

The Application of Time-Resolved Laser Induced Fluorescence Spectroscopy in the Complexation Studies of Eu(III) and Cm(III) with Humic Substances

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The application of time-resolved laser induced fluorescence spectroscopy (TRLIF) to the complexation studies of Eu(III) and Cm(III) with humic substances is described. Using this method, three different spectroscopic characteristics (excitation spectra, emission spectra, and lifetimes) of these aquo ions and their complexes can be directly measured. By observing shifts in the wavelength and changes in the lifetime and intensities of the fluorescence emission, the information on the complexation behavior of humic substances with these trivalent metal cations in an aqueous solution, as well as energy transfer mechanisms, can be obtained. In addition, this method allows precise spectroscopic quantification of the complexation processes at very low concentrations of both components.

Introduction

In recent years, the need for direct verification and quantification of chemical species in the investigation of physicochemical systems has lead to the development of ultra sensitive analytical methods based on spectroscopic techniques. One such technique is the time-resolved laser induced fluorescence (TRLIF) spectroscopy, developed from the laser excitation in time-resolved fluorimetry used since the 1960s^{1,2}. The high sensitivity and selectivity of the TRLIF technique has been achieved by high power monochromatic pulse laser coupled to the time-gating electronics. Using this technique, the temporal behavior of the emission from a particular analyte can be distinguished from other components in the system by observing the luminescence decay. Furthermore, the signal of interest appearing in one region of time is recorded in the absence of other interfering signals which may occur at different time scales. Because of these advantages over the conventional absorption methods, the applications of TRLIF are being expanded to many new areas which demand high specificity, such as in speciation studies and trace analysis.

One such application of TRLIF is in the study of chemical reactions of heavy metal cations in natural aquifer systems³⁻⁵. Metal cations ($Z \geq 2+$) can remain as hydrated aquo ions or undergo complexation reactions with naturally occurring ligands to form a variety of species in natural aquifers. These ions can also undergo cation-exchange reactions with suspended clays or co-precipitates as carbonates or hydroxide with other cations of the aquifer such as Fe^{3+} , Mn^{2+} , and Al^{3+} ions⁶. Among natural organic species in surface and groundwaters, the most preponderant species are humic acid

(HA) and fulvic acid (FA). These naturally occurring organic acids are polyelectrolytes with high complexation affinity for metal cations, and are present as humic colloids in aquifer systems⁷. For the assessment of the migration behavior of the toxic heavy metal species in aquifer systems, each of these processes must be quantified. This requires thorough investigations of the nature of these processes, using advanced analytical tools available.

This work presents the study of the complexation reactions of humate and fulvate with trivalent lanthanide (Eu) and actinide (Cm) using TRLIF. The emphasis is placed on the determination of the changes in the fluorescence intensity and the lifetime of emission, and wavelength shift, which provide the information on the chemical nature and energy transfer mechanisms of these aquo ions and their humate or fulvate complexes.

Luminescence Characteristics of Eu(III) and Cm(III) Ions

The energy diagram of the Eu^{3+} ion, with $4f^6$ electronic configuration, is shown in Figure 1. The characteristic luminescences of the aquo Eu(III) ion and Eu(III) complexes have been reviewed in details by Richardson⁸. The diagram in Figure 1 shows that there are many energy transitions which are possible in an Eu(III) ion. Among them, the $^5D_0 \rightarrow ^7F_1$ (588-600 nm range) and $^5D_0 \rightarrow ^7F_2$ (610-630 nm range) transitions invariably provide the strongest emissions, although $^5D_0 \rightarrow ^7F_4$ (680-705 nm range) transition is also frequently observed in moderately strong fluorescence intensity. The other remaining $^5D_0 \rightarrow ^7F_j$ transitions are either very weak in intensity or are not observable. It can be further noted

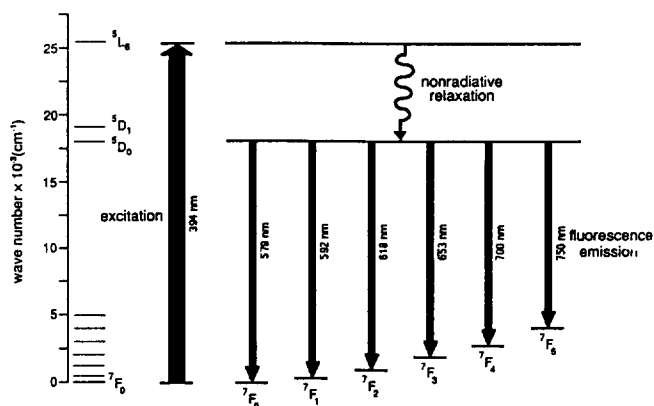


Figure 1. Energy level diagram of the Eu(III) ion displaying the spectroscopic features.

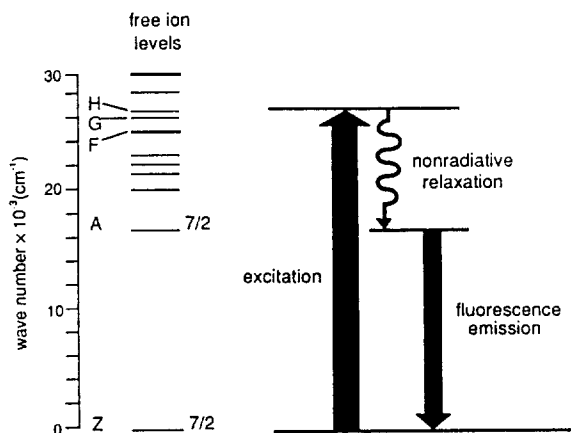


Figure 2. Schematic diagram of the energy levels of Cm(III) ion, showing the most important of the excitation and emission characteristics.

that the relative intensities of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions are extremely sensitive to the nature of the ligands surrounding the environment of a central metal cation. The splitting patterns of their emission are observed to be relatively simple even when the symmetry of the system is low. Therefore these two transitions ($^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$) are regarded as the important probe transitions for Eu(III) ion and its complexes. By examining the number, energy spacings, and relative intensities of these components, the detailed information about the symmetry, the chemical nature of the Eu^{3+} coordination sites, and the relative amounts of Eu species present in the aquifer systems, are obtainable.

The schematic energy level diagram, displaying the important excitation and emission states, of Cm(III)^{9,10} is shown in Figure 2. The excitation of Cm(III) is dominated by the strong f-f transitions from the Z-ground states ($^8S_{7/2}$ of the half-filled $5f^7$) to three excited states G, H and F. The absorption maxima of these excitation bands in an aqueous solution are observed at 369.0 nm ($\epsilon = 55.3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 381.3 nm ($\epsilon = 32.6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), and 375.5 nm ($\epsilon = 29.3 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) respectively¹¹. The first excited A-state ($J=7/2$) is populated by the subsequent deexcitation process, from which a radiative decay can occur down to the Z-groundstate with a relatively high quantum efficiency¹¹, yielding the emi-

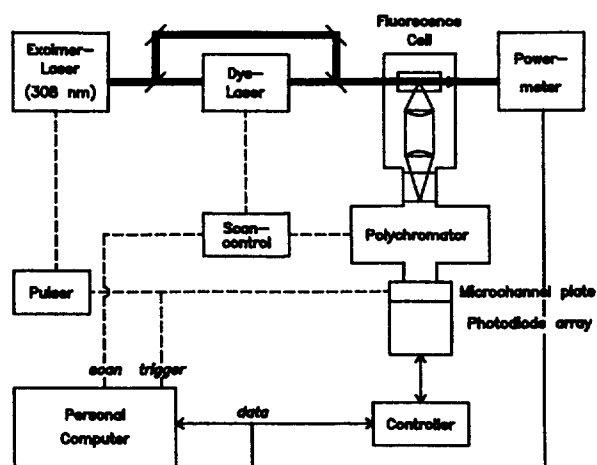


Figure 3. A diagram of the experimental setup of the time-resolved laser induced fluorescence spectroscopy.

ssion peak at 593.5 nm for aquo Cm(III) ions. The lifetime of this radiative emission (A $\rightarrow$ Z state) is measured to be 63 μs for Cm(III) ions in 1 M HClO_4 ^{9,12}.

Experimental

A block diagram displaying the experimental arrangement of the TRLIF used in this investigation is shown in Figure 3. The light source used in the setup consists of dye laser (Lambda Physik, FL2002), using both the PBO and BBQ dyes, which is pumped by an excimer laser (Lambda physik, EGM 201E) operating at 308 nm (XeCl mixture). This source delivers approximately 10 ns pulses with an average energy of 5 mJ at a repetition rate of 5 Hz. The focused output beam is directed to a rectangular quartz cuvette containing the relevant solution of investigation. The light source is coupled to a fluorescence center, which consists of a polychromator (Jobin Yvon, HR 320) and an optical multichannel analyzer (Princeton Spectroscopy Instr., OSMA IRY700GR). The detector system consists of a time-gating microchannel plate for light amplification and 1024 Si-photodiodes. A spectral resolution of 0.2 nm is attainable for a bandwidth of 40 nm at 1200 cm^{-1} grating.

The stock Eu(III) solutions, used in this investigation, are prepared by dissolving Eu_2O_3 (Fluka Co.) with 1.0 mL of 0.1 M HClO_4 and further diluting them with 0.1 M NaClO_4 , containing 10^{-3} M MES buffer (2-morpholineethane sulfonic acid), resulting in Eu(III) concentrations ranging from 1.0×10^{-7} to 5.0×10^{-6} M. The stock solutions are adjusted to pH at 6.0 with 0.1 M NaOH (carbonate free, Baker Co.). The stock Cm(III) solution (1.0×10^{-7} M) is prepared from ^{244}Cm , purified from its daughter nuclide ^{240}Pu by anion exchange, in 0.1 M NaClO_4 (10^{-3} M MES buffer) and pH adjusted to 6.0. A small ^{241}Am impurity ($\sim 10\%$) does not affect the measurement of Cm fluorescence, because ^{241}Am has a very short lifetime of fluorescence (30 ns) with low fluorescence yield¹³.

The humic and fulvic acids are extracted from soils sampled from the Okchun Metamorphic Belt region of Kuye San and are purified by the method recommended in the literature¹⁴. These soil humic substances, which contain rich com-

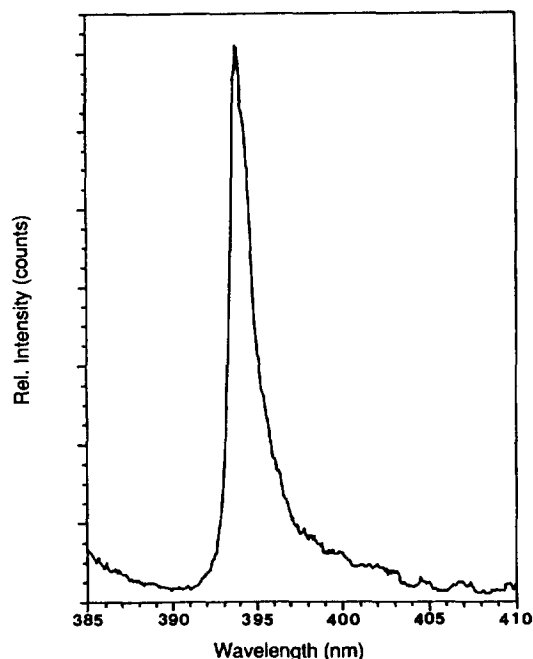


Figure 4. The excitation spectrum of the aquo Eu(III) ion in 0.1 M HClO₄ solution ($[Eu] = 1.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$).

ponents of polysaccharides and proteins, displayed characteristics unique of the monsoon rain-belt region of Korea. The details of the characterization of the humic substances from this area is described elsewhere¹⁵. For the complexation study, the stock solutions of humic and fulvic acids are prepared ($\sim 40 \text{ mg}/100 \text{ mL}$) by dissolving the appropriate organic acids with minimum quantities of 0.1 M NaOH (carbonate free, Baker Co.) and diluting them with 0.2 M NaClO₄ (10^{-3} M MES buffer) and pH adjusted to 6.0. The proton exchange capacity of HA (2.65 meq g^{-1}) and FA (7.07 meq g^{-1}), determined by a direct pH titration, is used for estimating the concentrations of the humic or fulvic acid in solutions.

Results and Discussion

Spectroscopic features of humic complexes of Eu(III) and Cm(III). The excitation spectrum of the aquo Eu(III) ion ($[Eu] = 1.0 \times 10^{-6} \text{ mol L}^{-1}$ in 0.1 M HClO₄), obtained by scanning the excitation wavelength and monitoring the emitted light over a constant range with a 40 nm window setting in the polychromator for the emission peak maximum, is shown in Figure 4. It shows a strong peak maximum at 394 nm, which is readily attributable to the transition from 7F_0 to 5L_6 state (see Figure 1), and is similar to the spectroscopic feature of its absorption spectrum. However, when a large excess HA or FA (200 fold excess) are added to the solution, the spectroscopic characteristics undergo a considerable change. The normally sharp and intense Eu(III) excitation peak at 394 nm is replaced by a very broad spectrum in the wavelength regions of 380–410 nm. Although no significant spectroscopic information can be derived from such a broad spectrum profile, this does provide an ample evidence of the strong interaction between humic substances and Eu(III) ions in aqueous media.

A similar phenomenon is observed in the excitation spec-

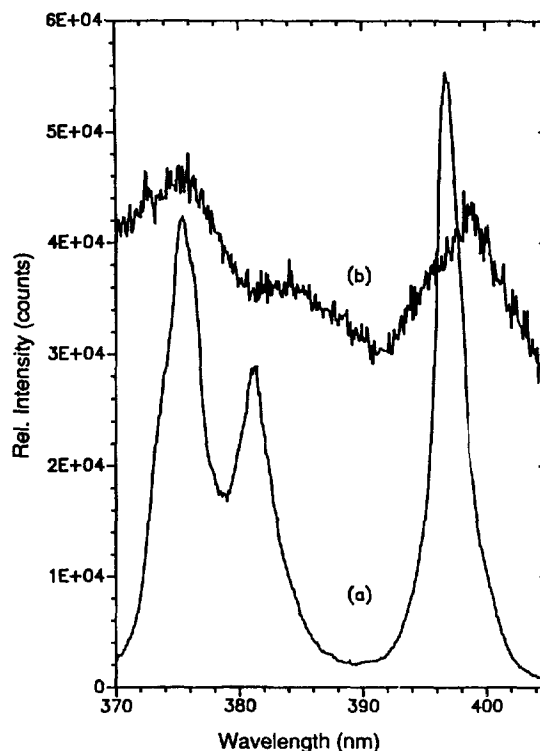


Figure 5. The excitation spectra of (a) aquo Cm(III) ion ($[Cm] = 8.2 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$; pH=6.0), and (b) Cm-humate ($[Cm] = 6.7 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$; $[HA] = 9.4 \text{ mg} \cdot \text{L}^{-1}$; pH=6.0).

tra of Cm(III) ion and its complexes. The excitation spectrum of the aquo Cm(III) ion ($[Cm] = 8.2 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$) is shown as the spectrum (a) in Figure 5, with three sharp excitation peaks of H (375.4 nm), G (381.4 nm), and F (396.5 nm) bands which are nearly identical to its absorption characteristics. When an excess HA is added to the Cm(III) ion solution ($[Cm] = 6.7 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$; $[HA] = 9.36 \text{ mg} \cdot \text{L}^{-1}$), the spectroscopic features undergo a considerable change as is seen in the spectrum (b) of Figure 5. All three peaks of the absorbing states show peak broadening accompanied by increase of baseline between the states. In addition, a small but significant peak shift, from 395.5 nm to 398.3 nm, is observed for the F band, which may be due to the non-selective energy transfer from the excess HA present in the solution to the Cm-humate complex. Similar phenomenon has been observed for the excitation spectrum of the Cm-fulvate complex, and has also been reported for other Cm complexes³.

Contrary to the absorption energy states, certain emission bands are highly sensitive to the nature of the ligands surrounding the central metal cation (see the review section on the luminescence characteristics of Eu(III) and Cm(III)). Therefore, the measurement of fluorescence emission is a viable method for the studies of the interaction of Eu(III) and Cm(III) ions with humic substances. The emission spectra of the aquo Eu(III) ion, Eu-fulvate and Eu-humate complexes are shown in Figure 6. It shows that the emission spectrum of the aquo Eu(III) ion, consists of the peaks at 592 nm ($^5D_0 \rightarrow ^7F_1$), 618 nm ($^5D_0 \rightarrow ^7F_2$), and 695 nm ($^5D_0 \rightarrow ^7F_4$), with the $^5D_0 \rightarrow ^7F_1$ transition showing the strongest radiation intensity. When HA or FA are added in large excess to the ion solutions, the emission spectra undergo considerable

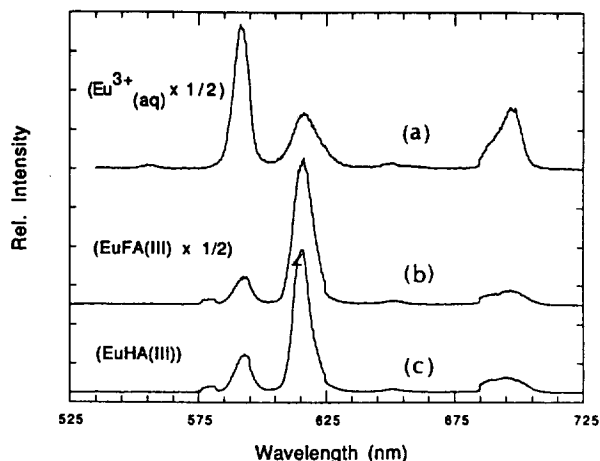


Figure 6. The spectra of fluorescence emission of (a) aquo Eu(III) ion ($[\text{Eu}] = 5.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; $\text{pH} = 6.0$), (b) Eu-fulvate ($[\text{Eu}] = 7.4 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$; $[\text{FA}] = 3.4 \text{ mg} \cdot \text{L}^{-1}$; $\text{pH} = 6.0$), and Eu-humate ($[\text{Eu}] = 7.4 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$; $[\text{HA}] = 8.9 \text{ mg} \cdot \text{L}^{-1}$; $\text{pH} = 6.0$).

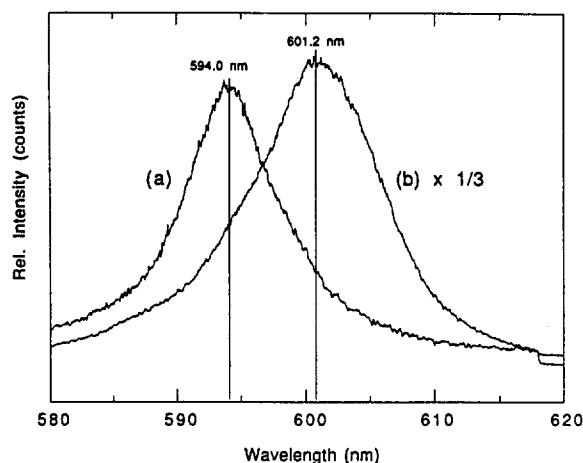


Figure 7. The spectra of fluorescence emission of the (a) aquo Cm(III) ion ($[\text{Cm}] = 5.7 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$; $\text{pH} = 6.0$), and Cm-fulvate ($[\text{Cm}] = 7.6 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$; $[\text{FA}] = 0.67 \text{ mg} \cdot \text{L}^{-1}$; $\text{pH} = 6.0$).

changes: Although no peak shifts are observed, the radiation intensities of the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_4$ transitions become relatively weaker, while that of the $^5D_0 \rightarrow ^7F_2$ transition becomes stronger. This reflects the hypersensitive character of the $^5D_0 \rightarrow ^7F_2$ transition state. Richardson⁸ in his review explained these observations in a following manners: Even in low symmetry systems, the $^5D_0 \rightarrow ^7F_1$ transition largely retains its magnetic dipole character, therefore its radiative transition probability is not significantly affected by the ligand environment; by contrast, the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_4$ transitions are predominately electric dipole in character, and their radiative transition probabilities are strongly dependent upon the structural characteristics of ligands.

Once excited by the dye laser, tuned for the excitation to the peak maximum of the H band (375 nm), the excited Cm species can undergo a non-radiative decay populating the A-state ($^6D_{7/2}$). A significant radiative decay can occur from this state to the ground state with relatively high quan-

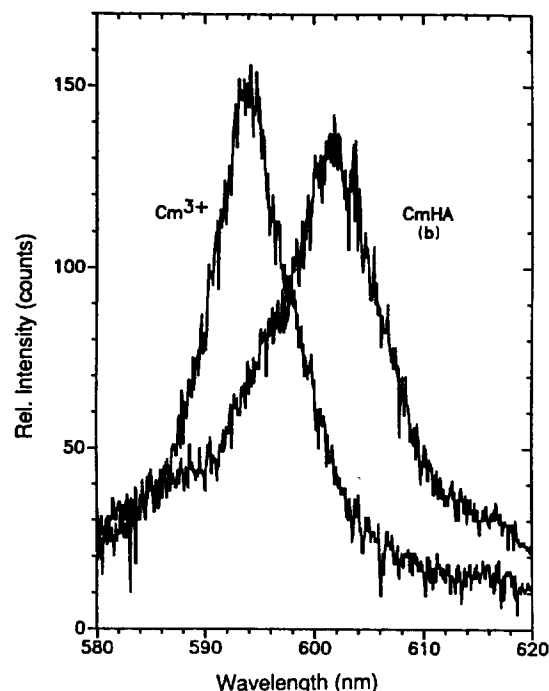


Figure 8. The spectra of the fluorescence emission of the (b) Cm-humate ($[\text{Cm}] = 6.3 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1}$; $[\text{FA}] = 16.8 \text{ mg} \cdot \text{L}^{-1}$; $\text{pH} = 6.0$).

tum yield. The emission spectra of the aquo Cm(III) ions and Cm-fulvate complex are shown in Figure 7. The spectrum (a) is characteristic of the emission band of the aquo Cm(III) ions, showing a peak maximum at 594.0 nm with a peak width of 8.0 nm (FWHM). On the other hand the spectrum (b) of the Cm-fulvate in a large excess of FA ($2.0 \text{ mg} \cdot \text{L}^{-1}$) shows a single emission band (a peak maximum at 601.2 nm) of somewhat broader peak width (FWHM: 11.0 nm). The emission spectrum of the Cm-humate complex displays a similar peak shift, and is shown in Figure 8 for comparison. It can be seen that the fluorescence yield of the Cm-fulvate emission (spectrum (b) in Figure 7) is approximately three times as large as compared to that of the Cm-humate (spectrum (b) in Figure 8). This suggests that the energy transfer from the excess FA to Cm-fulvate complexes in solutions is more efficient. All these results clearly show that the emission energy of the A band is strongly affected by the crystal field splitting, confirming that humate and fulvate are extensively complexed to the inner coordination sphere of Cm(III) ions. The peak shift of 7.2 nm, attributed to an increase of crystal field splitting of the A-state, is significantly large for the quantification of the FA and HA complexation reactions with Cm(III).

The lifetime of fluorescence emission. Humic and fulvic acids are natural organic polyelectrolytes which have similar structures, but contain a variety of oxygen containing functional groups (e.g. carboxyl, phenolic-OH and alcoholic-OH)¹⁶. These binding sites of humic substances can interact with metal cations to form complexes. The measurement of the lifetime of fluorescence can provide useful information about the nature of the interaction between humic substances and aquo ions of Eu(III) and Cm(III). The lifetime of an excited state is determined in part by a non-radiative

Table 1. Fluorescence Lifetime of Aquo Eu(III) ion, Eu-humate and Eu-fulvate Complexes in Differing Solution Media Measured by TRLIF (in μs); the Numbers in Paratheses Indicate the Relative Contribution of Each Time Components (in percent)

Species	Excitation Wavelength				Solution	pH	Remarks
	308 nm		394 nm				
	τ_1	τ_2	τ_1	τ_2			
Eu(III)			107		H ₂ O	6.0	[Eu]= 5×10^{-7} mol/L
			2290		D ₂ O	5.5	[Eu]= 1×10^{-7} mol/L
EuFA	86 (57%)	197 (43%)			H ₂ O	6.0	[Eu]= 5×10^{-8} mol/L
	81 (64%)	194 (36%)			H ₂ O	5.0	[FA]=18.8 mg/L
			84 (45%)	227 (55%)	H ₂ O	5.0	
	672 (67%)	1742 (33%)			D ₂ O	6.0	[Eu]= 5×10^{-7} mol/L
			640 (61%)	1785 (39%)	D ₂ O	5.5	[FA]=21.1 mg/L
EuHA	88 (55%)	197 (45%)	84 (69%)	227 (31%)	H ₂ O	6.0	[Eu]= 5×10^{-8} mol/L
	80 (49%)	200 (52%)			H ₂ O	5.0	[HA]=11.7 mg/L
	671 (49%)	1624 (51%)			D ₂ O	5.5	[Eu]= 5×10^{-7} mol/L
							[HA]=16.3 mg/L

pathway, namely by transferring energy from electronic to vibrational modes of coordinated water molecules. Therefore, the type and number of ligands which lead to the substitution of the coordinated water molecules from the central metal cation, can cause changes in the lifetime as well as the fluorescence yield.

The Eu(III)-coordinated water molecules (and OH⁻ ions) are known to be excellent non-radiative relaxer of the ⁵D₀ excited state of the aquo Eu(III) ions, and are much more effective than the coordinated D₂O (and OD⁻ ions) molecules. In fact Horrock and Sudnick¹⁷, in their investigation of the lanthanide ion probes of structure in biology, obtained laser-induced luminescence decay constants of Eu(III) and Tb(III) in both H₂O and D₂O solutions to measure directly the number of metal-coordinated water molecules. Accordingly, increase of the lifetime is expected when the number of metal-coordinated water molecules are reduced by the presence of complexing humate or fulvate.

The lifetime of the fluorescence emission of the aquo- Eu (III) ions, Eu-fulvate and Eu-humate complexes are measured in both H₂O and D₂O solutions, using either the excitation wavelength of the excimer laser (308 nm) or the dye laser tuned to 394 nm (⁷F₀→⁵L₆ transition), and the results are summarized in Table 1. The results show that the lifetime of the fluorescence emission of the aquo Eu(III) ions is dramatically increased from 103 μs in H₂O solution ([Eu] = 5.0×10^{-5} mol·L⁻¹) to 2290 μs in D₂O solution ([Eu] = 1.0×10^{-7} mol·L⁻¹), confirming that the modulation of the lifetime is ligand-dependent, and both the radiation and nonradiative ⁵D₀→⁷F_J transition probabilities are affected. The results also show that the lifetime of the fluorescence emission of the Eu-humate and Eu-fulvate complexes are comprised of two time components. The short time component (τ_1) which is somewhat similar to that of the aquo Eu(III) ions, and the longer time component (τ_2) is the result of dehydration of the metal-coordinated water molecules by HA or FA. The similarity of the measured lifetime of the Eu-humate and

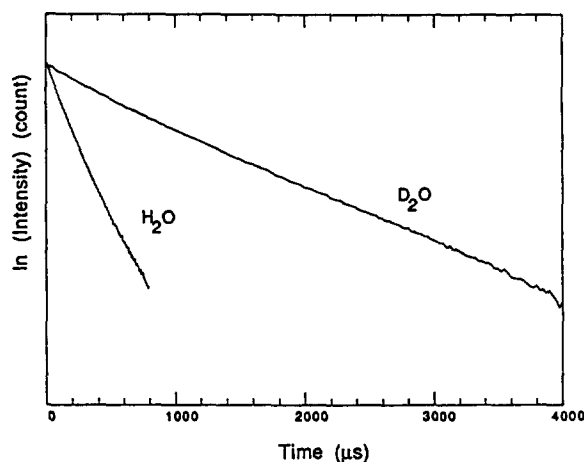
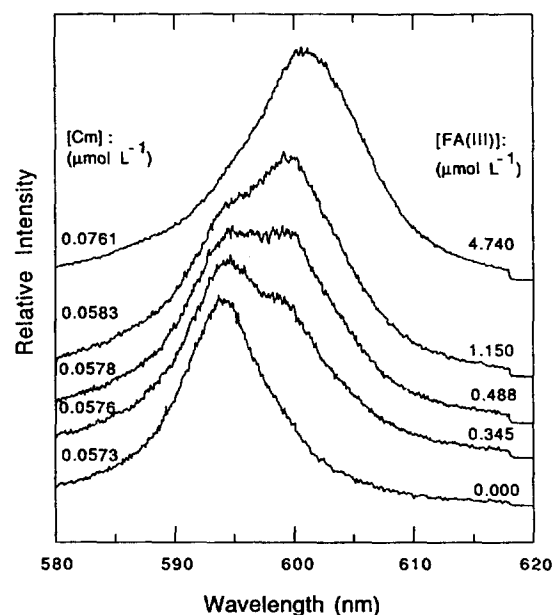
Eu-fulvate complexes proves that HA and FA are complexed to Eu(III) in the same manners. The mode of irradiation (308 nm or 394 nm) had little effect on the lifetime measured, suggesting that non-selective energy transfer is readily taking place between the excess HA or FA (with relatively short lifetime of <50 ns) and with the Eu-humate or Eu-fulvate complexes.

It is assumed that an aquo Cm(III) ion has between 8-9 molecules of H₂O coordinated to it. Beitz and Hessler¹² showed that the lifetime of the fluorescence emission of aquo Cm(III) ions in H₂O and D₂O solutions are 63 μs and 940 μs respectively, which is a clear evidence for the dominant roles played by the high frequency fundamental vibration modes of the Cm(III)-coordinated water molecules in the non-radiative decay processes. The lifetime of Cm-humate or Cm-fulvate complexes are expected to show an increase with respect to the aquo Cm(III) ions in H₂O solution.

The lifetime of the Cm-fulvate complex measured in differing solution pH is summarized in Table 2. The results show that the lifetime of Cm-fulvate also consists of two components in all cases. Both time components of the lifetime of Cm-fulvate show increases as pH of the solution is raised from 3.0 to 6.0. This is due to the increase in the number of negatively charged binding sites (e.g. increase in the degree of ionization of carboxyl groups) of FA, as pH of the solution is raised, which can interact intensely with Cm(III) ions. Further increase of pH to 7.0, resulted in the decrease of the lifetime components, caused by the hydrolysis of Cm(III) ions which is known to occur extensively at pH>6.0. The short time components (τ_1) of the Cm-fulvate, shown in Table 2, are similar to that of aquo Cm(III) ions (63 μs), while the longer time components (τ_2) are quite comparable to those values obtained for Cm-EDTA (126 μs) and Cm-carbonate (141 μs) complexes³. The lifetime of Cm-fulvate in D₂O solution is very much longer than that in H₂O solution (see Figure 9). These results suggest that Cm (III) ions are complexed predominately to the carboxyl

Table 2. Fluorescence Lifetime of Aquo Eu(III) ion and Cm Complexes in Aqueous Solutions of Differing pH Determined by TRLIF (in μs)

Species	Excitation Wavelength				Solution	pH	Remarks
	308 nm		394 nm				
	τ_1	τ_2	τ_1	τ_2			
Cm(III)			72		H ₂ O		[Cm]=3.7×10 ⁻⁸ mol/L
			65		H ₂ O		Ref. 12
			2290		D ₂ O		Ref. 12
CmHA	47	146			H ₂ O		[Cm]=6.3×10 ⁻⁸ mol/L [HA]=9.4 mg/L
CmFA	56 (50%)	102 (50%)			H ₂ O	3.0	[Cm]=7.6×10 ⁻⁶ mol/L
	62 (50%)	105 (50%)	55 (52%)	114 (48%)	H ₂ O	3.8	[FA]=2.0 mg/L
	63 (54%)	122 (46%)	60 (50%)	112 (50%)	H ₂ O	5.0	
	77 (53%)	143 (47%)	63 (50%)	138 (50%)	H ₂ O	6.0	
	63 (56%)	138 (44%)	53 (45%)	123 (55%)	H ₂ O	7.0	
	322 (42%)	641 (58%)	272 (46%)	653 (54%)	D ₂ O	6.0	[Cm]=7.6×10 ⁻⁶ mol/L [FA]=2.0 mg/L

**Figure 9.** Lifetime diagram of the Cm-fulvate in (a) D₂O and (b) H₂O solutions ([Eu] = 7.8×10^{-8} mol·L⁻¹; [HA] = 3.3 mg·L⁻¹; pH = 6.0).**Figure 10.** Emission spectra illustrating the complexation process of fulvate with Cm(III).

groups of FA; the formation of tridentate complexes (1:1 complex) of aquo-Cm³⁺ species. However, the sterically dispersive nature of binding sites and the involvement of somewhat different functional groups within FA should also be taken into consideration in the evaluation of these results.

Spectroscopic quantification of the complexation process. One of the key parameter, required for the assessment of the migrational behaviour of the toxic heavy metals in natural aquifer systems, is the complexation constant. The complexation of trivalent metal cations with humic substances have been investigated using solvent extraction¹⁸, ion-exchange¹⁹, spectrophotometry²⁰, gel permeation chromatography²¹, and ultrafiltration²² in the past. More recently, however, the application of laser induced photoacoustic spectroscopy (LPAS)²² and time-resolved laser fluorescence spectroscopy (TRLIF)^{4,5,10} to the same complexation studies have demonstrated the superior sensitivity of these modern spectroscopic methods. In the case of TRLIF, the measurement of fluorescence emission generated under energy-selection and time-gating, allows for spectroscopic distinction of aquo Cm(III) ion and Cm-fulvate complex, while discriminating the fluorescence of FA (<50 ns) present in excess.

The results obtained from the application of TRLIF to the study of fulvate complexation with Cm(III) are shown in Figure 10. The bottom spectrum represent the aquo Cm(III) ion, whereas the top spectrum is that of the Cm-fulvate complex.

The results obtained from the application of TRLIF to the study of fulvate complexation with Cm(III) are shown in Figure 10. The bottom spectrum represent the aquo Cm(III) ion, whereas the top spectrum is that of the Cm-fulvate complex.

plex. The fluorescence intensities (FI) of the aquo Cm(III) ion and Cm-fulvate complex are determined (excitation at 375 nm) for the purpose of calibration:

Species	FI (Counts $\text{mJ}^{-1} \cdot \text{L} \cdot \text{mol}^{-1}$)	Ratio
Aquo Cm(III) ion	3.73 ± 0.30 (594.0 nm)	1.00
Cm-fulvate complex	14.12 ± 0.50 (601.2 nm)	3.79 ± 0.06

The spectra in between stands for composites of the aquo Cm(III) ion and Cm-fulvate complex, obtained by varying the concentration of FA. The ratio of [Cm-fulvate]/[aquo Cm(III) ion] in each of the composite spectrum is being determined utilizing the top and bottom spectra as references. A more comprehensive study of the complexation constant of Cm(III) with the local sample fulvate¹⁰ and with model compounds (e.g. polymetaacrylic, polybenzoic, and polyphe-nolic acids) are in progress to better understand the complexation behavior of these natural organics.

Conclusion

This preliminary work has demonstrated that the time-resolved laser induced fluorescence spectroscopy, when applied to complexation studies, presents a rapid and direct method with high sensitivity and reliability. Using TRLIF, three different spectroscopic characteristics of Eu(III) and Cm(III) complexes can be measured, namely excitation spectra, emission spectra, and lifetime of fluorescence emission. They all provide useful information about the nature of interaction between Eu(III) or Cm(III) and humic substances. Furthermore, this method allows for investigations to be carried out at low concentrations of humic substances to avoid aggregation phenomena, and at concentrations of Eu(III) and Cm(III) below their solubility limits. Thus the investigation can cover a wider range of solution pH.

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