

Laser-Based Spectroscopic Studies of Actinide Complexes: Uranium

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1. Introduction

In the last year, a new book titled “The Heaviest Metals: Science and Technology of the Actinides and Beyond” was designed by John Wiley & Sons to cover both the fundamentals and recent advances in the science and technology of the “heaviest metals,” i.e., the actinide and transactinide elements, starting with actinium, up to the current end of the periodic table [1]. This book will also be published online as part of the Encyclopedia of Inorganic & Bioinorganic Chemistry. We contribute one chapter entitled “Laser-Based Spectroscopic Studies of Actinide Complexes” and we would like to present description of the techniques and several representative application studies introduced in the chapter in a series of three poster presentations. Each poster presentation is specific to uranium, plutonium and americium.

The chemical speciation of actinide complexes is considered to be a key concept for the safe management of spent nuclear fuels in the back-end of a nuclear fuel cycle. Methodological approaches for chemical speciation have been reported in detail in several studies [2, 3]. However, it appears that most nuclear and chemical engineers who work in nuclear industries are not familiar with laser-based spectroscopic techniques. In this presentation, applications of the laser-based spectroscopic techniques to the chemical speciation of actinide complexes are introduced for those who are interested in the highly sensitive analytical techniques applicable in the nuclear industry.

In the Uranium part, the spectroscopic properties of hydroxo complexes of U(VI) in aqueous solutions are demonstrated as representative examples. The luminescence characteristics of U(VI) species are

measured by using time-resolved laser fluorescence spectroscopy (TRLFS). We demonstrate here that TRLFS is a sensitive and specific technique, enabling the speciation of trace amounts of natural uranium in groundwater without any sample pretreatment. As an application, a few μM of Ca-U(VI)-carbonate complex is identified as dissolved uranium species in groundwater.

2. Experimental Considerations

The U(VI) sample preparation procedure and the experimental setup of TRLFS are described in detail in the previous literatures [4, 5].

3. Results and Discussion

The U(VI)-hydroxo complexes are denoted as (1,0), (1,1), and (2,2) species and $(\text{UO}_2)_m(\text{OH})_n^{2m-n}$ is usually denoted as (m, n) for simplicity. It is well known that the (1,1) and (2,2) species show relatively different luminescence lifetimes compared to that of (1,0) species. However, a direct comparison of spectral shapes of (1,1) and (2,2) species is still of interest. Fig. 1 shows the luminescence spectra measured from solutions containing U concentrations of 100 μM at pH 4.26 and 10 μM at pH 4.79 in 0.1 M NaClO_4 . The spectral shapes of (1,1) and (2,2) species are directly compared in Fig. 1.

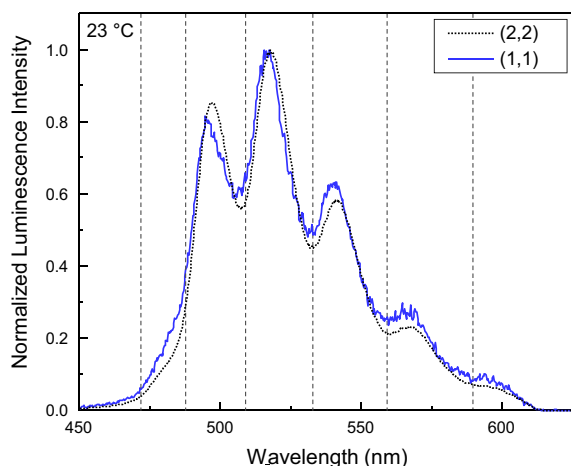


Fig. 1. Luminescence spectra of (2,2) and (1,1) species measured from solutions containing 100 μ M of uranium at pH 4.26 (dotted line) and 10 μ M of uranium at pH 4.79 (solid line). The dotted and solid lines are measured at $t_d = 20$ s, $t_w = 50$ s and at $t_d = 120$ s, $t_w = 50$ s, respectively. The vertical lines represent the peak positions of UO_2^{2+} .

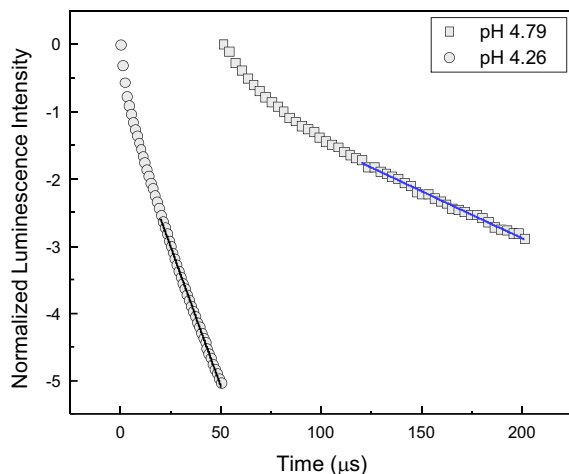


Fig. 2. The symbols represent the normalized luminescence intensity measured using the kinetic mode of ICCD. The solid lines represent fitting of the data to the linear regression. The luminescence lifetimes are $\tau = 12.0$ and 71.4 μ s at pH 4.26 and 4.79, respectively.

The symbols in Fig. 2 represent the normalized luminescence intensities in a natural logarithmic scale. For the solution at pH 4.26, the short- and long-lived species correspond to the (1,0) and (2,2) species, respectively. For the sample at pH 4.79, the short- and long-lived species correspond to the (2,2) and (1,1) species, respectively. The luminescence lifetimes of (2,2) and (1,1) species are determined to be 13.0 ± 2.0 and 57.4 ± 11.7 μ s, respectively.

4. Conclusion

The chemical speciation of actinides in aqueous solutions is important for the long-term isolation of high-level radioactive wastes. The laser-based spectroscopic technique, TRLFS is very useful for speciation studies of these elements in dilute concentrations. Speciation studies related to the identification of U(VI)-hydroxo and U(VI)-carbonate complexes in groundwater can be performed using TRLFS. The combined information on the luminescence spectrum with the luminescence lifetime, which depends on the nature of the ligands in aqueous solutions, makes the chemical speciation of U(VI) complexes at trace-level concentrations possible.

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