Time-resolved laser fluorescence spectroscopy of uranyl tricarbonate

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Introduction

Owing to the considerable concentration of carbonate in many natural waters, carbonate-complexed uranium (U) will become the major species when the U from a nuclear waste repository released into the environment comes into contact with the groundwater. Since the first observation of the fluorescence characteristics of Ca₂UO₂(CO₃)₃(aq) in calciumrich uranium mining-related waters [1], the following investigations have focused on the formation of ternary complexes of U(VI), CO32-, and alkaline earth metals using time-resolved laser fluorescence spectroscopy (TRLFS) [2]. In contrast to these complexes, TRLFS of pure uranyl tricarbonate, $UO_2(CO_3)_3^4$, was not performed for a long time owing to the very weak fluorescence intensity. Most recently, the fluorescence spectra of UO2(CO3)344 with a lifetime of 6-12 ns [3] and 11.6±0.1 ns [4] were reported. However, it is still generally considered that the pure uranyl tricarbonate species does not emit any fluorescence at room temperature because there have been no clear explanations in these studies [3] [4] regarding the reason for the failure of observation of fluolescence spectra in previous investigations [1] [2].

Discussion of Results

The objective of this work is to confirm the fluorescence characteristics of $UO_2(CO_3)_3^{4-}$ in detail. The peak wavelengths and lifetimes of $UO_2(CO_3)_3^{4-}$ were determined using several excitation laser wavelengths at 266, 355, 405, and 440 nm. Peak wavelengths in the fluorescence spectrum show hypsochromic shifts compared with those of UO_2^{2+} . The lifetime of 8.9 ± 0.9 ns was determined more accurately compared with the values reported in the literature [3] [4].

In addition, the experimental parameters (the insertion delay time of the intensified charge coupled device, primary inner filter effect, and the background emission of the sample solution), which may interrupt the measurement of weak fluorescence intensity owing to the very short lifetime, will be discussed.

[1] Bernhard *et al.* (1996) *Radiochim. Acta* **74**, 87-91. [2] Geipel (2006) *Coord. Chem. Rev.* **250**, 844-854. [3] Götz et al. (2011) *J. Radioanal. Nucl. Chem.* **287**, 961-969. [4] Lee & Yun (2013) *Dalton Trans.* **42**, 9862-9869.