

Energy transfer and quenching processes of excited uranyl ion and lanthanide ions in solutions.

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Deactivation processes of photoexcited uranyl ion by various lanthanide ions in aqueous solution were studied. Each lanthanide ions show different interaction with excited uranyl ion depending on its lowest excited energy level, the number of 4f electrons and the acid concentration of the solution.

keywords: excited uranyl ion, energy transfer, quenching, lanthanide ion

1. INTRODUCTION

Photochemistry of actinide and lanthanide ions have been attracted increasing interests in the field of inorganic photochemistry. We have been participated in the investigation of excitation process of lanthanide ions and revealed sensitization phenomenon of dysprosium ion by excited uranyl ion in aqueous system [1].

This system was revealed to show some characteristic behavior which arises from following points; (1) both donor and acceptor being metal ion, (2) excited state of donor species being triplet. In this paper, we present the energy transfer and a deactivation processes process involving paramagnetic metal ions.

2. EXPERIMENTS

Materials.

A stock solution of uranyl perchlorate was prepared by the method described previously[2]. Stock solutions of lanthanide perchlorate were prepared by dissolving G.R. grade lanthanide oxides into 5 mol dm^{-3} perchloric acid. Lanthanide solutions with low concentration of acid were prepared by dissolving lanthanide oxides into equimolar amount of 0.1 mol dm^{-3}

perchloric acid and its pH were adjusted with glass electrode pH meter (TOA ion meter MODEL IM-20E).

Emission Measurements.

Emission and excitation spectrum of samples were obtained by using Hitachi 850 fluorescence spectrophotometer. Laser flashphotolysis experiments were carried out by using a N₂-dye laser (Horiba NDL-100) with stilbene 3 and a nanosecond fluorometer (Horiba NAES-500) and a personal computer.

In solutions containing UO₂²⁺ and Ln³⁺, the irradiations were carried out at 414nm or 427nm, at which wavelength the lanthanide ion has no absorption peaks.

3. RESULTS AND DISCUSSION

Energy transfer in highly acidic solution.

Even in the region of high perchloric acid concentration, where both uranyl and lanthanide ions are not hydrolyzed, Dy³⁺ shows sensitization from excited uranyl ion [1]. In solutions containing UO₂²⁺ and Dy³⁺ ([HClO₄]=2.5 mol dm⁻³), the irradiation with 414nm laser resulted in the excitation of only UO₂²⁺, because Dy³⁺ has no absorption at this wavelength. The sensitized emission of dysprosium ion was not observed in fluorospectrophotometric measurements even in D₂O solutions [3], but observed in H₂O solution as the differential spectrum at 0.5μs by the flash photolysis method (Fig.1). The differential-transient-emission spectra have a maximum peak at 578nm and it agrees well with the transient emission spectrum measured for Dy³⁺ in the absence of UO₂²⁺.

The emission intensity $I(t)$ at 578nm was analyzed in the dual exponential function with time t :

$$I(t) = I_{0,UO_2^{2+}} \exp\left(-\frac{t}{\tau_{UO_2^{2+}}}\right) + I_{0,Dy^{3+}} \exp\left(-\frac{t}{\tau_{Dy^{3+}}}\right) \quad (1),$$

where $I_{0,UO_2^{2+}}$ and $I_{0,Dy^{3+}}$ referred to the emission intensity at time $t=0$ for two excited species, and $\tau_{UO_2^{2+}}$ and $\tau_{Dy^{3+}}$ the lifetimes of these species. The time $t=0$ is defined as the end of irradiation pulse. The lifetime of the first term $\tau_{UO_2^{2+}}$ decreases with increasing the concentration of dysprosium ion [Dy³⁺] and this behavior well explains the quenching of excited uranyl ion, whereas the second term $\tau_{Dy^{3+}} = (2.5-3.0) \times 10^6 s^{-1}$ is independent of [Dy³⁺]. These results clearly indicate that the energy transfer takes place from excited uranyl ion to dysprosium ion.

The sensitization is not observed for Eu^{3+} and Gd^{3+} ions entirely. The observation of sensitized emission for Sm^{3+} and Tb^{3+} ions, which are known as emissive metal ions in aqueous solution, have failed because those ions have absorptions around the absorption peak of uranyl ion (414nm) and the spectrum width of our dye-laser (<10nm) is not narrow enough.

The quenching rate constant of dysprosium ion for emission of uranyl ion is determined to be $k_q = 2.01 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ($[\text{HClO}_4] = 3.2 \text{ mol dm}^{-3}$) from the Stern-Volmer plot. The quenching rate constants of excited uranyl ion by various lanthanide ions (Table 1) and in different acid concentration (Table 2) were determined from Stern-Volmer plots.

The difference in the behavior of Dy^{3+} and Eu^{3+} to energy transfer could be explained by the difference in the overlap between the absorption spectra of lanthanide ions and the emission spectra of uranyl ion. The mechanism of energy transfer is considered to be a radiationless transfer due to electron-exchange interaction and a collisional transfer due to exciplex formation and dissociation, provided the excited state of uranyl ion is triplet. The overlap between absorption spectra $P_T(\nu)$ and emission spectra $\epsilon(\nu)$ is necessary for the mechanism due to electron-exchange interaction as:

$$k \propto (2\pi/\hbar) Z^2 \int_0^\infty P_T(\nu) \epsilon(\nu) d\nu \quad (2).$$

The overlap exists in the couple of UO_2^{2+} and Dy^{3+} , whereas it is negligible in the couple of UO_2^{2+} and Eu^{3+} .

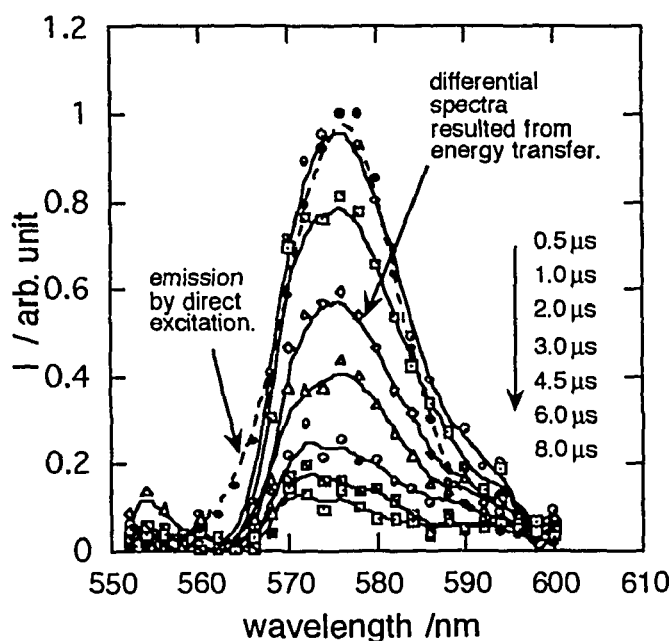


Fig.1 Transient-emission spectrum of Dy^{3+} obtained at 0.5ms after 337nm laser flash (dashed line), and differential-transient-emission spectra of Dy^{3+} resulted from energy transfer (straight line). [1]

Table 1. The quenching rate constants by lanthanide ions for triplet Naphthalene, triplet Anthracene and excited uranyl ion in solution at ambient temperature.

	Paramagnetic susceptibility (Bohr magnetons)	KSV	$10^5 k_q/\text{mol dm}^{-3} \text{s}^{-1}$		
			$^* \text{UO}_2^{2+}$ in $\text{H}_2\text{O}^{1)}$	$^3 \text{Naphthalene}$ in ethylene glycol ²⁾	$^3 \text{Anthracene}$ in pyridine ³⁾
Pr^{3+}	3.5	5.41	4.2		< 5
Nd^{3+}	3.5	10.9	7.9	4	
Sm^{3+}	1.5	45.4	39		< 5
Eu^{3+}	3.4	0	0		
Gd^{3+}	8.0	78.4	64	0.7	< 5
Tb^{3+}	9.72	0	0		
Dy^{3+}	10.6	38.2	29		
Ho^{3+}	10.4	31.4	23		
Er^{3+}	9.5	25.7	20		
Tm^{3+}	7.3	11.0	7.6		
Yb^{3+}	4.5	0	0		

1) this work; $[\text{UO}_2(\text{ClO}_4)_2]=5.0 \times 10^{-3} \text{mol dm}^{-3}$, $[\text{HClO}_4]=2.5 \text{mol dm}^{-3}$,
 2) ref. [5], 3) ref. [6]

Table 2. Quenching rate constants (k_q) in the system of UO_2^{2+} and Ln^{3+} in different acid concentrations.

Lanthanide	solvent	k_q	sensitization
		$\text{M}^{-1} \text{s}^{-1}$	
$\text{Eu}(\text{ClO}_4)_3$	$\text{H}_2\text{O}(\text{pH}4)$	---b)	+ a)
$\text{Eu}(\text{ClO}_4)_3$	0.4M HClO_4 + 0.6M NaClO_4	3.0×10^5	+
$\text{Eu}(\text{ClO}_4)_3$	2.5M HClO_4	0	-
$\text{Dy}(\text{ClO}_4)_3$	0.4M HClO_4 + 0.6M NaClO_4	3.65×10^6	+
$\text{Dy}(\text{ClO}_4)_3$	2.5M HClO_4	3.0×10^6	+
$\text{Gd}(\text{ClO}_4)_3$	2.5M HClO_4	6.4×10^6	-

a) Sensitization is observed by fluorospectroscopic measurement in this solution.
 b) considerable large value of k_q is supposed.

Energy transfer in low acidic solution.

In the region of low acid concentration (pH 3.8-4.0), in which uranyl ion should form hydrolysis species, the photosensitized emission of Eu^{3+} by UO_2^{2+} was certainly observed as reported before [10]. It had been suggested that both the formation of hydrolysis species of uranyl ion and its coordinative interaction with europium ion are required to happen the energy transfer.

The excitation spectrum of the system of UO_2^{2+} and Eu^{3+} drastically changed through pH 3.0 to pH 2.0, when the emission of Eu^{3+} was observed at 590nm. Our interests is concerning in the understanding of the behavior of the system in the region lower than pH 3.0 using flash photolysis method. The excitation at 427nm resulted in the emission of a dual exponential function observed at 617nm in the system ($[\text{UO}_2^{2+}] = 5.1 \times 10^{-3}$ M, $[\text{Eu}^{3+}] = 2 \times 10^{-2}$ M, $[\text{NaClO}_4] = 0.90$ M) and it was analyzed as following formula,

$$I_{617} = I_{\text{UO}_2^{2+},617} \exp(-k_{\text{UO}_2^{2+}} t) + I_{\text{Eu}^{3+},617} \exp(-k_{\text{Eu}^{3+}} t) \quad (3).$$

The value of $I_{\text{Eu}^{3+},617}/I_{\text{UO}_2^{2+},617}$ is almost zero at $-\log[\text{H}^+] = 0$ and increases with increasing pH (Fig.2). This dependence of the intensity of sensitized emission on pH of the solution is rationally explained by hydrolysis species involved. The concentration of the some hydrolysis species $[(\text{UO}_2)_n(\text{OH})_m]^{(+2n-m)}$ (denoted as $[n,m]$) are calculated using the published hydrolysis constants [11] as follows: $-\log[\text{H}^+] = 0$ $[1,0] = 5.0 \times 10^{-3}$, $[1,1] = 6.9 \times 10^{-7}$, $[2,2] = 5.1 \times 10^{-8}$, $[3,5] = 6.3 \times 10^{-16}$; pH 2.0 $[1,0] = 4.5 \times 10^{-3}$, $[1,1] = 6.2 \times 10^{-5}$, $[2,2] = 4.18 \times 10^{-4}$, $[3,5] = 4.7 \times 10^{-6}$ (total concentration of UO_2^{2+} is 5.01×10^{-3} mol dm^{-3}). It is elucidated that the $[2,2]$ or $[3,5]$ species plays an important role in the energy transfer from $^*\text{UO}_2^{2+}$ to Eu^{3+} .

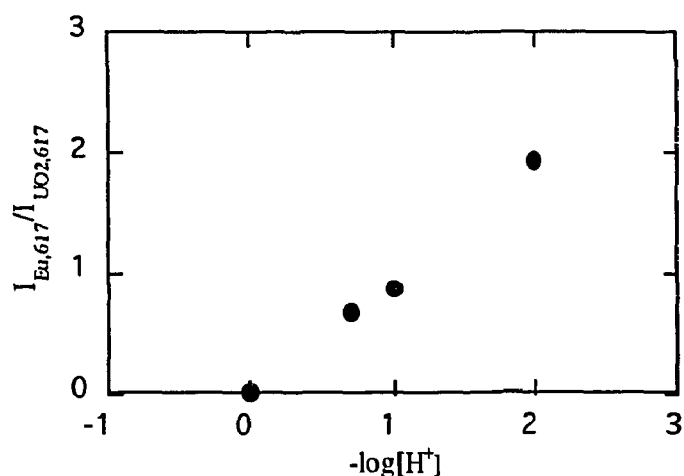


Fig.2 The plot of the value of $I_{\text{Eu}^{3+},617}/I_{\text{UO}_2^{2+},617}$ against the value of $-\log[\text{H}^+]$. The sample was irradiated at 427nm and emission was observed at 617nm.

Systematic paramagnetic quenching.

The quenching rate constants k_q for the excited uranyl ion have values of 10^5 order according to Table 1. These relatively large values cannot be rationalized simply by weak energy transfer found in the system with Dy^{3+} . And Gd^{3+} ion whose k_q is the maximum of the series of quenching constants indicates no sensitized emission from excited uranyl ion.

Matsushima et al. studied on the quenching phenomenon of uranyl emission by d-transition and f-transition metal ions [8]. The charge transfer mechanism was proposed to the quenching of $^*\text{UO}_2^{2+}$ by d-transition metal ions [8] and halogen and pseudo-halogen ions [2], whereas the quenching mechanism by lanthanide ions have been little known. The quenching process via the charge transfer mechanism is described as follows:



This scheme requests that k_q increases with decreasing the reduction potential of lanthanide ion $E_0(\text{III-IV})$. Such tendency, however, cannot be found in our result.

It is well known that 4f-transition metal ion have unpaired electrons and thus indicate the paramagnetism. The intersystem crossing from triplet excited state to singlet ground state is known to be assisted by the paramagnetic ions. Porter and Wright discussed on the paramagnetic quenching of triplet excited molecule and classified it into three cases depending on the paramagnetic compounds [5]. The typical value of k_q by lanthanide ion is about $2 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and the depressed value in comparison with $^3\text{O}_2$, ^2NO and the first transition metal ions is attributed to the deep shielding nature of 4f orbital.

In Table 1, the value of k_q obtained in our study for the excited uranyl ion is accompanied with the value of k_q for $^3\text{Naphthalene}$ and $^3\text{Anthracene}$ and also with paramagnetic susceptibility of lanthanide ions. The values of k_q for $^*\text{UO}_2^{2+}$ are almost coincide with the value presented by Porter et al., and a quite good correlation is obtained in the plot of the value of k_q against the number of 4f electrons except for Eu^{3+} and Tb^{3+} which have 6 electrons in 4f orbital (Fig.3). This result indicates an important role of paramagnetic quenching in the deactivation of excited uranyl ion.

There is a large spin-orbital coupling in uranyl molecule and the spin label is not justified. Thus the lowest excite state has been alternatively attributed to triplet or singlet and it has been thought that the quenching by spin-catalyzed deactivation appears to be unlikely because of poorly defined spin number. Our result in highly acidic solutions indicate the

excited species of uranyl ion is subjected to be deactivated by lanthanide ions via spin-catalyzed mechanism. Table 3 shows the comparison of our data with those of reported previously. It is worth while to note europium ion and terbium ion dose not quench the excited state of uranyl ion via outer shper mechanism and the sensitization process is of important in the case of these two ions.

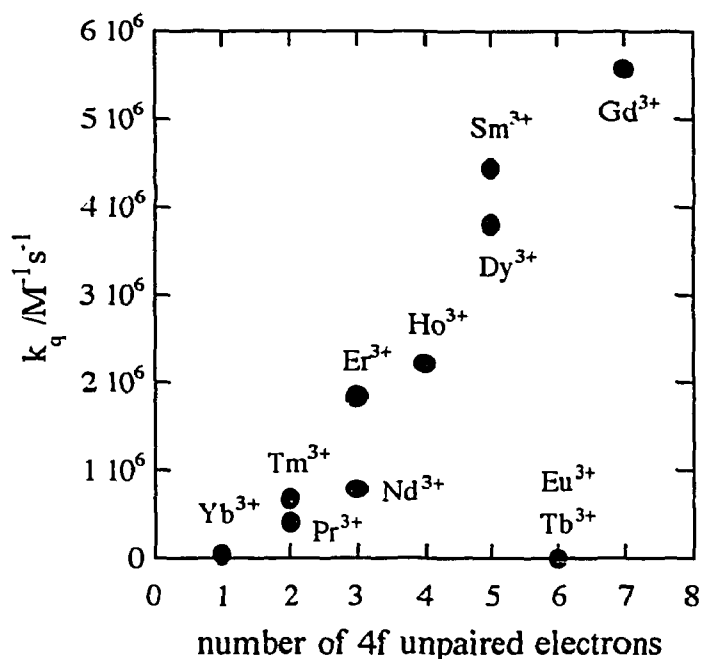


Fig.3 The plot of the quenching rate constants against the number of unpaired electrons.

Table 3. Comparison of present data with those of reported previously.

Lanthanide	uranyl	solvent	k_q	sensitization	quenching mechanism	ref.
			$M^{-1}s^{-1}$			
Eu(ClO ₄) ₃	perchlorate	pH 4(H ₂ O)	---	+	energy transfer	this work
Eu(ClO ₄) ₃	perchlorate	2.5M HClO ₄	0	-		this work
Eu(ClO ₄) ₃	perchlorate	0.4M HClO ₄ + 0.6M NaClO ₄	3.0×10^5	+	energy transfer	this work
Eu(ClO ₄) ₃	perchlorate	0.4M HClO ₄ + 0.6M NaClO ₄ + 0.2M CH ₃ COONa	1.5×10^6	+	energy transfer	this work
EuCl ₃	nitrate	0.2M CD ₃ COOK(D ₂ O)	2.7×10^7	+	energy transfer	ref.[7]
Eu(NO ₃) ₃	nitrate	0.67M H ₃ PO ₄	1.3×10^3	+	energy transfer	ref.[8]
Eu(NO ₃) ₃	nitrate	1M H ₃ PO ₄	1.0×10^6	+	energy transfer	ref.[9]
Eu(ClO ₄) ₃	perchlorate	pH 3.87(D ₂ O)	---*)	+	energy transfer	ref.[10]
Eu(ClO ₄) ₃	perchlorate	0.1M DClO ₄ (D ₂ O)	---*)	+		ref.[10]

*) not mentioned

4. CONCLUSION

In the region of low acid concentration where the hydrolysis species of uranyl ion are formed, energy transfer from $^*UO_2^{2+}$ to Eu^{3+} takes place effectively, which strongly suggests that both the formation of hydrolysis species of uranyl ion and its coordinative interaction with europium ion are required to undergo the energy transfer. In the region of high acid concentration where no inner-sphere mechanism could be considered, the energy transfer is observed in the case of Dy^{3+} , whereas it is not observed for Eu^{3+} . In addition to the energy transfer, the value of 10^5 order of quenching rate constants for excited uranyl ion are determined and quite good correlation is found between the k_q and the number of 4f electrons except for Eu^{3+} and Tb^{3+} . This is considered to be the first paramagnetic quenching for excited uranyl ion, despite the poorly defined spin number for uranyl ion.

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