· 12 H}_2\text{O} \text{ (def-TZVPP level).}

<table>
<thead>
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<td>2 Tc 12</td>
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<td>3.9</td>
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6.4 Ternary complex MgUO$_2$(CO$_3$)$_2^-$

Optimized structure without molecules of solvent in presented in Fig. 24. Two CO$_3^{2-}$ ligands are distorted out off equatorial plane and their coordination mode towards uranium is monodentate. Explicit inclusion of solvent molecules allow carbonate ligands to stay in the coordination plane, Fig. 25 shows two possibilities differing by 486 cm$^{-1}$ (the left one has been found as lower by energy and is presented first in Tab. 15).

Fig. 23. Struct. corresponding to ref. 8 in Tab. 13.

Fig. 24. Optimized structures (def-TZVPP basis) for MgUO$_2$(CO$_3$)$_2^-$ in vacuum.

Inclusion of 22 water molecules to model led Mg atom to stabilize closer to equatorial, ligation, plane (Fig. 26-28). Bond lengths are given in Tab. 24 (for description, please see Fig. 24 and Fig. 25).

Table 15: Ground electronic state properties of MgUO$_2$(CO$_3$)$_2^-$ (U-O$_3$) bond length $R$ in pm, vibrational frequency of modes containing significant part of UO$_2$: symmetric stretching mode $\omega_{b,1}$ and $\omega_{b,2}$ [cm$^{-1}$]) and vertical excitation energies $T_e$ [cm$^{-1}$].

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<td>15</td>
<td>Tc</td>
<td>22</td>
<td>0</td>
<td>21315</td>
<td>820</td>
<td></td>
<td>180</td>
</tr>
<tr>
<td>16</td>
<td>Tc</td>
<td>22</td>
<td>625</td>
<td>21206</td>
<td>826</td>
<td></td>
<td>178</td>
</tr>
</tbody>
</table>

Table 16: Lengths of important bonds in MgUO$_2$(CO$_3$)$_2^-$ · n H$_2$O model structures.

<table>
<thead>
<tr>
<th>ref</th>
<th>MgO$_{a1}$</th>
<th>MgO$_{a1}$</th>
<th>MgO$_{a2}$</th>
<th>UO$_{a1}$</th>
<th>UO$_{a2}$</th>
<th>UO$_{a3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>212</td>
<td>224</td>
<td>193</td>
<td>231</td>
<td>231</td>
<td>228</td>
</tr>
<tr>
<td>5</td>
<td>203</td>
<td>194</td>
<td>241</td>
<td>241</td>
<td>229</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>212</td>
<td>202</td>
<td>MgO$_{b1}$</td>
<td>260</td>
<td>245</td>
<td>234</td>
</tr>
<tr>
<td>11</td>
<td>231</td>
<td>198</td>
<td>231</td>
<td>236</td>
<td></td>
<td></td>
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<tr>
<td>15</td>
<td>205</td>
<td>200</td>
<td>249</td>
<td>249</td>
<td>241</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>200</td>
<td></td>
<td>239</td>
<td>252</td>
<td>240</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 28. PES local minimum structure (def-TZVPPc) for MgUO₂(CO₃)₃²⁻ · 2H₂O. „Side view”. All carbonate ligands are bidentate coordinated and Mg atom position is in coordination plane, with coordination number 6. This structure is 625 cm⁻¹ higher than the one from Fig. 27.

Fig. 29. „Down view” on structure from Fig. 28.

6.5 Ternary complex CaUO₂(CO₃)₅²⁻

Detailed parametric study on number of explicit water included will be given in Supplementary Information. For highest number of explicit water molecules Ca atom preferred position slightly above coordination plane (Fig. 30-32) and tendency to coordination number 7 (Fig. 32).

Fig. 30. Top view on optimized CaUO₂(CO₃)₅²⁻ · 2H₂O structure (within def-SVP atomic basis set), associated with \( \omega_{gs,1} = 797 \) cm⁻¹, \( R = 181 \) pm and \( T_c = 21256 \) cm⁻¹.

Fig. 31. Side view on optimized CaUO₂(CO₃)₅²⁻ · 2H₂O structure (within def-SVP atomic basis set, see Fig. 30)

Fig. 32. optimized CaUO₂(CO₃)₅²⁻ · 2H₂O structure (within def-TZVPPc atomic basis set, see Tab. 17)

Spectroscopic properties are listed in Table 15 below.

**Table 15:** Calculated properties of CaUO₂(CO₃)₅²⁻ · 2H₂O

<table>
<thead>
<tr>
<th>b.</th>
<th>( E )</th>
<th>( T_c )</th>
<th>( \omega_{gs,1} )</th>
<th>( \omega_{gs,2} )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S</td>
<td>21256</td>
<td>797</td>
<td>181</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Tc</td>
<td>0</td>
<td>20401</td>
<td>811</td>
<td>794</td>
</tr>
<tr>
<td>3</td>
<td>Tc</td>
<td>1837 cm⁻¹</td>
<td>20475</td>
<td>824</td>
<td>180</td>
</tr>
<tr>
<td>4</td>
<td>Tc</td>
<td>2559 cm⁻¹</td>
<td>21184</td>
<td>810</td>
<td>181</td>
</tr>
</tbody>
</table>

6.6 Ternary complex Ca₂UO₂(CO₃)₄⁰

Similar features as in charged complex CaUO₂(CO₃)₅²⁻ has been found for neutral bicalcium analogue Ca₂UO₂(CO₃)₄⁰ as well (Fig. 33, 34, table 16)
species (ΔG°, ΔH°, ΔS°) should be calculated (for species listed in 1-4) to decide on their importance and eventually to include them inside the geochemical speciation modelling as well.

6.8 Summary

In the following tables, parameters 〈b3〉 (Tab. 17) and T\(_{00}\) (Tab. 18) estimated from

\[ T_{00,m} \pm T_{e,m} + \Delta T_e, \]  

(where \(\Delta T_e = T_{00,bc} - T_{e,bc} = 677 \text{ cm}^{-1}\) is an average of difference of adiabatic \(T_0\) and vertical \(T_e\) excitation energies computed for \(\text{UO}_2(\text{CO}_3)^{2-}\) (807 cm\(^{-1}\)) and \(T_e - T_s\) computed for \(\text{UO}_2(\text{CO}_3)^{4+}\) (547 cm\(^{-1}\)) are compared to experimental values resulting from PARAFAC individual component assignment (“PF”), FATS results for samples S9 and S4 (f = 4) and to laboratory data.

Table 17: 0' → 0 transition energies \(T_{00}\) compared. QCH = from quasirelativistic TD-DFT/B3LYP quantum chemical calculation presented here (bold underlines values of \(T_s\) in Tab. and relation (31)), PF = PARAFAC derived experimental value, FATS = FATS derived exp. value, Lit. = transition energy derived from linear fit of last three peak positions in HZDR report [66], with ref. being the corresponding literature source.

Table 18: Symmetric stretching vibrational mode of uranyl group \(\text{UO}_2^{2+}\) in ground electronic state, sense of symbol is identical to that in previous Tab. 17.

---

**Table 16**: Calculated properties of \(\text{Ca}_2\text{UO}_2(\text{CO}_3)^{3-}\), \(n\text{H}_2\text{O}\) models.

<table>
<thead>
<tr>
<th>b.</th>
<th>n</th>
<th>(T_e)</th>
<th>(\langle b_3 \rangle)</th>
<th>(\langle b_2 \rangle)</th>
<th>(R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Tc</td>
<td>840</td>
<td>179</td>
<td></td>
<td></td>
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<tr>
<td>3</td>
<td>S</td>
<td>32</td>
<td>21311</td>
<td>832</td>
<td>842</td>
</tr>
</tbody>
</table>

6.7 On other molecular formation

Except for \(\text{UO}_2\text{SO}_4\) (which has been studied in [1]) all uranyl complex species present in list of assigned species in Tab. 8 has been investigated by quasirelativistic (TD)DFT/B3LYP/D3 methodologies here. However, the yet used geochemical models doesn’t consider theoretically possible creation of

1) ternary alkaline metal-uranyl-carbonate species (e.g. \(\text{Na}_2\text{UO}_2(\text{CO}_3)^{3-}\), ..., \(\text{Na}_3\text{UO}_2(\text{CO}_3)^{4+}\)) [103]

2) ternary metal-uranyl-carbonate species with less than three carbonate ligands (e.g. \(\text{Ca}_2\text{UO}_2(\text{CO}_3)^{4+}\), \(\text{Na}_2\text{UO}_2(\text{CO}_3)^{5+}\), ...) 

3) uranyl complex species with two or more different ligands (e.g. \(\text{UO}_2(\text{HCO}_3)(\text{CO}_3)^{3-}\))

4) quaternary metal-uranyl-carbonate species (e.g. \(\text{CaMgUO}_2(\text{CO}_3)^{6+}\)) [102]

As a future prospect, thermodynamic constants determining stability/equilibrium concentrations of...
Gray highlighted values in Tab. 17 and 18 have uncertain assignment to the corresponding two chemical species UO$_2$CO$_3$ / UO$_2$SO$_4$ (they could be swapped (but either in both tables simultaneously or not at all)).

7 Conclusions

Since the signal:noise ratio in measured natural water samples has been very low (yet very low differences between all spectroscopic parameters of individual components (in few to tens cm$^{-1}$) imply the decomposition into individual components is ill-conditioned problem and would demand signal:noise ratio to be rather high instead), for most samples, PARAFAC as a robust (exploiting correlations across wider set of data) chemometric method should be used. For eight component model (one component corresponds to artifact due to software background correction) individual component concentration profiles has been correlated to geochemical modelling prediction (done in [66] with EQ3/6 program [68], reproduced by us within PherqC [69] as well). Assignment of individual component spectra and luminescence decay curves is presented in Tab. 8. In following Tab. 9 literature data on spectroscopic parameters of assigned chemical components are listed. From comparison of identical parameters in aforementioned tables we can conclude that internal consistency of PARAFAC data analysis is relatively good (in particular for luminescence life-times $\tau$ and symmetric mode stretching frequency of uranyl group $\omega_{gs}$).

Samples S4 and S5 are specific since they were produced by acidification of the sample S3 by HCl. In particular, sample S4 ($\text{pH} = 5.5$) should have qualitatively different speciation than other samples (Fig. 19, for S4 species UO$_2$CO$_3$ and UO$_2$SO$_4$ should be dominant over ternary tris(carbonato) complexes $\text{M}_2\text{UO}_2(\text{CO}_3)_{2n-4}$ ($M = \text{Ca,Mg, } n = 0,1,2$). This might be overlooked by PARAFAC, but should be visible in detailed interpretation of FATS results for the samples S3, S4 and S5.

And FATS method truly indicate a one or two chemical components in S4 qualitatively different from the three seen as main constituents of all other samples – $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3n}$, $\text{CaUO}_2(\text{CO}_3)_{2}$ and $\text{MgUO}_2(\text{CO}_3)_{2}$.

Quantum chemical modelling led to realistic values of vibrational frequencies of each species individually (few percent errors) and geometry of $\text{Ca}_2\text{UO}_2(\text{CO}_3)_{3n}$ well comparable with literature [96,97]. And because the differences between $\omega_{gs}$ of different species are, in some cases, rather positive in percent (i.e. $< 8 \text{ cm}^{-1}$) than the several percent error of their QM prediction, direct usage of here applied quantum chemical methodologies (quasirelativistic TDDFT geometry optimization of nanoscale water droplets with studied complex inside) would be too ambitious. Existed state properties (including $T_d$) haven’t been predicted with certainty useful in practical individual component assignment. The reason might be that most uranyl compounds has highly multi-reference character of excited states (excited states are not dominated by a single electron configuration as the UO$_2^{2+}$ ground state) and more advanced, ab initio, method should be used (rather than TD-DFT). Spin-orbit coupling should be also included for excite state properties (going beyond quasirelativistic approximation). Further improvement planned will connect quantum chemical calculations to ambient temperature molecular dynamics to generate more realistic statistical ensembles of spectroscopic properties for each species / its simulated luminescence spectrum.

Even though rigorous chemometric method has been used, the data are not enough to provide more certain insight into uranium speciation of given samples. However, the methodology presented as a road to qualitative results is itself of great importance for future use.

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