Time resolved laser induced fluorescence spectroscopy at FNSPE

Czech Technical University in Prague
Faculty of Nuclear Sciences and Physical Engineering
Dept. of Nuclear Chemistry
Motivation

- Nuclear systems and fuel cycles are significantly evolving - efficiency of the resources consumption, safety of reactors, waste repository and a resistance towards proliferation.
- Different options allowing decreasing waste volume, toxicity and residual heat have to be studied.
  - Among others, recycling minor actinides, particularly americium, is of high interest due to its major contribution to waste long term toxicity and heat power.
- Processes for minor actinides recycling were developed e.g.
  - The recovery of all transuranium elements from the high activity spent fuel dissolution solution
  - or the recovery of Am and Cm together
  - or the separation of Am alone.
Motivation

- Different extraction processes based on coordination chemistry were designed for each option, but a representative process modelling needs an description of the structure and the thermodynamics aspects of the systems.
  - Due to the electron configuration Ln and MA are difficult to be distinguish chemically
  - They have different optical properties
  - **Remove chemically, but testing optically**
    - Advantage - Work in small amounts
- Various spectroscopic techniques could provide information; TRLFS could be powerful tool to identify the extracted species and evaluate the effectiveness of the extraction process.
  - Complexation Ln and MA
  - Reaction kinetics
  - Long-term stability of the complex
  - Molecule architecture
Time Resolved Laser Induced Fluorescence Spectroscopy

- Is a modern laser spectroscopic method used for studying chemical forms (species) in which elements are present even in trace concentrations.
- Non-destructive measurements of liquid and solid samples in real time
  - Selectivity
  - Sensitivity (ability to work at concentrations <10^{-8} M and lower)
  - Speed (optional kinetic studies)
- Studied mainly
  - lanthanides Eu, Tb, Gd, Dy, Sm, Ce, Tm, Nd, Ho, Er, Yb…
  - actinides U, Cm, Am, Cf, Es, Bk, Np, Pu…
TRLFS – method principles

- Is based on short-pulse laser excitation of various forms of the studied element and measurement of the luminescence signal characteristics.
  - The sample is irradiated with laser pulses of a selected wavelength - absorption
    - Quantum system (central atom) absorbs a photon enters into the excited state
  - Transition to the ground state follows
    - Non-radiative transitions (very fast) quantum system goes to the lowest excited state. Usually energy transfer direction to the solvent
    - Excited component (complex) emits a photon and system returns to the basic state
TRLFS – how to identify

- Following the spectra of emitted wavelengths (spectra shape)
  - Emitted photons are characteristic for the element
  - Spectrum of fluorescence signal is done by a difference of energy levels between which the luminescent transition occurs, depends also on the form (ion, complex, solvated molecule, etc.)
TRLFS – how to identify

- Following the lifetime
  - To each specie correspond a characteristic fluorescence lifetime (radiation intensity drops to $1/e = 36.8\%$ of initial value)
  - The changes in the emission spectra are due to variations in the first coordination sphere of the fluorescent central metal ion and indicate inner-sphere complexation processes.
  - The fluorescence lifetime increases with decreasing number of quenching molecules in the first sphere.

- This creates a 3D spectrum showing the dependence of the intensities of luminescence for the respective wavelength in time
  - Time resolution is achieved by successive delaying of spectra acquisition against the excitation pulse.
• For each time interval, determine the total fluorescence intensity

• Specify local maxima and determine the lifetime of a given maximum
What we have

• **Tunable laser** NT342C Ekspla, OPO based 210-2600 nm
  - Wavelength range 410-2600 nm, pump on 355 nm Nd:YAG (150 mJ). Signal 410-710 nm, Idler 710-2600 nm
  - Extension in to UV via module SH/SF generator 210-410 nm
  - Output for THG-355 nm and FHG-266 nm.
  - Length of output laser pulse 3-5 ns following the wavelength

• **Attenuator**
  - Made from two Glan polarizers, Beam dumps (to dissipate heat)
  - Attenuation range from 0.1% to ~ 80% in 350-2000 nm
What we have

- **Monochromator/spectrograph** MS257 LOT-Oriel with four gratings (150 l/mm 190-800 nm, 300 l/mm 250-1150 nm, 600 l/mm 280-1200 nm, 1200 l/mm 280-1600 nm).
  - Resolution 0.1 nm

- **Detection part with ICCD** (Intensified Charge Coupled Device) and detection had Andor (DH720i-18F-03), image intensifier (photocathode, MCP (microchannel plate)).
  - Gate step 2.4 nm

- **Temperature tuneable cell holder** TC 101 Quantum Northwest, to avoid fluctuation of the temperature-dependent luminescence signal

- **Joulmeter** Field Max II Coherent with J-50 MB-YAG probe
  - 0.5 mJ - 3 J, 266-2100 nm

- **Fiber spectrometer** Black comet with Concave Grating
  - measurements in the 190-850 nm range, resolution (<0.4nm)
Uranium carbonates results

- Study of behaviour of uranium in the natural environment - species creation is highly dependent on the pH.
- We studied systems in which are present alkaline earth metal – Mg, Ca, Sr and Ba.
- Samples were prepared near its composition of natural samples.
- Formation of species was studied in dependence on the concentration of the alkaline earth metal in solution at a given pH.
- Uranium concentration in all samples was the same \(10^{-5}\) mol/l, the concentration of alkaline earth metal was varied from \(2.10^{-2}\) mol/l to \(6.10^{-3}\) mol/l. Samples were measured at interval of pH \(~7\) to \(~8.5\).
\[
\begin{align*}
\text{specie} & & \text{lifetime [ns]} & & \text{lifetime [ns]} \\
\text{literature} & & \text{literature [ns]} \\
\text{UO}_2(\text{OH})^+ & & 6058 \pm 1526 & & 11300 \pm 4500 \\
\text{UO}_2(\text{OH})_3^- & & 313 \pm 88 & & 800 \pm 100 \text{; } 400 \\
\text{UO}_2^{2+} & & 1718 \pm 42 & & 2000 \pm 100 \\
(\text{UO}_2)_3(\text{OH})_5^+ & & 31180 \pm 660 & & 33300 \pm 5200 \\
\text{SrUO}_2(\text{CO}_3)_3^{2-} & & 18,4 \pm 1,5 & & 18,2 \pm 2,1 \\
\text{Sr}_2\text{UO}_2(\text{CO}_3)_3 & & 26,2 \pm 3,5 & & 28,2 \pm 7,1 \\
(\text{UO}_2)_3(\text{OH})_5^+ & & 27779 \pm 5096 & & 33300 \pm 5200 \\
(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^- & & 2243 \pm 446 & & -
\end{align*}
\]

c(U(VI)) = 1,00E-05 mol.l\(^{-1}\)
c(Ca\(^{2+}\)) = 7,50E-03 mol.l\(^{-1}\)
Uranium concentration measurements

- The linear responses of the uranyl luminescence signal to its concentration at a given intensity of the excitation radiation

- The complexant
  - It serves to reduce the impact of non-irritating processes
  - Reduces the effect of the matrix

- Determination of the amount of uranium in natural waters
  - Surface water, mine water, wells, water supply system, Soil contamination

- Barrier proposals

- Testing of ionex function
**Matrix effect**

- measurement with URAPLEX

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<tr>
<th>added salt, conc. (mol.L⁻¹)</th>
<th>NaCl</th>
<th>KCl</th>
<th>CaCl₂</th>
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<tr>
<td>100 μg.L⁻¹U 10 μg.L⁻¹U</td>
<td></td>
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<tr>
<td>1 × 10⁻⁵</td>
<td>103.3 ± 0.3  11.3 ± 0.1</td>
<td>102.4 ± 1.5  11.8 ± 1.0</td>
<td>102.5 ± 1.0  11.78 ± 0.02</td>
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<td>1 × 10⁻⁴</td>
<td>101.1 ± 1.3  11.8 ± 0.4</td>
<td>103.5 ± 0.1  13.5 ± 2.2</td>
<td>101.1 ± 1.9  10.6 ± 0.5</td>
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<td>1 × 10⁻³</td>
<td>96.8 ± 0.1   10.0 ± 0.1</td>
<td>98.2 ± 0.3   11.3 ± 0.1</td>
<td>97.5 ± 0.1   10.93 ± 0.01</td>
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<td>1 × 10⁻²</td>
<td>72.6 ± 3.9   7.7 ± 0.2</td>
<td>74.0 ± 0.8   7.5 ± 0.3</td>
<td>65.0 ± 0.1   6.6 ± 0.1</td>
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<td>111.4 ± 0.8  10.8 ± 0.3</td>
<td>102.4 ± 0.1  10.7 ± 0.1</td>
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<tr>
<td>1 × 10⁻⁴</td>
<td>116.2 ± 1.0  11.1 ± 0.01</td>
<td>106.0 ± 7.4  12.2 ± 0.1</td>
<td>102.8 ± 1.2  10.5 ± 0.7</td>
</tr>
<tr>
<td>1 × 10⁻³</td>
<td>109.4 ± 1.4  14.8 ± 0.1</td>
<td>101.6 ± 1.8  11.8 ± 0.2</td>
<td>109.9 ± 1.0  11.7 ± 0.2</td>
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<td>1 × 10⁻²</td>
<td>105.2 ± 0.8  12.4 ± 0.5</td>
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Results of europium speciation in the presence of succinic acid

Figure 2: Spectrum deconvolution of Eu(Suc)$^+$ complex (left) and three-dimensional time-resolved luminiscence spectrum of Eu(Suc)$^+$ complex (right).
Results of europium speciation in the presence of succinic acid

Figure 1: Distribution diagram of Eu in the presence of succinic acid as a function of pH (left), distribution diagram of Eu in the presence of succinic acid as a function of ligand-to-metal ratio (middle) and two-dimensional luminiscence spectra of samples containing Eu and succinic acid as a function of pH.
TRLFS and Am

- Up to now TRLFS studies have been already published with e.g. U(VI), U(IV), Eu(III), Cm(III) and others
- Particularly the europium is often used as a model of fission products from the group of lanthanides and minor actinides.
  - The 5f analog of europium(III) is americium(III).
- Despite the first observation of Am fluorescence emission is more than 25 years old only very few TLRFS investigations of the americium have been performed.
- The interest of Am complexes with TLRFS is limited by the short lifetime of Am (23.4 ± 1.2 ns in H₂O) which implies a dedicated detection system.
- Absorption of Am (\(^5\)L\(_6\)) 504 ± 1 nm (355, 337 nm), emission \(^5\)D\(_1\) → \(^7\)F\(_1\) (691 nm)
Short fluorescence decay time

- We tested the detection system from point of view
  - of sensitivity especially for weak signal
  - and short fluorescence decay time measurements.

- For a testing system some species of uranium carbonates were selected because of their relatively short fluorescence lifetime at certain condition.
  - $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ decay time is $40 \pm 5$ ns close to the pH ~ 8
  - $\text{SrUO}_2(\text{CO}_3)_3^{2-}$ is $18,4 \pm 1,5$ ns close to the pH ~ 8.
  - ...

- We were able to measure and calculate the decay times of such species even in this relatively short time scale.

- The speciation study for preliminary measurement were performed.
Thank you for your attention