8.2 Laser spectroscopy

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Introduction

Laser based spectroscopy techniques are very useful in the nuclear waste disposal field because of their ability to provide speciation information at trace levels or detection of colloidal species with highest sensitivity. Nowadays there are several laser based speciation methods used at INE – including LIBD, TRLFS, LIBS or LA-ICP-MS (the latter in collaboration with JRC Karlsruhe), mostly for studies in the context of the migration behavior of different actinide (An) species (or chemically homologue lanthanides (Ln)) after their hypothetical release from a nuclear waste repository. In order to broaden the TRLFS speciation capabilities at INE, new instrumental set-ups and upgrades of already existing instrumentation have been carried out in 2016. The design of a cell for high temperature/high pressure TRLFS measurements previously developed at INE has been improved to extend its applicability to high pH solutions or highly corrosive media. Additionally, a new portable set-up for luminescence measurements of uranyl species at ambient, high and low temperature has been designed and constructed, offering the capability to be coupled to different detection systems.

Development of a high-temperature/high-pressure cell for TRLFS measurements

Understanding An behavior in (geo)chemical systems is essential when assessing the safety of an envisaged nuclear waste repository. Hydrolysis or complexation mechanisms of these elements in aquifers possibly neighboring the repository site have been extensively studied during the past decades. Radionuclide (RN) migration or retention behavior in the multi-barrier system isolating the repository from the biosphere are not only influenced by the (geo)chemical environment, but also by thermal or pressure conditions given at or near the repository [1,2].

TRLFS is a laser based technique routinely used for An and Ln speciation studies. Although most of the experiments are performed at ambient temperature/pressure conditions, one needs to consider that the temperature in some parts of the repository after waste emplacement and closure might exceed 90°C due to the persistent radioactive decay heat. Nevertheless, a rather limited number of studies has been published in the past with the focus on possible effects of elevated temperatures on An/Ln complexation behavior [3-5]. With the aim to carry out systematic high-temperature experiments on radioactive solutions, about a decade ago a high-pressure cell for TRLFS and XAFS speciation studies was developed and successfully employed at INE (Fig. 1(a)) [6-8]. In this first design all parts of the cell (main body, windows (alternately quartz or beryllium), O-rings and PEEK

fittings) are in direct contact with the sample solution. A special Ti/Pd alloy for the main body and Kalrez® O-rings for window sealing – parts exposed to the highest temperatures during operation – were chosen for their high corrosion resistance. Those parts not exposed to high temperatures are made of PEEK. Quartz windows are embedded into the Ti/Pd body to easily couple a fiber optic bundle for delivery of the excitation laser beam and collection of the optical fluorescence. In case of XAFS measurements at the INE-Beamline, two of the quartz windows are replaced by metallic beryllium windows coated with Kapton® tape. The possibility to increase the working pressure up to 13 - 15 bar facilitates to suppress the formation of bubbles when analyzing samples at T > 100°C. With this original cell design, a regular filling requires sample volumes above 2 ml.

Although the original cell was working very reliably, some specific drawbacks exist. When analyzing highly corrosive media, persistent contamination of the cell body or even structural damages were detected. Due to these limitations and the high costs of the cell body material, the original cell was only used for specific analytical tasks with less corrosive samples and for combined TRLFS and XAFS studies.

In the last two years, an improved cell design has been conceived, built and recently successfully tested (Fig. 1(b)) in order to overcome the aforementioned drawbacks. The new cell design resembles an autoclave comprising a stainless-steel body with an interior holder for standard Suprasil® spectroscopy cuvettes. The holder can be moved up and down, allowing the adjustment of the cuvette height to the beam path – a very important feature when analyzing small sample volumes. Additionally, the cuvette holder can be easily exchanged to adapt to different cuvette geometries. As in the previous design, the new cell possesses four quartz windows allowing for a similar
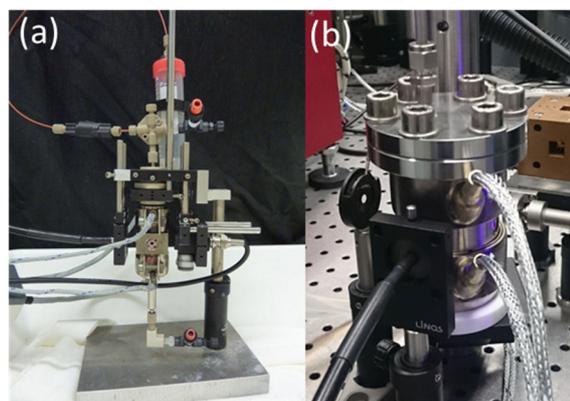
Fig. 1: *(a) Original high-temperature TRLFS cell built at INE. (b) Advanced cell design (cf. text for details).*
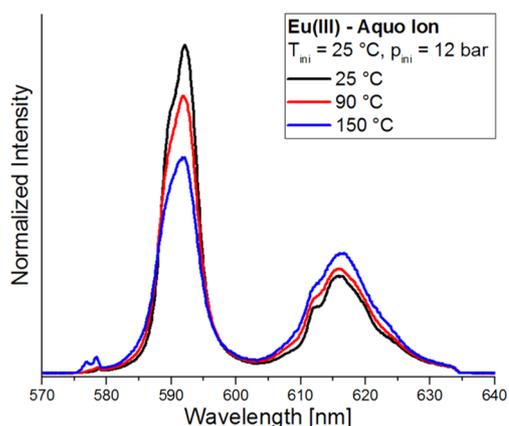
Fig. 2: *TRLFS of Eu(III) aquo ion measured with the new cell at 25, 90 and 150°C. Initial pressure: 12 bar; pressure at 150°C: ~20 bar.*

fiber optic coupling. The main advantages of the new design are: easy decontamination of cuvette and cell body, reduced sample volume, the possibility to use similar media for high-temperature and room temperature measurements, exclusion of sample induced cell damage and reduction of material costs.

As a result of preliminary tests, the cell has been proven to be airtight at 30 bars for almost 5 days with the maximum applied pressure being 66 bar. The first TRLFS signals measured for an aqueous sample containing the Eu(III) aquo ion at temperatures up to 150°C are plotted in Fig. 2. This experiment demonstrates that the new cell design is well applicable for An/Ln high-temperature speciation investigations. For these measurements the 3rd harmonic of a Nd:Yag Laser at 355 nm was used to pump a dye Laser, using Exalite 398 as a dye and an excitation wavelength of 394 nm. The fluorescence emission was dispersed with a polychromator and detected by using an intensified CCD camera. The new cell, with some small modifications, will be also available in the future for XAFS measurements at the INE-BL and ACT experimental stations at ANKA.

Development of a TRLFS set-up for U(VI) speciation studies

Uranium (U) is by far the most abundant radioactive element in nuclear wastes originating from various steps of nuclear power generation (including uranium mining, fuel fabrication or spent fuel disposal). U contaminants in the environment may be present in different chemical forms depending on the actual (geo)chemical conditions. Changes of the oxidation state will affect U solubility in aqueous solution and its sorption properties on mineral surfaces. Under oxidizing conditions U predominantly exists as U(VI) species, which is highly water soluble in form of the linear trans-dioxo uranyl cation (UO_2^{2+}).

TRLFS has been used for many years to follow uranyl migration in environmental compartments at rather low U concentrations [9-10]. Here the position of the emission bands in uranyl luminescence spectra

and the radiative lifetimes provide useful speciation information. Dedicated to this analytical purpose, a new portable luminescence excitation set-up has been designed and built at INE in 2016 (Fig. 3). The system will be applied to characterize UO_2^{2+} aqueous species or for uranyl analyses in soils or solid mineral phases (e.g., to follow carbonate induced dissolution of uranium containing precipitates possibly forming near a nuclear waste repository). Depending on the ligand system, uranyl luminescence emission at room temperature is very weak (e.g., for pure uranyl carbonate complexes), but easier to detect at liquid helium temperature [11]. To overcome this limitation and to offer high flexibility when simulating repository conditions, the new set-up allows analyses at ambient as well as at high and low temperatures.

The excitation source is a Nd:Yag laser (SpitLight Compact 100, InnoLas Laser) equipped with crystals for the 4th harmonic generation (266 nm), providing energies up to 30 mJ/pulse with 7 ns pulse duration and 10 Hz repetition rate. Excitation at this wavelength induces the typical green emission of the $(UO_2)^{2+}$ cation due to deactivation of a formally triplet ligand-to-metal charge transfer (LMCT) excited state. The laser has been installed in a carbon fiber reinforced optical bench from CarbonVision GmbH (300 mm × 900 mm). The bench is integrated into an aluminum rack with wheels. The entire instrument is movable and can be attached to different detection set-ups. In the optical set-up two dichroic mirrors positioned in a 90° configuration relative to the laser beam enable easy and fast alignment and increase the rigidity of the optical system. The beam energy is measured with a thermopile sensor (Newport Corpo-
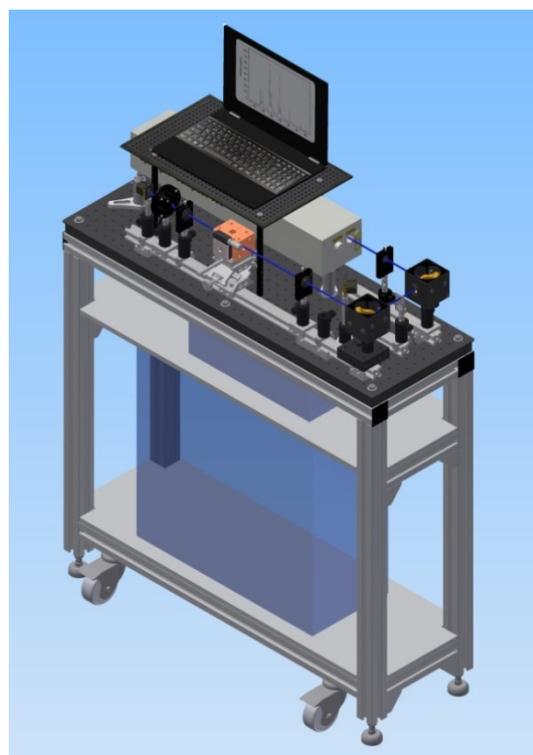
Fig. 3: *New portable laser excitation setup for TRLFS speciation studies.*

ration) by using a beam splitter between the two dichroic mirrors. Its value can be fixed between 0.5 and 10 mJ/pulse depending on the sample. Additional optical elements have been introduced in the set-up to reduce the primary inner filter effect (PIFE) and to avoid second order diffraction of the laser stray light at 532 nm.

For the analysis of liquid samples at room temperature the laser passes through a quartz cuvette (Helma) introduced in a home-built copper holder mounted on the optical bench and equipped with a mini stirrer. The luminescence propagating in a perpendicular direction to the laser beam is collected by a customized bundle-type fiber optic connected to the copper holder. The output of the fiber optic can be easily fed into different detection systems. During initial tests of the set-up it was coupled to the variable entrance slit of a Czerny-Turner Shamrock SR 303i spectrometer (Andor Technology) with a triple grating turret (400, 1200 and 2400 l/mm gratings) using an intensified CCD camera (Andor iStar) for luminescence detection. Time resolution is achieved by synchronizing the data acquisition by the CCD camera with the sync output signal delivered by the laser system. The time interval between the trigger signal of the laser and data acquisition by the camera is adjusted by an external digital delay generator (Stanford Research Systems). The delay values can be optimized depending on the lifetime of the analyzed species. For species with short luminescence lifetimes the delay inherent to the laser electronics as well as the insertion delay time of the CCD must be taken into account. The capability of the system to detect short lifetime species has been demonstrated by analyzing a cerium chloride ($CeCl_3 \cdot 7H_2O$) sample, obtaining a lifetime of 24.5 ns. Note that Cerium luminescence can be as well excited at a laser wavelength of 266 nm (the $CeCl_3$ crystal structure is of the UCl_3 structure type).

For TRLFS measurements at low temperature, one of the mirrors has been mounted on a kinematic magnetic base (Newport) to allow its easy removal and reinsertion into the beam path with high reproducibility. The portable laser table is fixed next to the He cryostat (CryVac). The samples introduced in the custom-made vacuum chamber of the cryostat with a capacity for two sample cuvettes can be cooled down to 4 K. Operation of the cryostat and the vacuum system are controlled by a home-made LabView program. The low-temperature sample luminescence is collected at an angle of 45° relative to the exciting laser beam by an optical fiber bundle connected to an x/y alignment stage coupled to the cryostat chamber. Detection of low-temperature TRLFS spectra is normally performed with the spectrometer/camera system described above. The luminescence of a $Cs[UO_2(NO_3)_3]$ crystal sample measured with the new set-up at room temperature is shown in Fig. 4 (a). When analyzing the same sample in the cryostat at liquid helium temperature (4 K) and with a 2400 l/mm grating, the electronic-vibrational spectra of the uranyl species in the crystal are easily discernible (Fig. 4 (b)) [12]. The
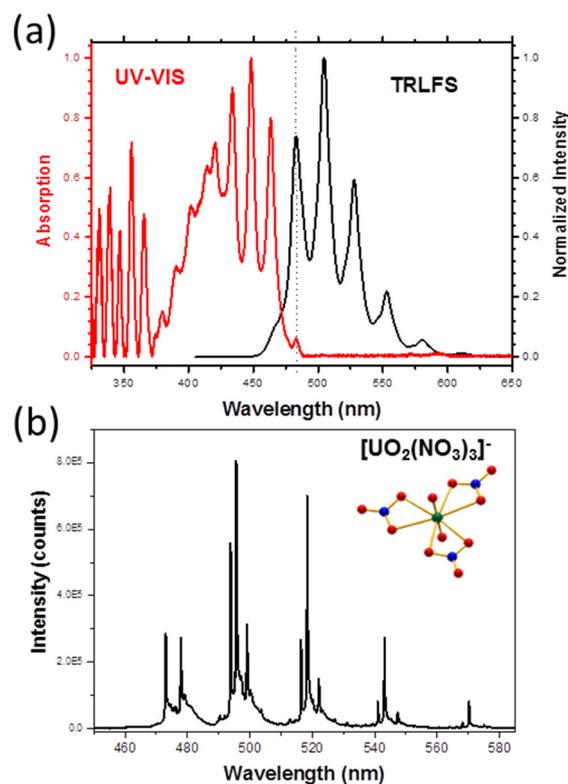
Fig. 4: TRLFS spectra of $Cs[UO_2(NO_3)_3]$ measured with the new set-up (a) at room temperature and (b) at 4 K. For comparison purposes the UV-VIS spectra of the same sample is shown in graph (a).

good spectral resolution allows to investigate the effect of the crystal lattice on the vibrational structure of the spectra.

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