

Laser-Based Spectroscopic Study on the Speciation of U(VI)-OH Complexes in Aqueous Media

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1. Introduction

Chemical speciation of actinides is fundamental for improving our understanding of their behavior under natural aquatic conditions for the safety assessment of a nuclear waste disposal [1]. In past decades, a number of spectroscopic techniques were developed for the direct speciation of ionic actinide species (hydrated metal ions, hydrolyzed ions and binary or ternary complexes) in an aqueous phase. Conventional absorption spectroscopy by using a UV/VIS spectrophotometer is a useful method for a speciation and most researchers are familiar with this method. But the poor detection sensitivity of a conventional UV/VIS spectrophotometer prevents the speciation of actinides in trace concentrations ($<10^{-6}$ M). Therefore laser-based spectroscopic techniques with a much higher detection sensitivity, such as TRLIF (Time-Resolved Laser-Induced-Fluorescence) and LPAS (Laser Photo-acoustic Spectroscopy), have been developed in recent years [2].

The aim of the present work is to estimate the performance of a newly constructed TRLIF system in our laboratory. In this paper, we report on the laser-induced fluorescence characteristics; e.g., emission spectra and lifetimes, of the UO_2^{2+} (free uranyl), $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and $(\text{UO}_2)_3(\text{OH})_5^+$ in an aqueous solution. The speciation sensitivity is estimated at about 10^{-7} M. We compared this data with the absorption and fluorescence spectra measured by a conventional UV/VIS spectrophotometer and fluorophotometer, respectively. These conventional methods provide a speciation sensitivity of about 10^{-4} - 10^{-5} M.

2. Experimental

A uranium stock solution was prepared with natural ^{238}U purified by a H_2O_2 precipitation in 6 M HClO_4 . U(VI) samples in the concentration range of 10^{-2} - 10^{-6} M with a pH range of 1.0-6.0 were prepared from a stock solution at room temperature being equilibrated with air. All the samples were appropriately diluted with 0.1 M HClO_4 (analysis grade, Merck), 0.1 M NaOH (Titrisol, Merck) and 0.1 M NaClO_4 solutions to maintain a 0.1 M ionic strength. For a purification, $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (analysis grade, Merck) was carefully recrystallized and then dissolved in ultra-pure water (Millipore). The pH measurement was carried out by a Ross-type combination glass electrode calibrated with several pH buffer solutions. The uranium concentration of a stock solution was determined by using a kinetic phosphorescence analyzer (Chemchek, KPA-11).

An experimental setup is shown in Fig. 1. The samples were irradiated by the third harmonic of a Nd:YAG laser (Spectron, 355 nm, 10 Hz, 10 ns pulse duration). The laser beam was focused into a quartz sample cell ($10 \times 10 \times 35 \text{ mm}^3$) by a plano-convex lens of 100 mm in focal length. TRLIF spectra of uranium were measured with a spectrometer (JOBIN-YVON, HR 250) coupled to an air-cooled photomultiplier tube (Hamamatsu, R955). Data processing was performed by a gated integrator and boxcar averager (SRS, SR250). Fluorescence lifetime measurement was performed by a digital oscilloscope (Tektronix, TDS 460A). For a comparison of the detection sensitivity, a UV/VIS spectrophotometer (CARY 3E) and a fluorophotometer (Edinburgh, FS900) were used.

3. Results and Discussion

Figure 2 shows the fluorescence spectrum of the UO_2^{2+} ion measured at a concentration of 1×10^{-5} M and pH 1. The well known six peaks are observed. The four main peaks (488, 509, 533, 559 nm) of the spectrum have a full-width at a half-maximum of about 12 nm. Figure 3 shows the fluorescence decay curve for the same data of Fig. 2. Fluorescence lifetime designated as a solid line, which is fitted to the data, is about 1.90 μs with the correlation coefficient of 0.99. The measured peak positions and lifetime agree well with the reported values in the literature [3,4].

Based on these fluorescence spectrum and lifetime of UO_2^{2+} ion, we can identify the polynuclear species such as $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$, which show wavelength shifts in their peak position with much longer lifetimes in the order of a few tens μs .

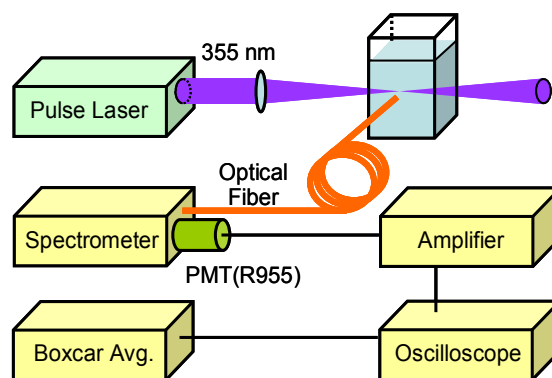


Figure 1. An experimental setup of the TRLIF.

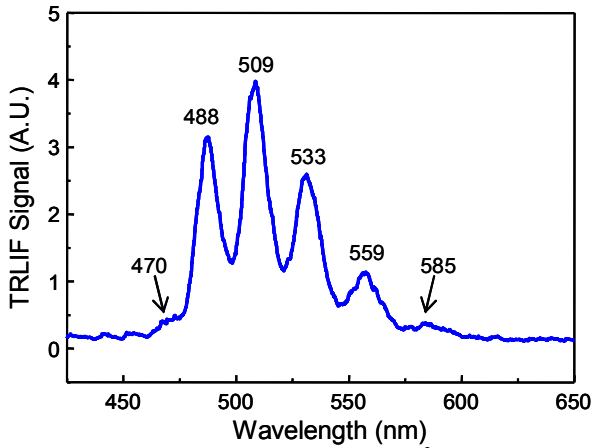


Figure 2. Fluorescence spectrum of UO_2^{2+} ion at uranium concentration of 1×10^{-5} M, pH 1, and $1 \mu\text{s}$ time delay for the gated integrator.

To estimate the speciation sensitivity, several fluorescence spectra were measured in the concentration range from 10^{-6} to 10^{-3} M at pH 1. The result is shown in Fig. 4. The symbols illustrate the peak value at the wavelength of 509 nm in the fluorescence spectrum. The calibration curve designated as a solid line illustrates a precise linear dependency with a regression coefficient of 0.99. The speciation sensitivity of the UO_2^{2+} species defined as a 3σ of the background is about 3×10^{-7} M. For polynuclear species formed at a pH value higher than 3.3, several times higher speciation sensitivity can be achieved due to a strong increase in an absorbance with a hydrolysis [5].

In the framework of the nuclear fuel cycle, speciation of actinides for macro concentration ($> 10^{-6}$ M) is also important for a routine analytical work. Thus, it is worthwhile to measure the sensitivity achieved by a conventional spectrophotometry. For the same samples of Fig. 4, speciation sensitivities of about 4×10^{-4} M and about 1×10^{-5} M for the UO_2^{2+} ion were measured by using a UV/VIS spectrophotometer and a fluorometer, respectively. In the case of quantitative analysis, the detection sensitivity was estimated to be one order of magnitude higher than the speciation sensitivity.

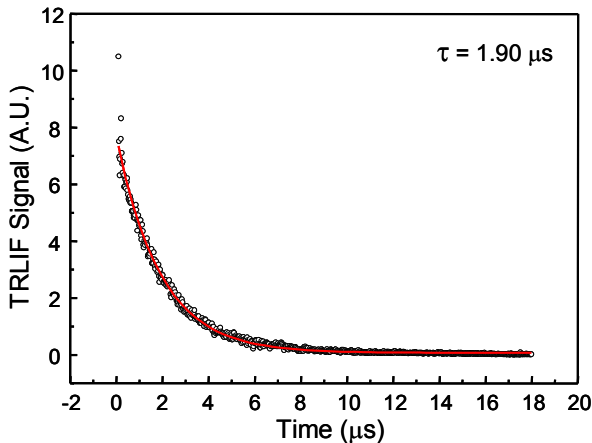


Figure 3. Fluorescence decay curve of UO_2^{2+} ion at uranium concentration of 1×10^{-5} M, pH 1, and wavelength of 509 nm.

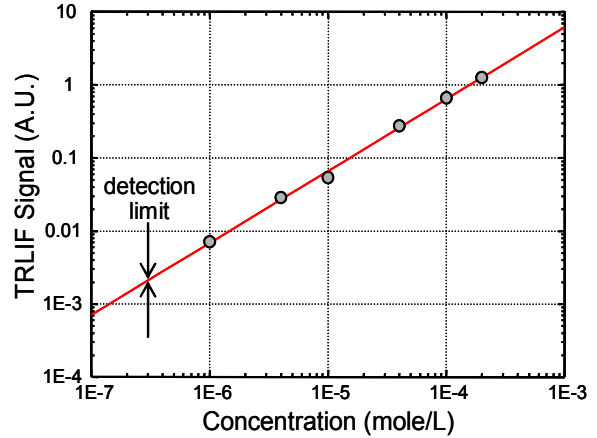


Figure 4. Calibration curve of UO_2^{2+} ion at the wavelength of 509 nm and pH 1. Speciation sensitivity is estimated to be about 3×10^{-7} M.

4. Conclusions

Chemical speciation of actinides at low concentrations (below the solubility limit) requires a very sensitive detection method. TRLIF experiments have been performed for the speciation of U(VI)-OH complexes in an aqueous media. Characteristics of the laser-induced fluorescence signals; e.g., spectral and time resolutions, were investigated for the UO_2^{2+} ion, and its hydrolyzed species, such as $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and $(\text{UO}_2)_3(\text{OH})_5^+$. Speciation sensitivity reached for the free uranyl ion is down to about 10^{-7} M in the present experimental geometry. The sensitivity can be improved to be about 10^{-9} M by increasing the light collection and detection efficiencies. We also report on the speciation sensitivity in the range of 10^{-4} - 10^{-5} M achieved by means of a conventional spectrophotometry.

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