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Emission Spectra of the Uranyl Ion in Aqueous Solutions at 77 K

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The deactivation mechanism of the photo-excited dioxo-uranium(VI) (uranyl) ion, $^*UO_2^{2+}$ in aqueous solutions has been studied extensively since the late 1970s.¹⁻⁷ However, the mechanism remains a matter of controversy. The luminescence of $^*UO_2^{2+}$ in aqueous solutions has been reported to decay exponentially or not with the lapse of time depending on experimental conditions. It is of greatest interest that the luminescence decay is biexponential in the aqueous solutions where the uranyl ion is predominant. Marcantonatos *et al.* measured lifetimes with a single photon counting nanosecond spectrometer, and interpreted the biexponential decay in terms of exciplex formation between $^*UO_2H^{2+}$ and UO_2^{2+} .²⁻⁴ In their interpretation the formation of UO_2^+ and U(IV) ions are involved, but no evidence has been observed yet for the formation of the U(IV) ion even by the long-time exposure of UO_2^{2+} ion in aqueous solutions to light. On the other hand, Formosinho *et al.* studied excited uranyl decays using nanosecond flash-photolysis apparatus with a pulsed nitrogen laser.^{5,6} They proposed the deactivation mechanism

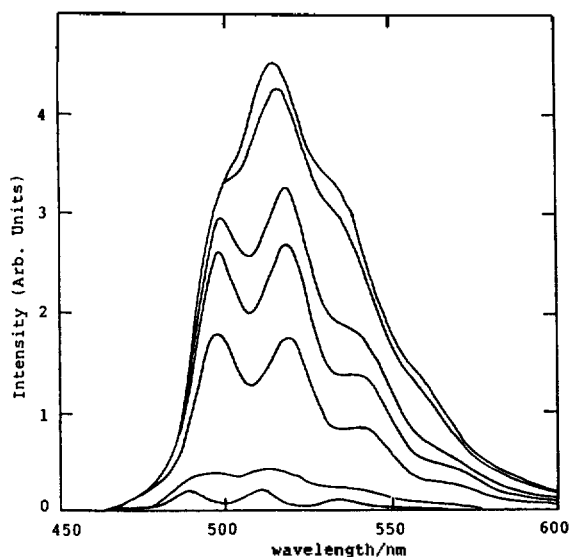


Figure 1. Emission spectra of uranyl ion in aqueous perchlorate solutions as a function of pH at ambient temperature: $[UO_2^{2+}]_T = 0.01$ M; pH (from the bottom) = 2.24, 3.01, 3.36, 3.49, 3.64, 3.76, and 3.82.

involving a reversible crossing process between two almost degenerate states of $^*UO_2^{2+}$. It has been reported that the luminescence decay of $^*UO_2^{2+}$ is four times or more faster than that of the other emitting species or state (*X).

In order to establish the identity of *X , we investigated emission spectra of UO_2^{2+} ion in aqueous solutions at ambient temperature and 77 K. The emission spectra were measured by using a Hitachi model 850 fluorescence spectrophotometer. Uranyl perchlorate solutions were prepared from $[UO_2(H_2O_9)](ClO_4)_2$, which was synthesized by the same method as described in a previous paper.⁸ The total uranyl ion concentration, $[UO_2^{2+}]_T$ of all sample solutions was 0.01 M (1 M = 1 mol dm⁻³). The pH readings of the solutions were carried out on a Toa IM-20E pH meter. The pH was adjusted with NaOH and HClO₄ solutions.

Figure 1 shows the emission spectra (excitation at 337 nm) of UO_2^{2+} ion in aqueous solutions as a function of pH at ambient temperature. The spectra changed markedly with increasing pH and thereby increasing hydrolysis products of UO_2^{2+} ion. The major hydrolysis products are known to be $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$ ions.⁹ The red shift of the bands corresponding to the $0' \rightarrow 0''$ transition is considered to be due to the formation of the hydrolysis products. This fact is in good agreement with the low-field shift of ¹⁷O NMR resonances of uranyl oxygen atoms by the hydrolysis because ¹⁷O chemical shifts of uranyl oxygen atoms in uranyl complexes increase with the decrease in their lowest electronic transition energies.^{10,11} The other characteristic aspect of the emission spectra is that band intensities increased significantly as hydrolysis proceeded. The intensities varied with pH to a greater degree than did those expected only from a consideration of change in the distribution of uranyl species in the ground state. For example, the emission spectrum at pH 3.36 is considerably different from that of $^*UO_2^{2+}$ at pH 2.24, in spite of the fact that the ratio of $[(UO_2)_2(OH)_2^{2+}]$ to $[UO_2^{2+}]$ is only ca. 0.05 at pH 3.36.

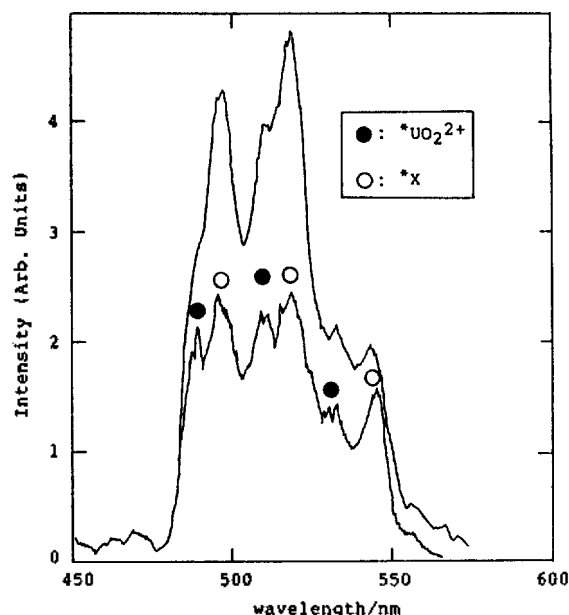


Figure 2. Emission spectra of uranyl ion in aqueous perchlorate solutions at 77 K: $[\text{UO}_2^{2+}]_T = 0.01 \text{ M}$; $\text{pH} = 3.32$ and 3.58 (upper) at 25°C .

The emission spectra measured at 77 K, though they were of low signal-to-noise ratio, were well resolved (Figure 2). Each band observed at ambient temperature was splitted into two bands. The main bands at shorter wavelengths were at almost the same positions (488, 510 and 533 nm) as the emission bands of the excited uranyl ion, which were measured in strongly acidic solutions at ambient temperature. Therefore, the bands are assigned to those of $^*\text{UO}_2^{2+}$, while the other bands at longer wavelengths to those of $^*\text{X}$ in question. Comparison of the emission spectra of $^*\text{UO}_2^{2+}$ and $^*\text{X}$ shows that the band at 533 nm red-shifts to a greater degree than those at 488 and 510 nm. The emission spectrum of $^*\text{X}$ is similar to that reported by Formosinho *et al.*,⁵ which was obtained from the comparison of the emission spectra at low and high temperatures. The proportion of $(\text{UO}_2)_2(\text{OH})_2^{2+}$ is expected to be higher at 23°C than at 4°C under their experimental conditions because hydrolysis reactions of UO_2^{2+} ion are endothermic.⁹

It may be concluded on the basis of the previous discussion that two emitting species responsible for the biexponential decay of uranyl luminescence are $^*\text{UO}_2^{2+}$ and $^*(\text{UO}_2)_2(\text{OH})_2^{2+}$ ions. Tomiyasu *et al.* also assigned $^*\text{X}$ to $^*(\text{UO}_2)_2(\text{OH})_2^{2+}$ ion in their study on rates of luminescence decay of various uranyl complexes in aqueous solutions.⁷ The question now arises as to why the luminescence intensity of $^*(\text{UO}_2)_2(\text{OH})_2^{2+}$ is stronger than that of $^*\text{UO}_2^{2+}$. This question may be solved by considering the following facts: upon the electronic excitation the transition probabilities of hydrolysis products are higher than that of UO_2^{2+} ion¹⁰ and $^*(\text{UO}_2)_2(\text{OH})_2^{2+}$ is more long-lived than $^*\text{UO}_2^{2+}$.

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Multienzyme-Catalyzed Synthesis of D-Fructose-1,6-Diphosphate

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Enzymes are now widely accepted as useful catalysts for enantioselective transformations.¹⁻⁴ Much of the work concerned with enzymes as synthetic catalysts has centered on reactions involving one or two enzymes, partly because they are operationally simple and straightforward. Examples are the reactions catalyzed by lipases,⁵ esterases,⁶ acylase I,⁷ alcohol dehydrogenases,⁸ glycerol dehydrogenase,⁹ lactate dehydrogenase,¹⁰ glycerol kinase,¹¹ and aldolases.¹² In these reactions the enzymes transform their substrates with high stereoselectivity and provide optically active products. Thus the transformations by these enzymes offer alternative routes to a wide variety of chiral molecules.

On the other hand, less effort¹³ has focused on reactions involving three or more enzymes cooperating in sequence or in parallel. Although they look more complex and less practical, multienzyme systems offer opportunity to carry out multistep processing of substrates in one pot with advantage that processes of seaperation and purification or protection