

Luminescence properties of uranyl-acetate species

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Time-resolved laser-induced fluorescence spectroscopy (TRLFS) was applied to characterize uranium(VI)-acetate species based on their luminescence properties. In contrast to previous interpretations, no indications were detected for the existence of the 1 : 3 complex.

EXPERIMENTAL. TRLFS experiments were performed in solutions with 50 μM uranyl perchlorate and 0.25 M acetic acid (AcOH; one sample contains no AcOH and is marked with an asterisk) at an ionic strength of 1 M (NaClO_4). NaOH and HClO_4 were used to adjust the pH of the samples between 1 and 4. The samples were measured at 25 $^\circ\text{C}$ and -120 $^\circ\text{C}$. To excite the samples the fourth harmonic (266 nm, ~ 0.3 mJ) of a pulsed Nd:YAG laser (Continuum) was used and the luminescence was detected in a time dependent manner with an intensified CCD camera (Horiba Jobin Yvon IHR 550).

RESULTS. The static luminescence spectra of the test series are shown in Figs. 1 and 2. The spectra were taken at the same delay time after excitation and were normalized in Fig. 2 to emphasize the spectral changes. The band positions and lifetimes were summarized in Tab. 1.

The band positions and the lifetime of the sample without AcOH can be assigned to the free uranyl-ion and are in accordance with literature values.^[1] The addition of AcOH and the increase of the pH, which correlates with the total amount of deprotonated acetate, lead to a quenching of the uranyl-luminescence (Fig. 1, left) and a decrease of the uranyl lifetime. This behavior was extensively discussed in literature and is caused by static and dynamic quenching.^[2] Hence, the $\text{UO}_2(\text{AcO})^+$ complex showed no luminescence properties. In a second phase (Fig. 1, right), the luminescence intensity increases and the emission bands were shifted to higher wavelengths (Fig. 2, left). A new band occurs at 460 nm. These changes can be assigned to the formation of the $\text{UO}_2(\text{AcO})_2$ complex, showing a very short luminescence lifetime of 0.48 μs . To minimize the dynamic quenching the luminescence properties were measured at -120 $^\circ\text{C}$. Below pH 2.2, a constant lifetime of 319 μs and no band shifts were observed for the uranyl-ion at -120 $^\circ\text{C}$ (Fig. 2, right) which is in good agreement with literature data.^[1] Significant band shifts are only present at pH values above pH 2.4, which can be assigned to the formation of the $\text{UO}_2(\text{AcO})_2$ complex with a much longer lifetime of 922 μs compared to those measured at 25 $^\circ\text{C}$.

Under the chosen experimental conditions, the third uranyl-acetate complex $\text{UO}_2(\text{AcO})_3^-$ should be formed, according to published stability constants for uranyl-acetate species. But no spectral changes (e.g. band shifts, quenching) or a third lifetime were observed, giving evidence for the 1 : 3 complex at 25 $^\circ\text{C}$ and -120 $^\circ\text{C}$. Since these results give sufficient reasons to assume that the 1 : 3 complex does not exist and are therefore in big contrast to previous investigations, more effort will be put in this apparently simple system to clarify the formed species.

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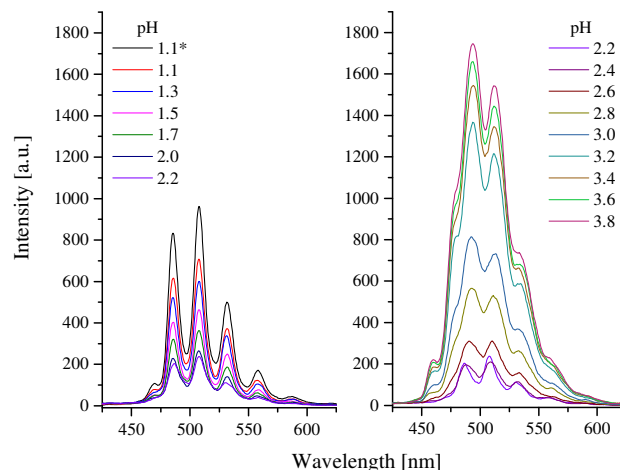


Fig. 1: Luminescence spectra of uranyl-acetate samples at 25 $^\circ\text{C}$ ($[\text{UO}_2^{2+}] = 50$ μM , $[\text{AcOH}] = 0.25$ M, $I = 1$ M (NaClO_4)).

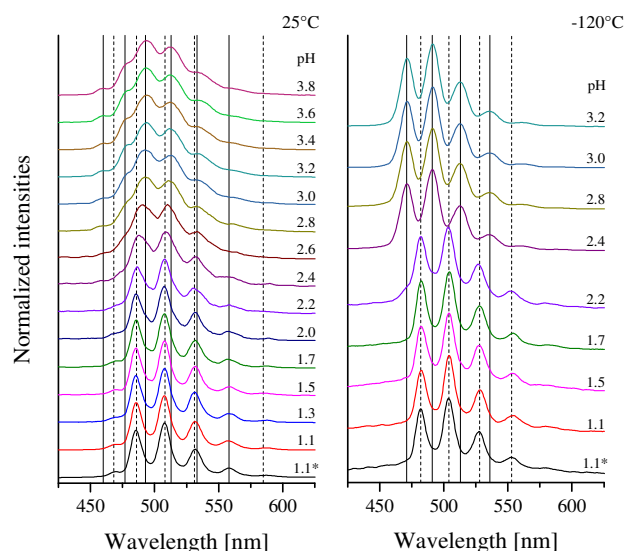


Fig. 2: Normalized luminescence spectra of uranyl-acetate samples at 25 $^\circ\text{C}$ (left) and -120 $^\circ\text{C}$ (right).

Tab. 1: Emission bands and calculated lifetimes.

Species	Emission Bands (nm)		Lifetimes (μs)	
	25 $^\circ\text{C}$	-120 $^\circ\text{C}$	25 $^\circ\text{C}$	-120 $^\circ\text{C}$
UO_2^{2+}	468, 486, 508, 532, 558, 585, 619	482, 504, 528, 553	2.11 ± 0.04 *	319 ± 22
Species 2 ($\text{UO}_2(\text{AcO})_2$)	460, 493, 513, 533, 562, 477	471, 491, 513, 536	0.48 ± 0.03	922 ± 11

[1] Günther, A. *et al.* (2011) *Radiochim. Acta* **99**, 535–542.

[2] Sladkov, V. (2014) *J. Photochem. Photobiol., A* **295**, 40–45.