

The yield of purified polymer was generally 0.3–0.5 g.

The chalcone/styrene copolymer was prepared and purified in a similar fashion, starting from chalcone (0.5 g), freshly distilled styrene (5.0 g), azobis(isobutyronitrile) (0.1 g), and benzene (7 mL). The yield of purified polymer was 0.35 g.

The compositions of the above polymers were determined by UV spectroscopy, from the absorbances at 345 nm of standard samples in benzene solution. The extinction coefficient of the  $n, \pi^*$  absorption in these copolymers was assumed to be the same as that of propiophenone in benzene. The compositions of the polymers determined in this way corresponded to incorporation of 8–12% ketone.

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## Aqualigand Dissociation of $[\text{Ce}(\text{OH}_2)_9]^{3+}$ in the $5d \leftarrow 4f$ Excited State

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**Abstract:** Hydrated  $\text{Ce}^{3+}$  ions in aqueous solution are predominantly in a tricapped trigonal structure of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$ . However, an equilibrium between  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  and  $[\text{Ce}(\text{OH}_2)_8]^{3+}$  exists in aqueous solution. Upon the  $5d \leftarrow 4f$  excitation, one of the aqualigands of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  dissociates in the excited state and an emission band exclusively comes out from  $*[\text{Ce}(\text{OH}_2)_8]^{3+}$ . In ethylene glycol, however, the emissions not only of the long-lived excited species  $*[\text{Ce}(\text{OH}_2)_8]^{3+}$  (48 ns) but also of the short-lived excited species  $*[\text{Ce}(\text{OH}_2)_9]^{3+}$  (430 ps) were detected upon intense laser pulse excitation. The rise transient which indicates an increase of  $[\text{Ce}(\text{OH}_2)_8]^{3+}$  immediately after the excitation was also observed in ethylene glycol. The lifetime of  $*[\text{Ce}(\text{OH}_2)_9]^{3+}$  in solution is controlled by the rate of aqualigand dissociation.

Five absorption bands are observed in a region between 37 and  $51 \times 10^3 \text{ cm}^{-1}$  with single crystals of  $\text{Ce}^{3+}$  doped lanthanum(III) ethylsulfate enneahydrate (Ce:La·ES).

In the crystal,  $\text{Ce}^{3+}$  is in a ligand field of nine water molecules such as in  $[\text{Ce}(\text{OH}_2)_9]^{3+}$ . The ultraviolet bands are assigned to five Kramers doublets which are the excited  $^2D(5d^1)$  multiplet split by the ligand-field interaction and the spin-orbit coupling of a cerium 5d electron.<sup>1,2</sup>

Two resolved luminescence bands are also detected at 30 and  $32 \times 10^3 \text{ cm}^{-1}$  at liquid-nitrogen temperature. The excitation spectrum of the luminescence conforms to the absorption spectrum. The twin emission bands, which cannot be resolved at ambient temperatures, are ascribed to the transitions to the  $^2F_{5/2}$  and  $^2F_{7/2}$  substates, two components of the ground  $^2F(4f^1)$  multiplet, which are split almost exclusively by the spin-orbit coupling of a cerium 4f electron.<sup>1,2</sup>

Hydrated  $\text{Ce}^{3+}$  ions in aqueous solution show the absorption bands which correspond to those observed with Ce:La·ES. The hydrated ions must be in a similar structure as found in the single crystal. However, the aqueous solution displays an extra weak absorption band at  $34 \times 10^3 \text{ cm}^{-1}$ . The band cannot be detected with Ce:La·ES even if a high concentration of  $\text{Ce}^{3+}$  and/or a thick crystal are used.<sup>1</sup> The ligand-field splitting of the  $^2D(5d^1)$  manifold gives not more than five Kramers doublets. A partial dissociation of the coordinated waters in aqueous media has been proposed.<sup>3</sup> Recent X-ray studies on the aqueous solutions concluded that the hydrated ions  $\text{La}^{3+}$  through  $\text{Nd}^{3+}$  are nine coordinated and those between  $\text{Nd}^{3+}$  and  $\text{Tb}^{3+}$  are transitional between nine and eight.<sup>4,5</sup> However, the weak band at  $34 \times 10^3 \text{ cm}^{-1}$  provides sound evidence of the partial dissociation. For the aqueous solution of  $\text{Ce}^{3+}$  ion, an emission band is observed at  $28 \times 10^3 \text{ cm}^{-1}$  instead of the band

observed at  $30\text{--}32 \times 10^3 \text{ cm}^{-1}$  with the Ce:La·ES regardless of the excitation wavelengths in the band of the dissociated species or in the five-component absorption bands of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$ .<sup>1</sup> The luminescence comes out exclusively from a dissociated species such as  $[\text{Ce}(\text{OH}_2)_8]^{3+}$ . The luminescence of the hydrated  $\text{Ce}^{3+}$  ion in aqueous media decays in a single exponential of 45 ns regardless of the excitation wavelengths, while that of Ce:La·ES decays in a shorter lifetime of 27 ns.<sup>2</sup>

Upon the  $5d \leftarrow 4f$  excitation of  $\text{Ce}^{3+}$  ion, one of the aqualigands in  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  dissociates in solution. However, a greater Stokes shift observed on Ce:La·ES indicates that a deformation of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  occurs in the excited state but does not result in bond dissociation in the crystal.

In the present work, a very fast aqualigand dissociation of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  in the excited state was studied.

### Experimental Section

**Materials.** Cerium(III) ethylsulfate enneahydrate (Ce·ES) was obtained by the method of Ketelaar.<sup>6</sup>  $\text{Ce}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ ,  $(\text{C}_2\text{H}_5)_2\text{SO}_4$ , and  $\text{BaCO}_3$  were commercially available and of reagent grade.

Ethylene glycol was purified by distillation under reduced pressure.

**Solutions for Measurements.** For measurements, the crystals of Ce·ES were dissolved in  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and ethylene glycol. Absorption, emission, and excitation spectra of Ce·ES in solution were exactly coincident with the spectra of  $\text{Ce}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$  in solution. The perchlorate is a weaker ion pair forming salt; however, it is too deliquescent to be used for quantitative preparation of solutions.

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**PVA Films.** PVA films 0.2-mm thick were prepared by spontaneous evaporation of an aqueous solution of PVA (degree of polymerization: 1400) on a glass plate at ambient temperature over 10 days and then heating the films at 80–90 °C for 1 h. The PVA film was swelled in water and then dipped in an aqueous solution of  $\text{Ce} \cdot \text{ES}$  (ca. 0.2 M) at ambient temperature for 10–20 s. The surface of the film was washed with the smallest possible portion of distilled water and then its attached water was wiped out by filter paper. The film was soaked in methanol for 2 min. After that it was allowed to dry at room temperature on a sheet of filter paper. The PVA film dyed with hydrated  $\text{Ce}^{3+}$  ion exhibits absorption, emission, and excitation spectra which conform to those of the aqueous solution.

**Spectroscopic and Fluorescence Decay Lifetime Measurements.** Absorption spectra were recorded on a Hitachi 220A spectrophotometer. Emission and excitation spectra were taken on a Hitachi 850 spectrofluorometer, which was equipped with a Hamamatsu Photonics R928 photomultiplier. The spectral response was calibrated by use of a concentrated ethylene glycol solution of rhodamine B.<sup>7,8</sup> The recorded spectra were read into a Hewlett-Packard 9825A personal computer by digitizing on a Hewlett-Packard 9872A plotter and then all corrections to the emission spectra were achieved on the computer. The quantum yields of fluorescence were determined with reference to a solution of 2-aminopyridine in 0.1 N  $\text{H}_2\text{SO}_4$  as a standard ( $\phi = 0.74$  at 25 °C).<sup>9</sup>

Measurements of the fluorescence decay in the nanosecond time scale were carried out by means of the single photon counting method. The sample was excited by pulses of 2 ns duration obtained from a hydrogen-gas lamp (PRA Model 510B) through a monochromator (Jobin-Yvon Model H10). The photon emission was detected through a glass filter (Toshiba UV-33) by a Hamamatsu Photonics photomultiplier R212P and counted on a Norland Model 5300 multichannel analyzer. The lifetime was determined by fitting the decay curve exponentially by means of the least-squares method on a microcomputer NEC PC-8801 interfaced with the multichannel analyzer.

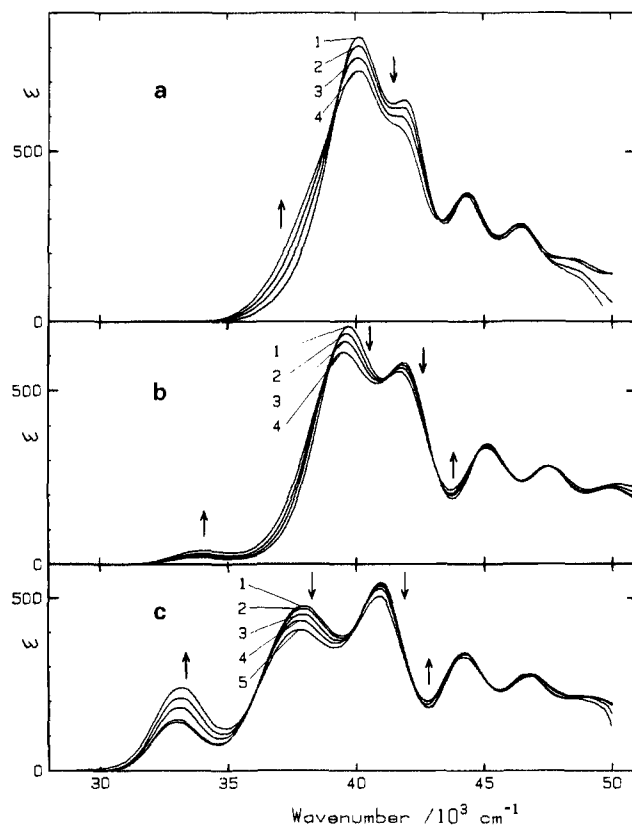
The decay and rise transients of fluorescence in the picosecond time scale were recorded by a Hamamatsu C-979 streak camera upon excitation of the sample by the fourth harmonic (266 nm, 15 ps fwhm) of a mode-locked Nd:YAG laser. The fluorescence was detected through a Toshiba L-42 or UV-30 filter which cuts the wavelength shorter than 420 or 300 nm, respectively. The streak image was detected by a TV camera and analyzed with a Hamamatsu temporal analyzer C-1098. The time scales were calibrated by recording multiple reflection of a pulse with a parallel half reflector in a fixed distance. The decay and rise transients were reproduced by use of the method of nonlinear least-squares iterative reconvolution on a Hewlett-Packard 9825A personal computer.

## Results and Discussion

The absorption spectrum of hydrated  $\text{Ce}^{3+}$  ion in aqueous media displays five bands corresponding to the  $^2\text{D}(5d^1)$  multiplet in  $[\text{Ce}(\text{OH})_9]^{3+}$  and a weak band at  $34 \times 10^3 \text{ cm}^{-1}$ . The intensity of the weak band was independent of the hydrogen ion concentration in solution. Even in high concentrations of  $\text{HClO}_4$ , no spectral variation was observed. Thus the band which lacks  $[\text{Ce}(\text{OH})_9]^{3+}$  doped in the crystal is ascribed to the lowest component band of a ligand-dissociated species in solution such as  $[\text{Ce}(\text{OH})_8]^{3+}$  but not to a proton-dissociated species such as  $[\text{Ce}(\text{OH})(\text{H}_2\text{O})_8]^{2+10}$  or its condensation aggregates.<sup>11</sup>

Elevation of temperature increases the intensity in the absorption band of  $[\text{Ce}(\text{OH})_8]^{3+}$ , but it decreases the intensity the intrinsic bands of  $[\text{Ce}(\text{OH})_9]^{3+}$ . Figure 1 shows that spectra vary with an increase in temperature, displaying isosbestic points. The spectral change is reversed by cooling of the solution.

In aqueous solution an equilibrium is present between two different species  $[\text{Ce}(\text{OH})_9]^{3+}$  (A) and  $[\text{Ce}(\text{OH})_8]^{3+}$  (B). The predominant species in the solution is A. However, an emission band is detected at a longer wavelength than that observed for A in the crystal regardless of the excitation of A or B. The emission excitation spectra were coincident with the absorption spectra regardless of the emission-monitoring wavelengths. The emission band is attributable to the excited B species ( $\text{B}^*$ ). This implies that the  $5d \leftarrow 4f$  excitation of  $\text{Ce}^{3+}$  ion gives rise to a shift



**Figure 1.** Temperature variations of the absorption spectra of hydrated  $\text{Ce}^{3+}$  ion: (a) ethylene glycol (1, 14 °C; 2, 26 °C; 3, 35 °C; 4, 48 °C); (b) aqueous solution (1, 5 °C; 2, 20 °C; 3, 35 °C; 4, 55 °C); (c)  $\text{CH}_3\text{OH}$  (1, 5 °C; 2, 10 °C; 3, 25 °C; 4, 37 °C; 5, 47 °C).

of the equilibrium in solution up to an exclusive predominance of  $\text{B}^*$ .

The temperature variation of the excitation spectra conformed to that of the absorption spectra. However, no variation of the emission spectrum was observed in the range of temperature used. The emission intensity was dependent only on the total concentration of A and B species in the ground state but not the individual concentrations of A and B, which were varied with temperature. This indicates that the equilibrium shift in the excited state gives rise to an exclusive species  $\text{B}^*$ . The emission from the species  $\text{A}^*$  cannot be detected since only a very low concentration of  $\text{A}^*$  is obtained by the stationary irradiation used for fluorescence measurements. The quantum yields of emission were also measured with a variety of excitation wavelengths. The yields vary with the media but not with the excitation wavelengths. This also supports the dissociation of the aqualigand of  $[\text{Ce}(\text{OH})_9]^{3+}$  in the excited state.

Similar spectral behaviors were also observed with hydrated  $\text{Ce}^{3+}$  ion in  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , ethylene glycol, and PVA media.

The emission decay of hydrated  $\text{Ce}^{3+}$  ion in the nanosecond time scale is of single exponential as shown in Figure 2 and gives an invariant lifetime regardless of the excitation wavelengths, including those in the  $34 \times 10^3 \text{ cm}^{-1}$  band.

Even if the dissociation of the ligand in  $\text{A}^*$  is fast, the emission which comes out from  $\text{A}^*$  could be detected immediately after intense pulse excitation. Therefore, the emission decays were measured in the picosecond time scale. In fact, the decay observed with an ethylene glycol solution of hydrated  $\text{Ce}^{3+}$  ion shown in Figure 3 is not of a single exponential, but it can be reproduced by superposition of double exponentials. The reconvolution of the decay curve yields a fast component lifetime of 430 ps. The fast component decay was also observed with a PVA film dyed with hydrated  $\text{Ce}^{3+}$  ion. Some of the lifetimes and the yields measured in a variety of media are summarized in Table I.

For the PVA film, the decay of emission was measured with the emission-monitoring wavelength varied by use of band-pass

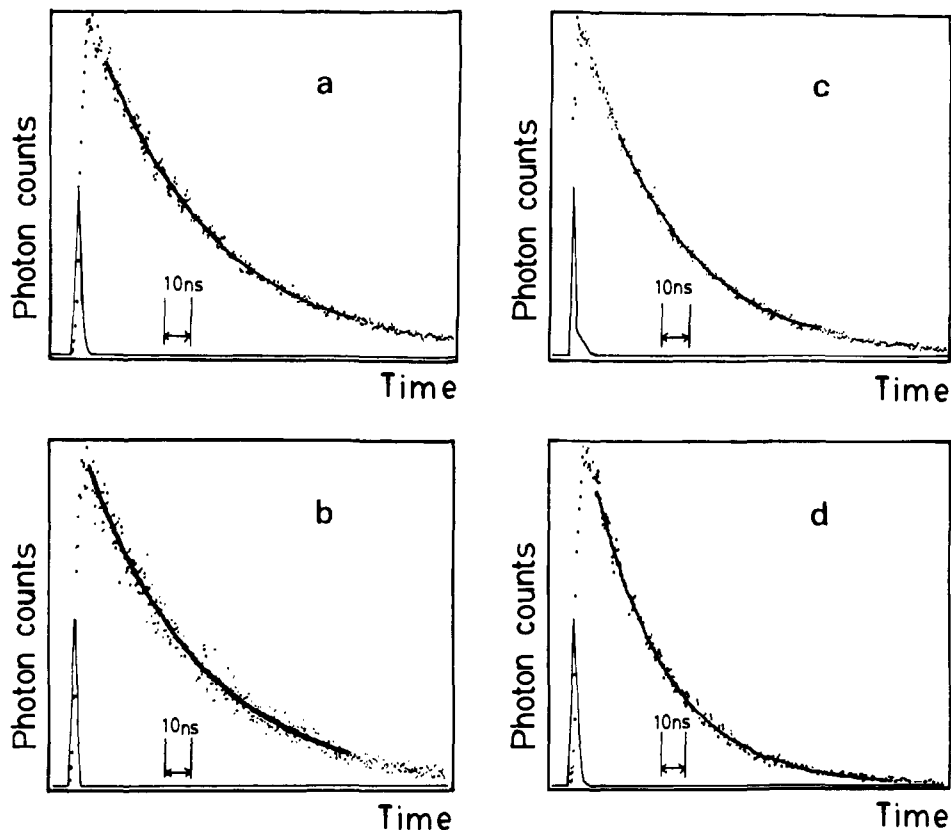
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**Figure 2.** Emission decay curves of hydrated  $\text{Ce}^{3+}$  ion in the nanosecond time scale: (a) ethylene glycol ( $\tau = 48$  ns); (b) aqueous solution ( $\tau = 45$  ns); (c)  $\text{CH}_3\text{OH}$  ( $\tau = 43$  ns); (d) PVA ( $\tau = 29$  ns). The solid line is the best fit.

**Table I.** Lifetimes and Quantum Yields of Hydrated  $\text{Ce}^{3+}$  Ion in Various Media

medium	ns lifetime	ps lifetime	quantum yield at 25 °C <sup>a</sup>	
			250 nm	350 nm
doped crystal <sup>b</sup>	27	<sup>c</sup>		
$\text{H}_2\text{O}$	45	nd <sup>d</sup>	1.0	1.0
PVA	29	410		
$\text{CH}_3\text{OH}$	43			
$\text{C}_2\text{H}_5\text{OH}$	33	970	0.8	0.8
ethylene glycol	48	430	0.7	0.8 <sup>e</sup>

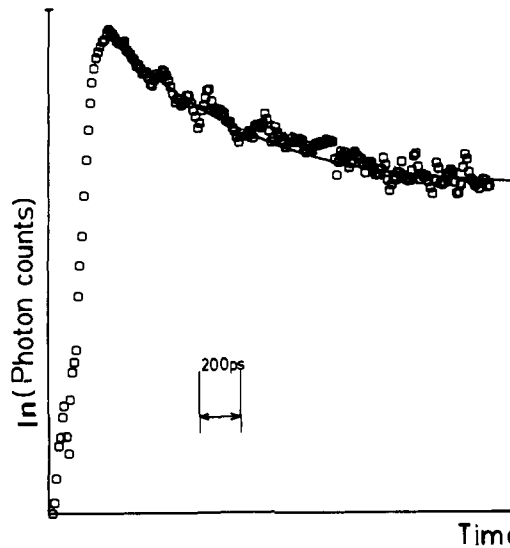
<sup>a</sup> Measured for the excitation wavelength set at 250 or 300 nm.

<sup>b</sup> Doped in Lanthanum(III) ethylsulfate enneahydrate. <sup>c</sup> Unsuccessful to detect for dispersed light. <sup>d</sup> The fast component lifetime was not detected. <sup>e</sup> Excited at 273 nm, since no appreciable absorption arises at 300 nm.

filters. Figure 4 shows that the decays are dependent upon the monitoring wavelength. The fluorescence band observed upon irradiation of an intense laser pulse is a superposition of the longer wavelength band of long-lived  $\text{B}^*$  and the shorter wavelength band of short-lived  $\text{A}^*$ . The emission decay observed at 401 nm is attributable to that of the long-lived  $\text{B}^*$ , but the decay at 295 nm is mainly due to that of the short-lived  $\text{A}^*$ .

The rise transients were recorded with ethylene glycol solutions of hydrated  $\text{Ce}^{3+}$  ion for the monitoring wavelength varied by means of cutoff filters. The emission detected in a longer wavelength region than 300 nm is a sum of those of  $\text{A}^*$  and  $\text{B}^*$ , while the emission in a longer wavelength region than 420 nm is ascribed to that of  $\text{B}^*$ . The rise was observed only for the emission of  $\text{B}^*$  but not for the superposed emission of  $\text{A}^*$  and  $\text{B}^*$  as illustrated in Figure 5. The observed rise indicates an increase of  $\text{B}^*$  in a very early stage after pulse excitation.

The relaxation of the hydrated  $\text{Ce}^{3+}$  ion in the excited state is described as in a scheme given in Figure 6. An equilibrium between A and B in solution is established in the ground state. In the excited state, however,  $\text{A}^*$  dissociates one of the ligands and results in  $\text{B}^*$ . The dissociation rate  $k_3$  is much greater than



**Figure 3.** Emission decay curve of hydrated  $\text{Ce}^{3+}$  ion in ethylene glycol in the picosecond time scale: (—) the best fit.

$k_1 + k_2$  and  $k_4 + k_5$ . The lifetime of  $\text{A}^*$ ,  $1/(k_1 + k_2) = 27$  ns, measured with the crystal is shorter but not so much different from that of  $\text{B}^*$ ,  $1/(k_4 + k_5) \approx 45$  ns, observed with aqueous solutions. The concentrations of  $\text{A}^*$  and  $\text{B}^*$  in solution after pulse excitation are given as a function of time as follows

$$[\text{A}^*] = [\text{A}^*]_0 \exp[-(k_1 + k_2 + k_3)t] \quad (1)$$

$$[\text{B}^*] = -\frac{k_3[\text{A}^*]_0}{(k_1 + k_2 + k_3) - (k_4 + k_5)} \exp[-(k_1 + k_2 + k_3)t] + \left\{ [\text{B}^*]_0 + \frac{k_3[\text{A}^*]_0}{(k_1 + k_2 + k_3) - (k_4 + k_5)} \right\} \exp[-(k_4 + k_5)t] = -[\text{A}^*]_0 \exp[-(k_1 + k_2 + k_3)t] + \frac{([\text{A}^*]_0 + [\text{B}^*]_0) \exp[-(k_4 + k_5)t]}{([\text{A}^*]_0 + [\text{B}^*]_0) \exp[-(k_4 + k_5)t]} \quad (2)$$

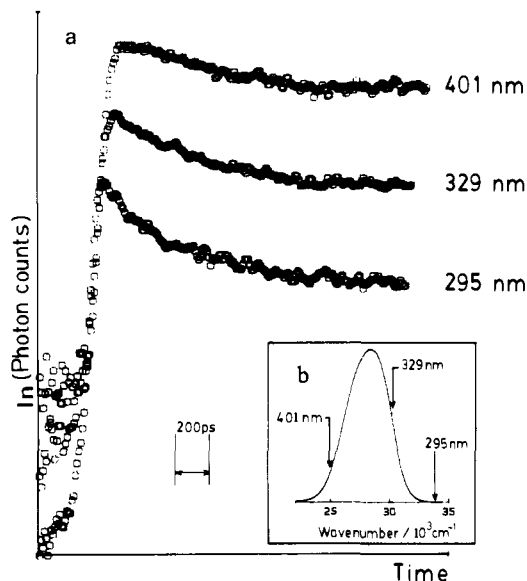


Figure 4. Dependence of the emission decay of hydrated  $Ce^{3+}$  ion in PVA film (a) on the emission-monitoring wavelengths (b).

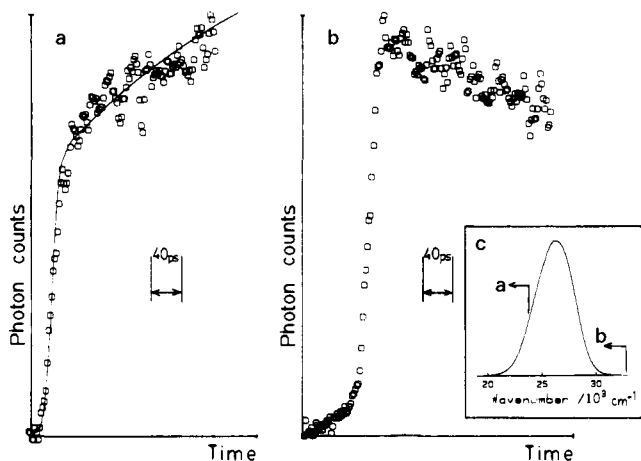


Figure 5. Emission rise transients of hydrated  $Ce^{3+}$  ion in ethylene glycol. The emission was detected with the monitoring wavelength varied by means of cutoff filters: (a)  $>420$  nm; (b)  $>300$  nm. The solid line is the best fit.

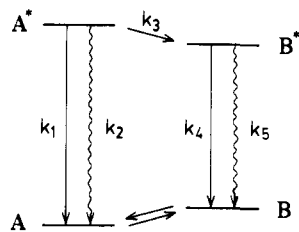


Figure 6. Relaxation processes of the excited  $Ce^{3+}$  ion in solution.

where it is assumed that  $k_3 \gg k_1 + k_2$ ,  $k_4 + k_5$ , and  $[A^*]_0$  and  $[B^*]_0$  are the initial concentrations of  $A^*$  and  $B^*$ , respectively. The emission intensity is given by

$$I = k_1[A^*] + k_4[B^*] \\ = [A^*]_0(k_1 - k_4) \exp\{-(k_1 + k_2 + k_3)t\} + \\ ([A^*]_0 + [B^*]_0)k_4 \exp\{-(k_4 + k_5)t\} \quad (3)$$

The short-lived  $A^*$  decays in the fast component rate ( $k_1 + k_2 + k_3$ ), which is governed by  $k_3$ . On the other hand,  $B^*$  rises in the fast component rate, while  $B^*$  decays in the slow component rate ( $k_4 + k_5$ ). The reciprocal of the fast component lifetime 430 ps ( $2.3 \times 10^9$  s<sup>-1</sup>) is comparable to the rise rate of  $B^*$  ( $3.0 \times 10^9$

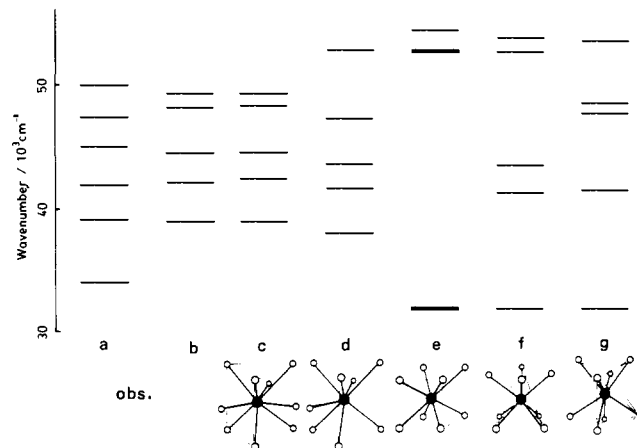


Figure 7. The  $5d \leftarrow 4f$  excited states of  $[Ce(OH_2)_8]^{3+}$  calculated for typical octacoordinate structures. (a) and (b) are the excited states observed in aqueous solution and the crystal, respectively. The calculated excitation energies are given for  $[Ce(OH_2)_9]^{3+}$  in tricapped trigonal prism (c), and  $[Ce(OH_2)_8]^{3+}$  in bicapped trigonal prism (d), cube (e), square antiprism, (f), and dodecahedron (g).

s<sup>-1</sup>) detected with ethylene glycol solutions. The emission yield upon excitation of A is given by

$$\frac{k_1}{k_1 + k_2 + k_3} + \frac{k_3}{k_1 + k_2 + k_3} \frac{k_4}{k_4 + k_5} \quad (4)$$

where the emission comes out not only from  $A^*$  but also from the  $B^*$  of  $A^*$  origin, while the yield upon excitation of B is  $k_4/(k_4 + k_5)$ . Here the condition  $k_3 \gg k_1 + k_2$ ,  $k_4 + k_5$  predicts an identical yield  $k_4/(k_4 + k_5)$  regardless of the excitation wavelengths. For the condition, identical emission spectrum, quantum yield, and decay lifetime are also observed regardless of the excitation of A or B unless a high concentration of the species  $A^*$  is obtained upon intense laser excitation.

On the basis of the observed decay lifetimes, rise rate, and quantum yield, the rate constants were evaluated as  $k_3 = 2.3 \times 10^9$  s<sup>-1</sup>,  $k_4 = 1.6 \times 10^7$  s<sup>-1</sup>,  $k_5 = 0.5 \times 10^7$  s<sup>-1</sup>, and  $k_1 = 6 \sim 10 \times 10^7$  s<sup>-1</sup>, while  $k_2$  could not be determined.

The ligand dissociation process is detected, since the process is rather retarded in ethylene glycol and PVA film than in aqueous solution. In the media, the hydrated  $Ce^{3+}$  ion exhibits the absorption and emission spectra similar to those in aqueous solution, while the spectra of hydrated  $Ce^{3+}$  ion in  $C_2H_5OH$  is not necessarily coincident with those in aqueous media.

The structure of  $[Ce(OH_2)_9]^{3+}$  is a tricapped trigonal prism; six water molecules are on the vertexes of a trigonal prism and three equatorial waters above the centers of the prismatic faces. In the lowest substate of  $^2D(5d^1)$ , the promoted electron occupies the  $d_{z^2}$  orbital which extends in the direction of the  $C_3$  symmetry axis. Thus the excitation results in a shift of the vertex water molecules to the equatorial, and thus one of the equatorial water molecules is eliminated. A structure of bicapped trigonal prism which lacks one of the equatorial ligands has been found in  $Nd(acac)_3(OH_2)_2$  (acac: acetylacetonate).<sup>12</sup> However, a variety of structures are possible for the octacoordinate species  $[Ce(OH_2)_8]^{3+}$ . In fact, octacoordinate cerium(III) and lanthanum(III) complexes have been found in a distorted dodecahedron,<sup>13</sup> a square antiprism,<sup>14</sup> and a transition of square antiprism and cube.<sup>15</sup> Since the antibonding character of the 5d orbitals is greater than that of 4f orbitals, the 5d ← 4f excitation gives rise to a destabilization of the coordination bond. The angular overlap model calculations were carried out by taking into account

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spin-orbit coupling.<sup>2</sup> The theory can predict the lowest  $5d \leftarrow 4f$  excited Kramers doublet of  $[\text{Ce}(\text{OH}_2)_8]^{3+}$  present in an energy region much lower than the lowest component of  $[\text{Ce}(\text{OH}_2)_9]^{3+}$  as shown in Figure 7 in which the distance Ce-O is assumed to be conserved in  $[\text{Ce}(\text{OH}_2)_8]^{3+}$  and  $[\text{Ce}(\text{OH}_2)_9]^{3+}$ . A ligand-field stabilization is obtained at the expense of the bond dissociation. Since the calculations do not take proper account of variations in the repulsion energies, the model cannot determine exactly which configuration is the most stable. For their small energy differences, however, the structure of the excited octacoordinate

species in solution must be fluxional between dodecahedron, square antiprism, and/or cube.

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**Registry No.**  $[\text{Ce}(\text{OH}_2)_9]^{3+}$ , 59922-22-4;  $[\text{Ce}(\text{OH}_2)_8]^{3+}$ , 70273-04-0.

## Detection of $\text{H}_2$ , HD, and $\text{D}_2$ by Raman Spectroscopy: A Powerful Aid for the Elucidation of Reaction Mechanisms

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**Abstract:** The detection of  $\text{H}_2$ , HD, and  $\text{D}_2$  by gas-phase Raman spectroscopy has shown that the photochemical and thermal dehydrogenation of dioxabicyclo[ $n.2.2$ ]alkanes occurs by an intramolecular process. The general applicability of the Raman technique for the identification of dihydrogen produced in the course of a reaction is based upon the high-scattering cross section of dihydrogen, which allows the ready detection of submicromolar quantities of the gas.

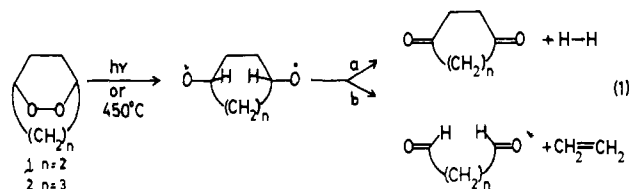
There are many chemical reactions in which dihydrogen is evolved. For some of these, a determination of the isotopic composition of the gas that is produced from reactants labeled at specific sites with deuterium could provide valuable mechanistic information. However, at present there appears to be no generally recognized method for effecting such an analysis, especially where the reactions are carried out on a small scale. One of us (R.J.H.C.) has previously shown that Raman spectroscopy can be used for this purpose in a study of the photolysis of pentamethylcyclopentadiene.<sup>1</sup> In the present work, we have extended the use of the technique to investigate the mechanism by which certain saturated bicyclic peroxides (dioxabicyclo[ $n.2.2$ ]alkanes) undergo dehydrogenation when pyrolyzed in the gas phase<sup>2</sup> or photolyzed in solution.<sup>3</sup> In addition to reporting these results, we wish to draw attention to the sensitivity and convenience of Raman spectroscopy as a method for detecting and distinguishing between  $\text{H}_2$ , HD, and  $\text{D}_2$ . The mechanistic value of this capability has been demonstrated, and the potential now exists for the application of this technique to a wide range of systems.

### Results and Discussion

Bicyclic peroxides were photolyzed or thermolyzed in sealed vessels, and the gaseous phase above each sample was then examined by Raman spectroscopy. The photolyses were carried out in benzene solution with benzophenone as sensitizer, whereas the thermolysis was effected in the gas phase by a flash pyrolytic technique. The following samples were examined: (i) photolyzed 2,3-dioxabicyclo[2.2.2]octane (**1**), (ii) thermolyzed 6,7-dioxabicyclo[3.2.2]nonane (**2**), (iii) photolyzed **2** (in  $\text{C}_6\text{D}_6$ ), (iv) photolyzed 1:1 mixture of **1** and 1,4-dideoxio-2,3-dioxabicyclo[2.2.2]octane (**1-d<sub>2</sub>**), and (v) photolyzed **1-d<sub>2</sub>**.

Previous work has established that photolysis<sup>3</sup> or flash vacuum pyrolysis<sup>2</sup> (FVP) of the [ $n.2.2$ ] peroxides **1** and **2** affords good yields of cycloalkane-1,4-diones, and it was suggested that these arise by extrusion of molecular hydrogen from intermediate cy-

cloalkanedioxy (eq 1a). Competitive formation of  $\alpha,\omega$ -di-aldehydes was detected under FVP conditions and was attributed to an alternative mode of double  $\beta$ -scission in which ethylene is extruded (eq 1b).



The presence of ethylene among the thermolysis products was confirmed, but the detection of dihydrogen was precluded by the nature of the analytical techniques used.

The Raman spectrum of the gas above a photolyzed sample of the [2.2.2] peroxide [experiment i] is shown in Figure 1a. The presence of dihydrogen is unambiguously established by the observation of lines assigned to the  $J = 0 \rightarrow 2$ ,  $J = 1 \rightarrow 3$ ,  $J = 2 \rightarrow 4$ , and  $J = 3 \rightarrow 5$  transitions, i.e., to the pure rotational  $S_0(J)$  lines of dihydrogen.<sup>4,5</sup> The relative intensities of these lines are governed by the nuclear spin and by the populations of the relevant states<sup>6</sup> and provide additional confirmation of the assignment of these transitions. Evidence for the presence of ethylene is also available, through the observation of its pure rotational spectrum,<sup>7</sup> particularly in the highly structured region between 60 and 100  $\text{cm}^{-1}$ , along with bands attributed to the  $\nu_1$  ( $a_g$ , 3019  $\text{cm}^{-1}$ ),  $\nu_2$  ( $a_g$ , 1625  $\text{cm}^{-1}$ ), and  $\nu_3$  ( $a_g$ , 1344  $\text{cm}^{-1}$ ) fundamentals.<sup>8</sup> Under the conditions of the experiment, the rotational structure associated with these bands was not resolved. The remaining bands are assigned to the  $\nu_1$  ( $a_g$ , 3073  $\text{cm}^{-1}$ ),  $\nu_2$  ( $a_g$ , 992  $\text{cm}^{-1}$ ), and  $\nu_2$

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