

Luminescence study of tetravalent uranium in aqueous solution

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The luminescence spectrum of U⁴⁺ in aqueous solution was observed in the UV-Vis region with the lifetime < 20 ns at room temperature by excitation light corresponding to the 5f–5f electronic transition. All the luminescence peaks were assigned to individual electronic transitions.

Luminescent transitions of actinide ions in solution have been studied on Am(III), Cm(III), Bk(III), Cf(III), Es(III)¹ and U(VI).² Some spectroscopic speciation methods of these elements based on their luminescence properties using laser-induced fluorescence were developed and made it possible to perform the direct analysis of their hydration numbers or ligand coordination states. On the other hand, luminescence of tetravalent and pentavalent actinides in solution has been practically unreported until now, although no theoretical or experimental fact has proved luminescent transition not to exist. In regard to this subject, we found there was a possibility of U⁴⁺ exhibiting luminescence in aqueous solution from an analysis of the transition energy level structure of the 5f electron. So far, U(IV) in solution has been considered to have no luminescence³ except for phosphate complex in solution.⁴ However, the energy gap⁵ of U⁴⁺ in aqueous solution between ¹S₀ and ³P₂ is so broad (about 17400 cm⁻¹) that the deexcitation process from ¹S₀ might include luminescence emissions. From this assumption, we carried out spectroscopic experiments on U⁴⁺ in aqueous solutions and discovered the emission spectrum consisting of 10 bands in the range 280 to 560 nm. This paper reports the first observation of luminescence of U⁴⁺ in aqueous solution.

U(IV) sample solutions were prepared by the hydrogen reduction, i.e., 0.01 M UO₂²⁺ in 1 M HClO₄ was reduced to U(IV) by bubbling pure hydrogen gas with a platinum black catalyst for 1 hour with 0.02 M hydroxylammonium chloride as a holding reductant. Absorption spectrum of the U⁴⁺ in D₂O solution was measured in the range of 200 to 1800 nm using a UV-VIS-NIR spectrophotometer (Shimadzu UV-3100 PC). Emission and excitation spectra were measured using a fluorescence spectrophotometer (Hitachi F-4500). Deconvolution of the absorption and emission spectra was performed using Lorentzian-Gaussian functions for peaks with fitting parameters such as peak wavelength, peak height and full-width at half maximum. Time-resolved laser-induced fluorescence spectroscopy (TRLFS) was also applied to U⁴⁺ in solution. In order to excite U⁴⁺ from the ³H₄ to the ¹S₀ state, a 245 nm pulsed laser beam was used, obtained by frequency doubling of a 490 nm beam from the dye laser using a second harmonic generator (Lambda Physik, SCAN mate UV-SHG) with BBO-I crystal. The 490 nm beam was generated from a pulsed (5 Hz) 308 nm output of a XeCl excimer laser (Lambda Physik, COMPex201) pumping Coumarin-102 (Lambda Physik) in methanol solution in a dye laser head (Lambda Physik, SCANmate2). The pulse power was typically 2 mJ per pulse and the pulse width was about 20 ns. The luminescence lifetimes and time-resolved emission spectra were measured using a photomultiplier tube (Hamamatsu, R3896) and a gated multichannel diode array (Princeton Instruments, SMA), respectively.

The 5f–5f transition energy level structures of U⁴⁺ in aqueous solution were obtained by the deconvolution of the absorption

spectrum. The terms of absorption bands of U⁴⁺ (aq) have been assigned from the comparison of the bands among U⁴⁺ free ion⁵, U⁴⁺ (aq) and U⁴⁺ in ThBr₄ matrix.⁶ The ¹S₀ level of U⁴⁺ (aq) is 40820 cm⁻¹ which is about 2800 cm⁻¹ lower than that of free ion. With reference to the derived absorption bands, U⁴⁺ in sample solutions was excited by UV or VIS lights corresponding to the respective 5f–5f transition levels, and then emission spectra were measured in the range 250 to 900 nm. When the excitation light is 245 nm (= 40820 cm⁻¹) which corresponds to the energy of ³H₄ → ¹S₀ transition, the emission spectrum is distinctly observed as shown in Fig. 1. On the other hand, no structured emission spectrum appeared when other excitation wavelengths were employed. The deconvolution of the emission spectrum shown in Fig. 1 gives 10 peaks at λ_{em} = 525, 409, 394, 345, 338, 335, 320, 318, 291 and 289 nm. The excitation spectra for four emission wavelengths, i.e., 525, 409, 335 and 320 nm corresponding to peaks of the emission spectrum, have similar excitation peaks at λ_{ex} = 245 nm. This shows that the luminescence seen in Fig. 1 is arising from the ¹S₀ level. These results mean that the emission of U⁴⁺ in aqueous solutions exists only on the deexcitation process from the ¹S₀ state. The relative energies and spacings for the 17 absorption and 10 luminescence transitions of the U⁴⁺ ion in aqueous solution are shown in Fig. 2 with their spectra. Comparison of the luminescence bands with absorption bands readily assigns observed luminescence to the following transitions: ¹S₀ → ¹I₆, ¹S₀ → ¹G₄, ¹S₀ → ³P₀, ¹D₂, ¹S₀ → ³H₆, ¹S₀ → ³F₃, ³F₄, ¹S₀ → ³H₅. The emission spectrum seems to have an enantiomorphic relationship with the absorption spectrum.

To estimate the luminescence lifetime, luminescence decay curves were measured using the TRLFS system. Each emission decay curve at λ_{em} = 320, 336, 410 nm indicated that the luminescence lifetime was about 20 ns which was almost equal to the pulse width of the excitation light. This means the actual luminescence lifetime of U⁴⁺ is shorter than 20 ns and cannot be estimated by our TRLFS system since the luminescence decay curve is overlaid with the excitation beam signal. In con-

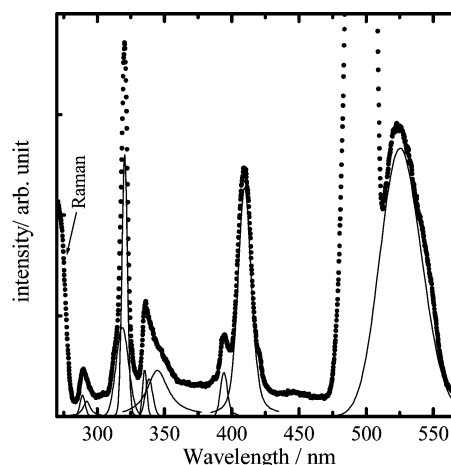


Fig. 1 Emission spectrum of U⁴⁺ in 1M HClO₄ at λ_{ex} = 245 nm.

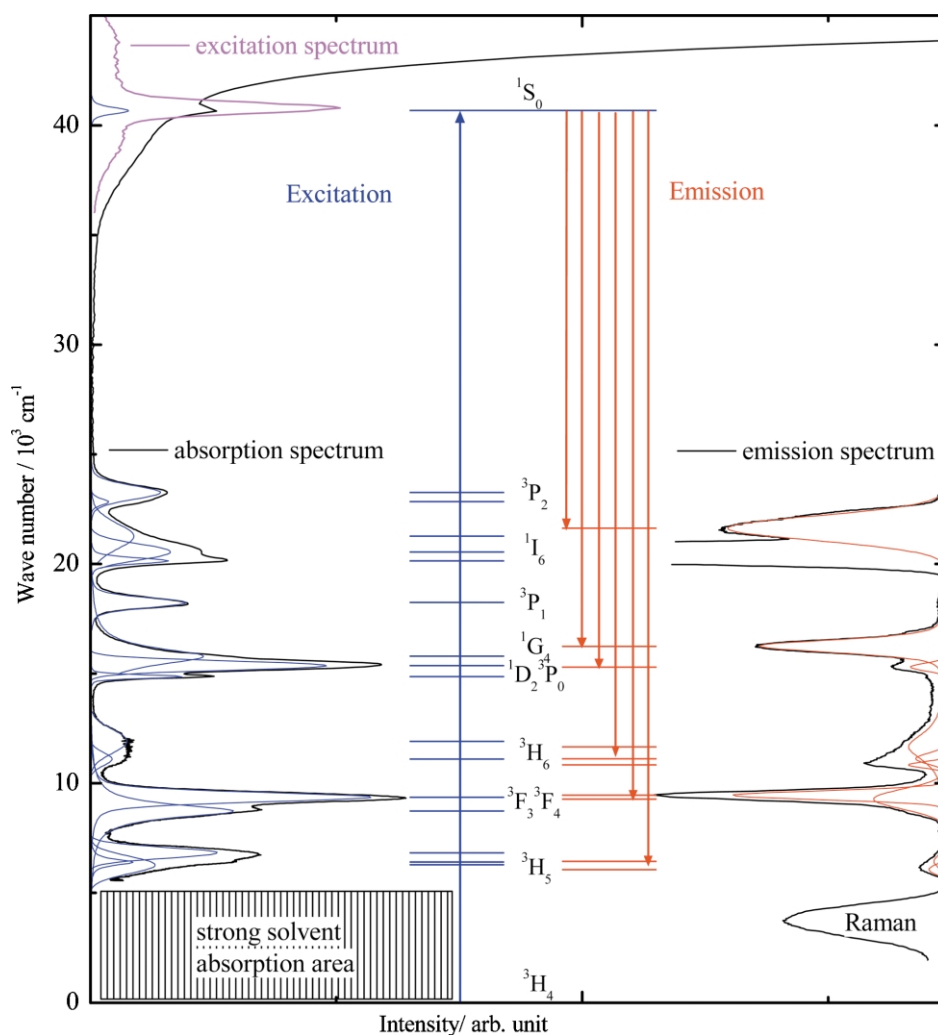


Fig. 2 Transition energies of the aqueous U^{4+} ion in perchlorate medium as determined from the resolved absorption and emission spectra.

sequence, a new laser system that provides the pulsed 245 nm beam having pico or femto second pulse width is required to measure the luminescence lifetime of U^{4+} . The intensities of laser-induced luminescence spectrum are much stronger than those measured with a fluorescence spectrophotometer since the excitation energy density of the laser pulse is much higher, therefore, the detectivity of the emission spectrum can be raised. At $[U^{4+}] = 1 \times 10^{-4}$ M where the absorption spectrum is hardly measurable quantitatively, the laser-induced luminescence system exhibits a clearly shaped spectrum of adequate intensity. This result suggests that the detection limit of the emission spectrum of U^{4+} in aqueous solution could possibly be down to the order of 10^{-6} M which is below the detection limit with LPAS⁷ (Laser-induced Photoacoustic Spectroscopy).

In conclusion, we have studied the luminescence property of tetravalent uranium in aqueous solution. The emission spectrum of U^{4+} is comparable to its absorption spectrum and its structure is definitely assigned to the terms of the 5f–5f electron transitions. These results imply the possibility of developing a

new speciation method for $U(IV)$ in aqueous solution based on this luminescence property, when an advanced laser technology becomes available enabling the measurement of its luminescence lifetime.

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