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Deactivation and luminescence lifetimes of excited uranyl ion and its fluoro complexes

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Abstract

The luminescence decay of uranyl fluoride complexes has been studied in broad fluoride concentration range. Biexponential decay were found with a shorter lifetime component varying between 1.7 and 19.1 μs, while a longer component is in the range from 49 to 156 μs. The fluoride saturated solution exhibits single exponential decay with a lifetime of 207 μs. The activation parameters for the decay of $[UO_2F]^+$ complex have been determined. The results have been compared to other studies and interpreted in terms of ligand exchange, which is proposed as a new deactivation pathway for excited uranyl fluoro complexes. © 1998 Elsevier Science S.A.

Keywords: Uranyl; Uranyl fluoro complexes; Luminescence; Lifetime; Deactivation

1. Introduction

The luminescence of uranyl compounds is known for a long time and was studied extensively. The reactivity of the excited uranyl ion and the luminescence quenching by various inorganic and organic substances is of particular interest [1–4]. Halogen and pseudohalogen ions act as quenchers [3], except fluoride which strongly enhances the uranyl luminescence.

Moriyasu et al. [4] studied the luminescence of uranyl–fluoro complexes with different coordination number. They determined the lifetime of the aquo ion, the 1:1 and 1:2 complexes, and proposed similar lifetimes for the higher coordinated complexes. They assumed that the formation of the 1:1 complex is slower than the deactivation rate of the uranyl aquo ion, but in case of two or more coordinated fluorides, equilibrium is attained between these complexes within their luminescence lifetimes.

Szabó et al. recently studied the ligand exchange reactions of uranyl–fluoride complexes by NMR spectroscopy [5,6]. They identified 15 different exchange pathways with two of them dominating: fluoride ion exchange between F^- (or HF) and one of the uranyl species, and fluoride exchange between two complexes. They determined the exchange rate constants and proposed an Eigen–Wilkins type mechanism.

The goal of the present study is to examine the luminescence behavior of the uranyl–fluoro complexes and use the above mentioned data to interpret the results.

2. Experimental details

The preparation of uranyl perchlorate stock solution was described earlier [7]. Sodium fluoride (Kanto) was recrystallized from distilled water. The ionic strength was kept at 1 mol dm^{-3} by $NaClO_4$ (GR grade, Merck). The solutions were prepared in distilled water for fluorometry (Kanto).

Most of the measurements were carried out as titrations by changing the total fluoride concentration in the sample while the total concentration of UO_2^{2+} was kept at 10 m*M*. The pH of the starting solutions was adjusted to 2 in order to avoid formation of uranyl–hydroxo complexes. These species interfere because of their high fluorescence intensity and long lifetime [7,8].

The excitation wavelength was 337 nm and the light source was a nitrogen laser (Molectron UV-22). The emission was detected by a photomultiplier (Hamamatsu R1509) mounted on a grating monochromator (Ritsu

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MC25NP). A digital memory (Iwatsu DM2350) controlled by a personal computer was used for data collection.

All the measurements were made at 25.0°C except the determination of activation parameters when the temperature was varied from 17 to 38°C.

3. Results

Time-resolved luminescence of uranyl samples was measured at 509 nm. The fluorescence decay in the presence of multiple emitting species can be described as:

$$I(t)=\sum_{i=0}^{5} I_{0,i} \exp\left(-\frac{t}{\tau_i}\right), \tag{1}$$

where i is the number of coordinated fluorides and τ_i is the lifetime of the ith species ($\tau_i = \mathrm{k}^{-1}$). The preexponential factor $I_{0,i}$ equals the initial fluorescence intensity and consists of several terms:

$$I_{0,i} = (I_{\mathrm{exc.}} l)(\varepsilon_i \eta_i) C_i. \tag{2}$$

Here $I_{\mathrm{exc.}}$ stands for the laser intensity, l the optical pathlength, ε_i is the molar absorbtion coefficient, η_i is the fluorescence quantum yield and C_i is the concentration of the ith species.

The luminescence decay of the uranyl ion at pH 2 was single exponential with a lifetime of 1.83 μs, in good agreement with the literature data [7,8].

After addition of a small amount of fluoride a second component appeared in the decay curve with a much longer lifetime. According to equilibrium calculations and Moriyasu et al. [4] this belongs to the 1:1 complex.

The decay rate of these species is temperature dependent, and the activation parameters were determined. Fig. 1 shows that the Arrhenius plots are linear. For the uranyl ion, the activation energy was 44.3±1.5 kJ mol^{-1}, and the activation entropy was 13.7±5 J mol^{-1} K^{-1}, in agreement with the literature data [8]. For the $[UO_2F]^+$ complex, these parameters were 29.4±0.6 kJ mol^{-1} and −63.6±2 J mol^{-1} K^{-1}, respectively.

Fig. 2 shows the concentration distribution of uranyl species, free fluoride and HF in a broad fluoride concentration range. The calculations were made by using the stability constants determined by Ahrland and Kullberg [9] and Ferri et al. [10] (for the $[UO_2F_5]^{3-}$ complex).

The decay curves of the first few samples were biexponential as shown in Fig. 3. The contribution of the longer lifetime increases with fluoride concentration and suppresses the shorter component. However, use of only single exponential fit was unsatisfactory even in the high fluoride concentration range.

After addition of solid NaF to the last sample, its decay curve became single exponential with $\tau = 207$ μs.

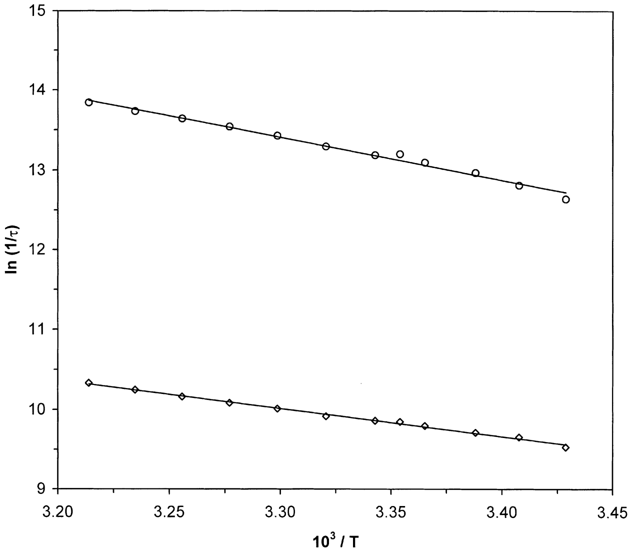

Fig. 1. Temperature dependence of the decay constants of the uranyl aquo ion (circles) and the $[UO_2F]^+$ complex (diamonds) at pH=2. $[UO_2^{2+}]_{\mathrm{tot.}}=$ 10 m*M*, $[F^-]_{\mathrm{tot.}}=1$ m*M*.

4. Discussion

Fig. 4 shows the lifetimes determined by fitting double exponentials. The longer component has a value around 50 μs in the first four samples, then starts to increase. The limiting value seems to be around 200 μs as measured in the saturated solution.

Moriyasu et al. [4] reported 150 μs as the maximum lifetime and it was already reached at $[F^-]$ =60 mM. They discussed the effect of fluoride exchange on the lifetime and proposed that its rate is high enough to attain equilibrium between the $[UO_2F]^+$ and $[UO_2F_2]$ complexes

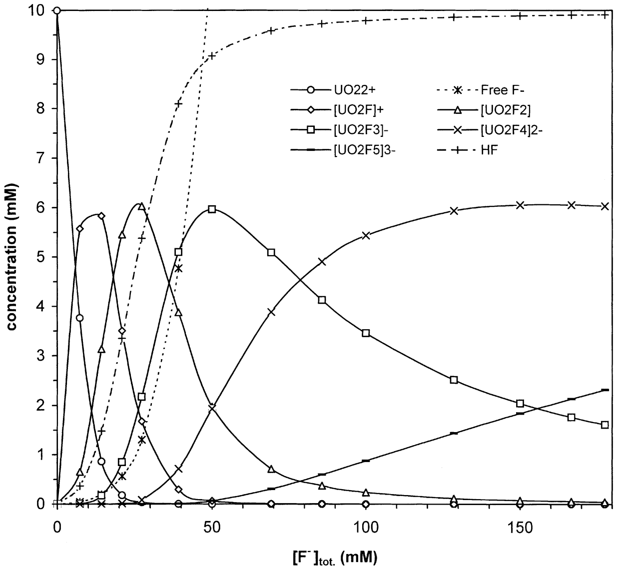

Fig. 2. Concentration distribution of the uranyl fluoro complexes as a function of total fluoride concentration. Starting pH=2, $[UO_2^{2+}]_{\mathrm{tot.}}=10$ m*M*.

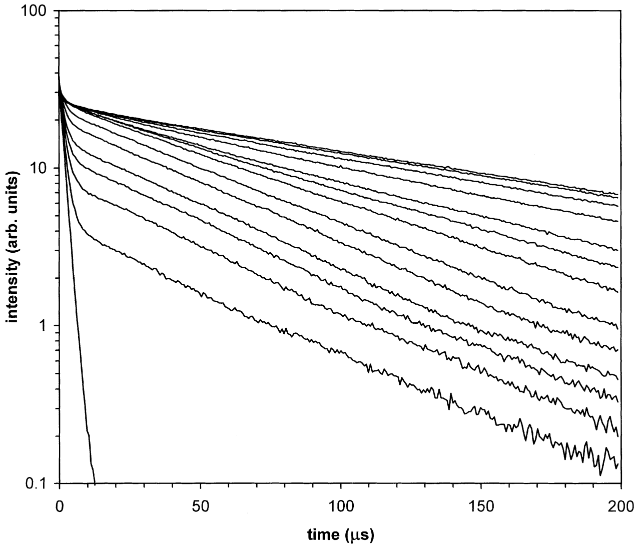

Fig. 3. Luminescence decay of samples from zero fluoride concentration to $[\mathrm{F}^-]_{\mathrm{tot.}}=0.18$ *M*. The curves from the bottom to the top correspond to the points of Fig. 2 from the left to the right. (For the sake of simplicity, only the first 200 μs was plotted, but during the measurements the decay was followed until it completely faded into the noise).

within the decay time, resulting in single exponential decay. In their model, quenching by water was the main deactivation pathway of the excited species.

According to Szabó et al. [6] the main exchange pathways in the system are:

$$[\mathrm{UO}_2^*\mathrm{F}_x]^{2-x} + [\mathrm{UO}_2\mathrm{F}_y]^{2-y} \rightleftharpoons \mathrm{UO}_2\mathrm{F}_x]^{2-x} + [\mathrm{UO}_2^*\mathrm{F}_y]^{2-y} \tag{3}$$

$$[\mathrm{UO}_2\mathrm{F}_x]^{2-x} + \mathrm{H}^*\mathrm{F} \rightleftharpoons [\mathrm{UO}_2^*\mathrm{F}_x]^{2-x} + \mathrm{HF} \tag{4}$$

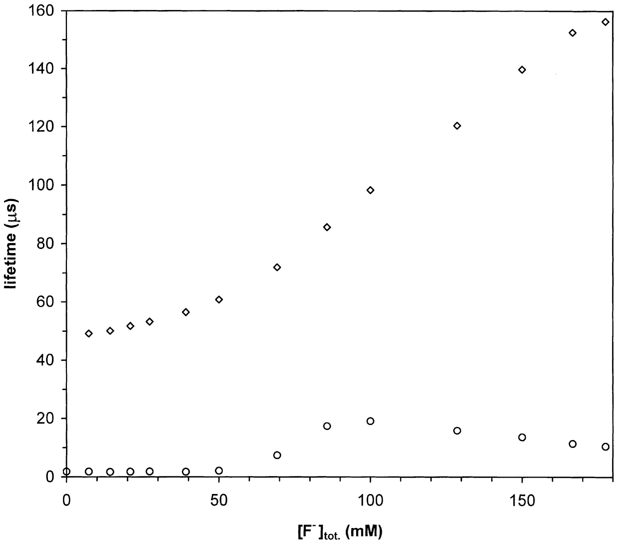

Fig. 4. The long (diamonds) and short (circles) lifetime components determined by fitting a double exponential to the decay curves shown in Fig. 3, plotted as a function of the total fluoride concentration.

$$\mathrm{UO}_2^{2+} + \mathrm{HF} \rightleftharpoons [\mathrm{UO}_2\mathrm{F}]^+ + \mathrm{H}^+ \tag{5}$$

$$[\mathrm{UO}_2\mathrm{F}_x]^{2-x} + {}^*\mathrm{F}^- \rightleftharpoons [\mathrm{UO}_2^*\mathrm{F}_x]^{2-x} + \mathrm{F}^-. \tag{6}$$

The rate constants of these reactions have a value around 5×10^4 M^{-1} s^{-1} (at -5°C) except those involving 4 or 5 coordinated complexes with fluoride. At room temperature these rates are comparable with the measured deactivation rates of fluoro complexes, so it is reasonable to assume that the ligand exchange and the deactivation occurs in the same step, simultaneously, because excitation weakens the uranyl–fluoride bond, and the leaving ligand can take away the excess energy. This is supported by the reported activation parameters for the reaction:

$${}^*\mathrm{UO}_2^{2+} + [\mathrm{UO}_2\mathrm{F}]^+ \rightleftharpoons [{}^*\mathrm{UO}_2\mathrm{F}]^+ + \mathrm{UO}_2^{2+} \tag{7}$$

where $\Delta H^{\neq}=31.2$ kJ mol^{-1} and $\Delta S^{\neq}=-56.2$ J mol^{-1} K^{-1} [6]. These are close to the ones obtained in this study for the deactivation of the $[\mathrm{UO}_2\mathrm{F}]^+$ complex.

The first four points in Fig. 4 show similar lifetime components (about 50 and 1.75 μs) indicating that the first and second complexes have similar deactivation mechanisms, presumably the fluoride exchange with the uranyl aquo ion, whose presence is indicated by the constant shorter lifetime component. The necessity of double exponential fitting for samples with negligible free uranyl ion concentration ($[\mathrm{F}^-]>40$ m*M*) hints at a different decay mechanism or slow exchange between complexes with different lifetimes (see the increasing shorter lifetime component in Fig. 4).

The difference between our results and the ones of Moriyasu et al. can be explained by the role of HF in the exchange process [Eqs. (4) and (5)]. Their experiments were carried out in 0.1 *M* HClO_4, where the concentration of HF is high enough to take part in the exchange and equilibrium can be reached even in low fluoride concentration.

NMR measurements showed that the exchange reactions for the $[\mathrm{UO}_2\mathrm{F}_4]^{2-}$ and $[\mathrm{UO}_2\mathrm{F}_5]^{3-}$ complexes are much faster [6,10]. The decay curves become closer to exponential in the case of high fluoride concentration (Fig. 3), which indicates rapid ligand exchange.

These results suggest the necessity for further investigations involving the use of time resolved fluorescence spectroscopy to identify the emitting species. These are in progress and the results will be presented in a forthcoming paper.

Acknowledgements

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