

4-5 Exploring the Valence of Uranium by Luminescence

— Time-Resolved Laser-Induced Fluorescence Spectroscopy for Short-Lived Species —

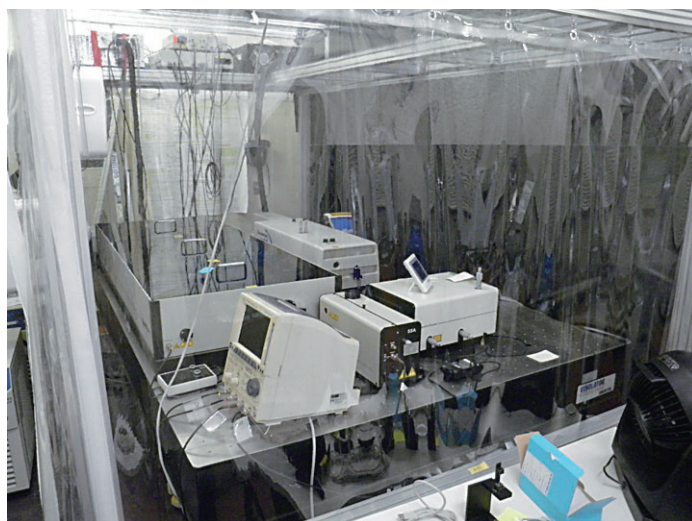


Fig.4-11 System using an ultrashort pulsed laser
The regenerative amplifier of a Ti:sapphire laser with a fast CCD camera hyphenated to a spectrometer enables us to obtain time-resolved luminescence spectra and lifetimes.

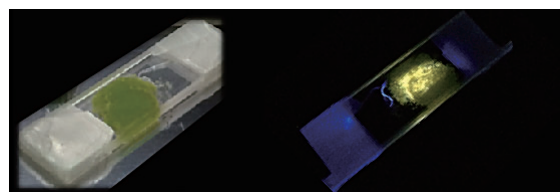


Fig.4-12 The color and luminescence of the U(IV) compound
The green U compound (left) emits white-to-light-yellow luminescence (right) under irradiation by ultraviolet light (365 nm).

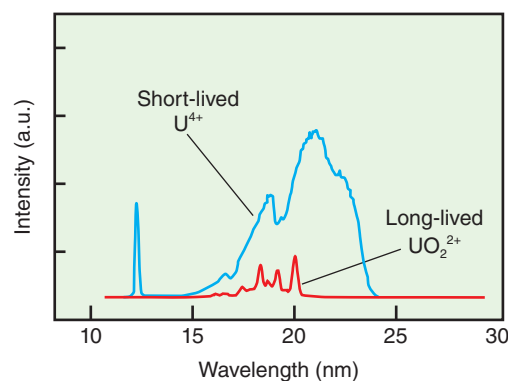


Fig.4-13 Time-resolved luminescence spectra of U_4 in $[emim][SCN]$
Upon the irradiation of ultraviolet pulsed light, emission from the short-lived U^{4+} occurs from 0–10 ns, and then that from the long-lived UO_2^{2+} occurs from 1–10 μs .

The environmental behavior of uranium (U), which is the major component of spent nuclear fuel, and techniques to analyze are key issues for future studies of the direct disposal of such fuel. U exhibits various valences. Among them, U(VI) is chemically favorable as the most stable state, which is abundant in the ambient condition. In the liquid state, the U(VI) ions bind oxygen, resulting in uranyl ions (UO_2^{2+}). Since these ions are intensely luminescent under the irradiation of UV light, this luminescence has been investigated in many analytical studies to understand the chemical state of U compounds. In contrast, U exists as uranous ions (U^{4+}) in reductive conditions such as in groundwater, where analytical observation of U^{4+} is of greater importance. The conventional absorption spectroscopy records spectra in which photon energy ranges widely from the ultraviolet to the near infrared. Conversely, the luminescence intensity is so weak and the luminescence lifetime so short that the measurement of U^{4+} might be difficult. Therefore, the spectral information available for U^{4+} is less than that for UO_2^{2+} and it is often challenging to determine the chemical states of U(IV) and U(VI) in a mixture solution by simultaneous observation.

Hence, we develop a laser system for the *in situ* detection of

U^{4+} using state-of-the-art laser technology with an intense light source. The laser, having ultra-short pulses of approximately 100 fs, was introduced to provide excitation pulses for samples having short-lived species. Moreover, a fast and highly sensitive CCD camera as was utilized as a detector to facilitate time-resolved laser-induced fluorescence spectroscopy (Fig.4-11). We aim to extend the spectral database of uranium in solutions.

To demonstrate the luminescence of U(IV) compounds, U_4 was dissolved in 1-butyl-3-methylimidazolium thiocyanate ($[emim][SCN]$), which is suitable for spectroscopy owing to its transparency (Fig.4-12). Consequently, we have succeeded in obtaining the luminescence data for U^{4+} and in distinguishing U(IV) from U(VI) in their mixture solution by changing the delay time after the irradiation of the excitation pulses; the lifetime of U^{4+} is 18.6 ns and that of UO_2^{2+} is 35.7 μs (Fig.4-13).

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Reference

Aoyagi, N. et al., Optical Properties of Tetravalent Uranium Complexes in Non-Aqueous Media, Journal of Radioanalytical and Nuclear Chemistry, vol.303, issue 2, 2015, p.1095-1098.