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ciable oscillator strength from the ground state. Our calculations indicate that for states with $v \geq 7$, the resonances will show asymmetric features due to the quantum interference between the binding $A^2\Sigma^+$ and the dissociative $^2\Sigma^-$ state. Figure 2 depicts the resonance corresponding to the F_2 level $(J_f = N+1)$ with $N=2$ and $v=9$ of the $A^2\Sigma^+$ state. $(J_f$ and v are the total angular momentum and vibrational quantum numbers, respectively, and N is the quantum number that describes the Hund's case (b) rotational levels). The total cross section as well as the partial cross sections to each spin orbit component $O(^3P_j, j=0, 1, 2)$ exhibit highly asymmetric features. The initial ground state is the $X^2\Pi_{2/3}$ state, which is of the lowest energy, with $J_i = 3/2$. The zero of energy is taken as the statistical average of the $O(^3P_j, j=0, 1, 2)$ fine structure splittings. The total cross section does not decay to zero near the resonance, in contrast to the predissociation of Cs_2[8] near 580 nm, since there is more than one (at least three repulsive states $^4\Sigma^-$, $^2\Sigma^-$ and $^4\Pi$) continuum state involved in the predissociation precess.[6] More importantly, the partial cross sections show different degrees of asymmetry, represented by different values of the parameter q.[6] The asymmetry of the partial cross sections to $O(^3P_0)$ can be understood easily, since the $^2\Sigma^-$ state correlates with this oxygen fine structure component,[14] and since this state is optically coupled with the ground $X^2\Pi$ state. However, it is very intriguing that the partial cross sections to $O(^3P_1)$ and to $O(^3P_2)$ exhibit asymmetric resonances as well, since the $^4\Sigma^-$ and $^4\Pi$ states, whose spin-orbit components dissociate to $O(^3P_j, j=1, 2)$ states,[14] do not carry oscillator strengths from the $X^2\Pi$ state. One possibility is that the $^4\Sigma^-$ and $^4\Pi$ states may borrow intensity from the bright $^2\Sigma^-$ state by continuum-continuum interactions[15,16] among these dissociative states. Further investigations are under way.

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Observation of Charge Transfer in Eu³⁺-Aliphatic Carboxylate Mixtures

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Studies on the luminescence intensity of lanthanide ions (Ln^{3+}) have been topics of great interest to numerous physical, chemical and biological systems.[1,2] Since the absorption cross sections of Ln^{3+} are small within the uv-visible spectral region,[3] a primary mechanism of luminescence from Ln^{3+} involves their sensitization by organic chelates.[4] In the previous work,[5] we reported the luminescence properties of PSMA-Ln^{3+} (Ln = Tb, Eu, Dy, Yb, Gd) complexes in aqueous solution, where PSMA stands for the sodium salt of styrene and maleic acid copolymer.

By considering spectral overlap integrals,[6] unlikely low efficiencies of energy transfer from the styryl moieties to Eu^{3+} in PSMA-Eu^{3+} was obtained as compared with PSMA-Tb^{3+}. Although a charge transfer (CT) band was not clearly observed, we proposed that the insignificant sensitized emission arises because of a low-lying ligand-to-Eu^{3+} CT band. The CT states were suggested to be the most effective acceptor states in many ligand-to-Eu^{3+} electronic energy transfer processes occurring in the near uv spectral range, and their existence accounted for the relatively large quenching efficiencies of Eu^{3+} toward intrinsic ligand luminescence.[7] To obtain the effectively sensitized emission from Eu^{3+}, better understanding of the energies of CT band is essential.

In this communication, we report the finding of CT bands in Eu^{3+} and some simple aliphatic carboxylate mixtures. Absorption spectra were recorded on a Hewlett Packard 8542A diode array spectrophotometer, and luminescence measurements were carried out by a Hitachi 650-60 spectrofluorimeter. Chloride salts of lanthanide ions (purity of 99.9% or greater from Aldrich) were used without further purification. All other chemicals of GR grade were used as received.

The absorption and excitation spectra of Eu^{3+}, sodium acetate, and Eu^{3+}-acetate mixture in aqueous solution are shown in Figure 1. The narrow bands in Figure 1b correspond to metal centered $4f \rightarrow 4f$ transitions,[8] which could be hardly observed in the absorption spectra (Figure 1a). Mixtures of acetate in the form of sodium salt and Eu^{3+} exhibit
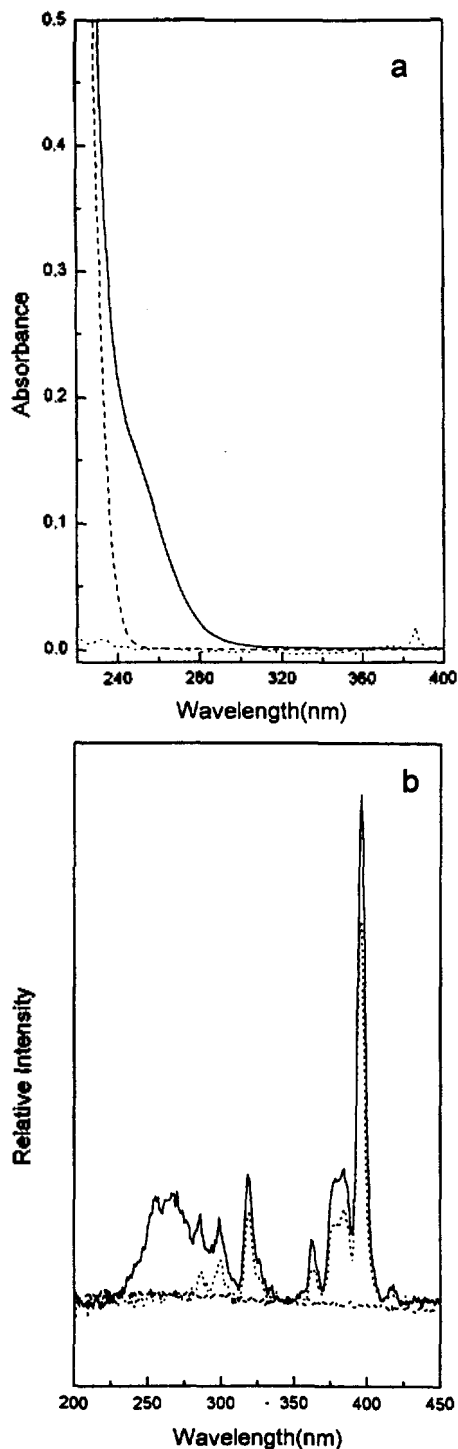
Figure 1. Absorption(a) and excitation(b) spectra of Eu^{3+} (dotted lines), acetate (dashed lines), and Eu^{3+}-acetate mixture (solid lines) in aqueous solution. $\lambda_{em} = 595$ nm. $[Eu^{3+}] = 1.0 \times 10^{-3}$ M, $[CH_3COO^-] = 0.10$ M.

a much broad and intense band both in the absorption and excitation spectra compared with f-f transitions in the near uv region with $\lambda_{max} = 265$ nm and FWHM $\cong 5,300$ cm^{-1} measured from the excitation spectrum, Figure 1b. The band is not shown by either Eu^{3+} or carboxylates seperately. The results suggest the presence of a charge transfer transition,

Table 1. Luminescence properties of Eu^{3+} in aqueous solution containing some aliphatic carboxylates. λ_{max} and FWHM are derived from the excitation spectra and I_{618}/I_{595} are calculated from the emission spectra. Concentration: Eu^{3+}, 1.0×10^{-3} M; carboxylate, 0.10 M

Carboxylate	λ_{max} (nm)	FWHM (cm^{-1})	I_{618}/I_{595}
formate	264	5200	1.7
acetate	268	5300	2.3
propionate	269	5400	2.8
TFA	–	–	0.7
none	–	–	0.5

which originated most likely from the coordinated oxygen donor atom of carboxylate to Eu^{3+}. The intensity ratio of the band at 265 nm to 396 nm in the excitation spectrum of Eu^{3+}-acetate (Fig. 1b) is much smaller than that in the absorption spectrum (Fig. 1a), implying that the conversion efficiency of this new band to the emitting state of Eu^{3+}, $^5D_0$, is smaller than that of the band at 396 nm to $^5D_0$. The relatively small extinction coefficients are quite normal for CT bands of Ln^{3+} because of the small overlap between the donor ligand orbitals and the acceptor $4f$ metal orbitals.[9] The properties of the CT states have intimate dependence on the oxidation or reduction potential of the ligand and on the ligand environments.[10] The CT band is not observed in carboxylate complexes with other lanthanide ions, such as Tb^{3+}, La^{3+}, Yb^{3+}, Sm^{3+} and Gd^{3+}, which are not easily reduced compared with Eu^{3+}. Eu^{3+} has a relatively low standard reduction potential of -0.43 V $vs.$ NHE in aqueous solution, whereas the standard reduction potential of Yb^{3+}, the next smallest one, is -1.05 V $vs.$ NHE.[3b]

To confirm further that the energy necessary for the CT transition is directly related to the ionization potential of a donor, luminescence properties of Eu^{3+} in aqueous solution were measured in the presence of some aliphatic carboxylates, such as formate, propionate, and trifluoroacetate (TFA) and summarized in Table 1. Except trifluoroacetate no noticeable changes were observed in terms of λ_{max}, FWHM, and I_{618}/I_{595}, where the latter is the ratio of the $^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$ relative peak intensities of Eu^{3+}. Upon addition of trifluoroacetate which is not easily oxidized compared with acetate, the CT band disappears in the spectral region where the mixtures of Eu^{3+} and other carboxylates exhibit the CT bands. However, from the definitely increased peak intensity ratio, I_{618}/I_{595},[11] measured from emission spectra, it is certain that trifluoroacetate weakly coordinates to Eu^{3+}. Further studies will reveal which is responsible for the absence of the CT band in the mixture of Eu^{3+} and trifluoroacetate, the high oxidation potential or weak coordinating ability.

One of the common criteria for the validity of a CT transition is the effect of solvent on the spectral shift of the CT band. Unfortunately, however, no suitable solvents were found because Eu^{3+} and aliphatic carboxylate are not very soluble in most of nonpolar solvents. Moreover, the availability of solvents is further limited because the CT bands are expected to have small absorption cross sections and to arise in the near uv region, where the solvent absorption predominates over the CT absorption. The absorption and excitation
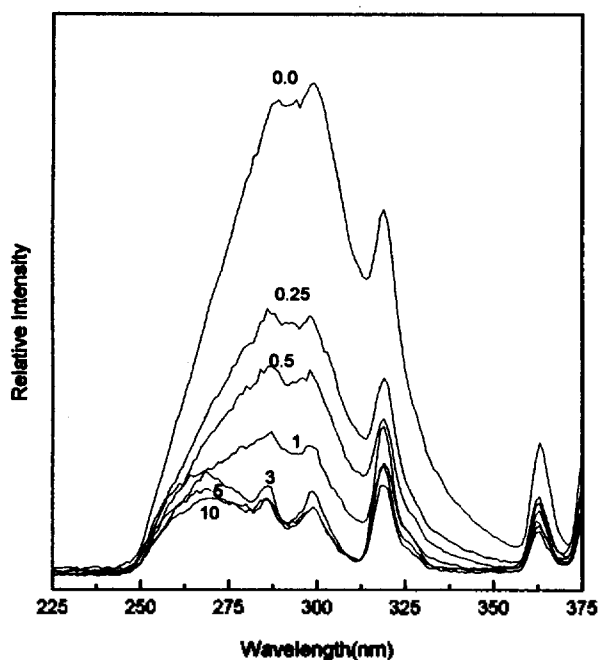
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Figure 2. Effect of water concentrations on the excitation spectra of 1.0×10^{-3} M $EuCl_3$ in acetic acid. The numbers in the figure are the molar concentrations of water. $\lambda_{em} = 595$ nm.

spectra obtained in different solvents such as D_2O and methanol closely resemble those obtained in water. However, the solution of $EuCl_3$ in pure acetic acid was found to exhibit a CT band whose relative oscillator strength, absorption maximum ($\lambda_{max} = 287$ nm) and FWHM (5,500 cm^{-1}) differ markedly from those found in aqueous medium. The band is attributed to a charge transfer transition from Cl^- to Eu^{3+}.[12] Upon addition of water to the solution of $EuCl_3$ in acetic acid, the peak position of the CT band is progressively shifted to the CT band from carboxylate to Eu^{3+} and the luminescence intensity is diminished as shown in Figure 2. The shift of the Cl^--to-Eu^{3+} CT band can be explained by considering that the association with acetate anion formed by the addition of water reduces the effective charge of Eu^{3+} followed by the subsequent increase in the energy of the ligand-to-metal CT transitions involving the carboxylates. In the solid state chemistry an example of this effect is found in mixed metal oxides containing six coordinated Eu^{3+}.[13]

More studies of the effect of solvents, *e.g.* ethanol and methanol, and dicarboxylates are in progress.

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