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## Laser-induced Fluorescence Studies of $\text{Cm}^{3+}$ Complexes in Solution

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*Complexation/Speciation/Photophysics/Laser-induced fluorescence*

### Abstract

Photophysical studies of complexed  $\text{Cm}^{3+}$  in solution have been carried out using a laser-induced fluorescence method. The luminescence decay rate of the first excited  $J=7/2$  state of  $\text{Cm}^{3+}$  was measured using carbonate, nitrate, and two extractant aminocarboxylic acids as complexing ligands in aqueous solution.  $\text{Cm}(\text{ClO}_4)_3$  dissolved in methyl sulfoxide also was studied. Solvent deuteration provided insight into the dominant nonradiative luminescence quenching mechanism which was found to be electronic-to-vibrational energy transfer. Emission spectra of  $\text{Cm}^{3+}$  complexed by the various ligands studied are reported. Prior spectroscopic and photophysical studies of  $\text{Cm}^{3+}$  in solution are reviewed.

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## Introduction

The first reported spectroscopic study of  $\text{Cm}^{3+}$  luminescence in aqueous solution was that of GUTMACHER, HULET and CONWAY, who observed luminescence peaking at 598.9 nm from  $\text{Cm}^{3+}$  in 10 mol/dm<sup>3</sup> LiCl[1]. The luminescence was assigned as arising from the first excited  $J=7/2$  state of  $\text{Cm}^{3+}$  to its  $J=7/2$  ground state and its excitation was attributed to radiolysis from alpha decay of <sup>244</sup>Cm (i.e., autoradioluminescence). The power of the laser-induced fluorescence method for probing the inner coordination sphere of  $\text{Cm}^{3+}$  in aqueous solution was first demonstrated by BEITZ and HESSLER[2] in a study of aquo  $\text{Cm}^{3+}$ . Since luminescence from aquo  $\text{Cm}^{3+}$  peaks at 593 nm[2], it is clear that complexation of  $\text{Cm}^{3+}$  in 10 mol/dm<sup>3</sup> LiCl results in readily observable spectroscopic changes. In the work reported here, the photodynamics of the first excited  $J=7/2$  state of  $\text{Cm}^{3+}$  are probed to provide insight into the nature of the complexes formed between  $\text{Cm}^{3+}$  and inorganic and organic ligands in solution. The high sensitivity provided by the laser-induced fluorescence technique makes it the method of choice for speciating  $\text{Cm}^{3+}$ , even in aqueous solutions where significant luminescence quenching occurs.

### Prior spectroscopy and photophysics studies of $\text{Cm}^{3+}$ in solution

CARNALL and RAJNAK[3] reported the first detailed study of the optical absorption spectrum of  $\text{Cm}^{3+}$  in dilute perchloric acid. These workers determined the free-ion energy level scheme of  $\text{Cm}^{3+}$ , based in part on a Judd-Ofelt theory[4,5] prediction of transition intensities for aquo  $\text{Cm}^{3+}$ . They concluded that the oscillator strengths of  $\text{Cm}^{3+}$  5f-5f bands are 10 to 100 times

greater than those of 4f-4f bands of  $Gd^{3+}$  ( $Gd^{3+}$  is the 4f analog of  $Cm^{3+}$ ). The work of CARNALL and RAJNAK built on the earlier study of GRUBER and co-workers[6] who carried out an f-state energy level structure determination of  $Cm^{3+}$  using  $^{244}Cm^{3+}$  doped into  $LaCl_3$ . NUGENT and co-workers[7] used sensitized luminescence (i.e., ligand to metal energy transfer) to measure the emission spectrum and lifetime of  $Cm^{3+}$  complexed by hexafluoroacetylacetonate in anhydrous ethanol. They reported that the luminescence quantum yield of the complexed  $Cm^{3+}$  was 7% and its lifetime was 120  $\mu s$ .

BEITZ and HESSLER[2] reported the first study of aquo  $Cm^{3+}$  photophysics, including measurement of the emission spectrum and lifetime of aquo  $Cm^{3+}$  in  $H_2O$  and  $D_2O$ . They selectively excited an f-state of  $Cm^{3+}$  using a tunable dye laser. CARNALL and CROSSWHITE[8], in their review of actinide ion electronic energy level structure, note that the purely radiative lifetime of the A state of aquo  $Cm^{3+}$  is 1.3 ms, based on Judd-Ofelt theory and the aquo  $Cm^{3+}$  oscillator strengths determined by CARNALL and RAJNAK[3].

YUSOV and co-workers have reported several luminescence studies of  $Cm^{3+}$  using sensitized and autoradioluminescence methods. The complexes of  $Cm^{3+}$  studied included several  $\beta$ -diketones and a variety of solvents including water, benzene and methyl sulfoxide. They stated that they could record curium at concentrations down to  $10^{-10}$  mol/dm<sup>3</sup> using curium thenoyltrifluoroacetate in benzene with pulsed 337 nm excitation[9]. YUSOV and co-workers[10] determined the influence of a wide range of ligands and potential quenchers on  $Cm^{3+}$  emission using an autoradioluminescence method and report that the luminescence of  $Cm^{3+}$  is linearly proportional to the D atom fraction in mixtures

of H<sub>2</sub>O and D<sub>2</sub>O. In a separate study, YUSOV and co-workers[11] reported emission spectra and lifetimes for tungstate complexes of Cm<sup>3+</sup>. These same workers[12] have also found an unusual method of creating electronically excited Cm<sup>3+</sup> in solution, namely Cm<sup>3+</sup> chemiluminescence arising from destruction of tungstate complexes of Cm<sup>4+</sup>. YUSOV[13] has also measured the radioluminescence yields of Sm<sup>3+</sup>, Eu<sup>3+</sup>, Tb<sup>3+</sup>, and Dy<sup>3+</sup> ions in solution using alpha decay of <sup>244</sup>Cm<sup>3+</sup>. DEM'YANOVA and co-workers[14] have reported the emission spectra and lifetimes of Cm<sup>3+</sup> complexed with methyltrioctylammonium thiocyanate using benzene as a solvent.

Using a pulsed dye laser tuned to a near-ultraviolet f-electron state of Cm<sup>3+</sup>, BEITZ and co-workers[15] demonstrated an aquo Cm<sup>3+</sup> detection limit of 1.8x 10<sup>-11</sup> mol/dm<sup>3</sup> in 0.1 mol/dm<sup>3</sup> HClO<sub>4</sub> which corresponded to 10<sup>8</sup> Cm<sup>3+</sup> ions in the laser beam. A similar detection limit was found for Cm<sup>3+</sup> in 0.1 mol/dm<sup>3</sup> NaCl at pH 7.5 and spectral and luminescence decay evidence for hydroxo complexation of Cm<sup>3+</sup> were reported. With detection system improvements, these workers estimated that as little as 0.08 parts per trillion of Cm<sup>3+</sup> should be detectable in aqueous solution.

## **Experimental methods**

The basic apparatus and data analysis procedures used in this work have been described previously[1,15]. Briefly, a nitrogen laser pumped dye laser was used as the excitation source. Long pass optical filters and a 20 cm focal length monochromator equipped with a holographic grating were used to isolate emission from Cm<sup>3+</sup>. A transient recorder connected to a computer, for signal

averaging, was used to acquire lifetime data. In all cases, the observed luminescence decays were well-fit by a single exponential decay model. The estimated uncertainty in the reported lifetimes is  $\pm 3\%$ . Emission spectra were acquired using a boxcar integrator and were normalized to the simultaneously measured dye laser energy. The dye laser was operated near 383 nm and its wavelength was adjusted to give the most intense fluorescence from each sample. The emission spectra were recorded with a spectral bandpass (full width half maximum) of 1 nm and have not been corrected for the wavelength-dependent response of the detection system (gradual decrease with increasing wavelength).

The samples were prepared using  $>97$  atom %  $^{248}\text{Cm}$  and measurements were carried out at  $295 \pm 1$  K. Typically, 1 mg of Cm was used in 2 ml of solution to minimize luminescence data acquisition time. The sample cells were made from mandril-shrunk rectangular (3 mm x 9 mm) Suprasil fused silica tubing. The trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA) and diethylenetriaminepentaacetic acid (DTPA) samples were prepared first in  $\text{H}_2\text{O}$  by dissolving the solid and then adding NaOH solution to obtain near-neutral pH. This solution was added to dried  $\text{Cm}(\text{ClO}_4)_3$ . The  $\text{Cm}(\text{ClO}_4)_3$  was prepared by taking a  $\text{Cm}^{3+}$  in  $\text{HClO}_4$  solution to dryness under a stream of dry nitrogen. The CDTA and DTPA in  $\text{D}_2\text{O}$  solutions were prepared by taking the corresponding protiated samples to dryness three times with the solid being redissolved in  $\text{D}_2\text{O}$  ( $>99$  atom % D) between drying cycles. Analytical reagent grade  $\text{Na}_2\text{CO}_3$  and Baker "Ultrex" grade nitric acid were used. The  $\text{Cm}^{3+}$  in perdeuteromethyl sulfoxide,  $(\text{CD}_3)_2\text{SO}$  (Aldrich,  $>99.96$  atom % D), solution was prepared using dried  $\text{Cm}(\text{ClO}_4)_3$  (from evaporation of  $\text{Cm}(\text{ClO}_4)_3$  in  $\text{DClO}_4$ ). The  $\text{Cm}^{3+}$  sample in  $(\text{CH}_3)_2\text{SO}$  (Aldrich spectro. grade) was prepared using

dried  $\text{Cm}(\text{ClO}_4)_3$  (from evaporation of an  $\text{HClO}_4$  solution). Dry nitrogen gas was bubbled through the aliquots of  $(\text{CH}_3)_2\text{SO}$  and  $(\text{CD}_3)_2\text{SO}$  immediately prior to their being added to  $\text{Cm}(\text{ClO}_4)_3$ .

## Experimental results

The observed luminescence lifetimes of the A state of complexes of  $\text{Cm}^{3+}$  are shown in Table 1 along with the resulting calculated nonradiative decay rates (see **Discussion** section below).

A comparison is shown in Figure 1 of the optical absorption spectrum of aquo  $\text{Cm}^{3+}$  and the free-ion f-states of  $\text{Cm}^{3+}$ [3] to the pump laser and luminescence energies in present work. The luminescence observed in the present work is attributed to the first excited  $J=7/2$  state of  $\text{Cm}^{3+}$ , termed the A state, based on the energy level structure of  $\text{Cm}^{3+}$  and the observed luminescence lifetimes. The observed  $\text{Cm}^{3+}$  A-to-Z state emission spectra of aquo  $\text{Cm}^{3+}$ [2] and  $\text{Cm}^{3+}$  complexed by several inorganic and organic ligands are shown in Figure 2. Also shown are the wavelengths of the 4 components of the first excited  $J=7/2$  state of  $\text{Cm}^{3+}$  in  $\text{LaCl}_3$  as reported by GRUBER et al.[6]. For purposes of comparison, the spectra have been normalized to the same peak intensity. Since the ground state of  $\text{Cm}^{3+}$  is  $^8\text{S}_{7/2}$  (i.e., spherically symmetric), little splitting of it is expected due to inner coordination sphere ligands. For example, the observed splitting of the ground state of  $\text{Cm}^{3+}$  in  $\text{LaCl}_3$  is only a few wavenumbers[6]. As a consequence, the structure of the observed emission bands is attributed to ligand field splitting of the emitting  $J=7/2$  state into at most  $(7/2 + 1/2) = 4$  components. In the case of aquo  $\text{Cm}^{3+}$ , the splitting of the A

state is evidently small enough that the individual components are not resolved whereas at least 3 components are evident in the emission spectrum of  $\text{Cm}(\text{ClO}_4)_3$  dissolved in  $(\text{CD}_3)_2\text{SO}$  (see Figure 2, panel a).

The solid line emission spectra in panels b and c of Figure 2 ( $\text{Cm}^{3+}$  in DPTA and  $\text{Na}_2\text{CO}_3$  solutions) show 4 distinct local maxima, suggesting predominantly a single  $\text{Cm}^{3+}$  complex. In the case of  $\text{Cm}^{3+}$  in DCTA and  $\text{Cm}^{3+}$  in  $16 \text{ mol/dm}^3 \text{ HNO}_3$ , the emission band tails off slowly at shorter wavelengths and the number of local maxima may exceed 4, suggesting the possibly presence of more than one  $\text{Cm}^{3+}$  complex or stronger vibronic interaction. Previous spectroscopic evidence for nitrate complexation of  $\text{Cm}^{3+}$  comes from the work of CARNALL and FIELDS[16] who examined the absorption spectrum of  $\text{Cm}^{3+}$  while varying nitric acid concentration. They observed a marked decrease in the molar absorption coefficients of the principal bands of  $\text{Cm}^{3+}$  with increasing nitric acid concentration, but did not attempt to determine the number of nitrate  $\text{Cm}^{3+}$  complexes present.

## Discussion

The observed lifetimes of complexed  $\text{Cm}^{3+}$ , shown in Table 1, fall between those reported by BEITZ and HESSLER[2] for aquo  $\text{Cm}^{3+}$  in  $\text{H}_2\text{O}$  ( $65 \mu\text{s}$ ) and aquo  $\text{Cm}^{3+}$  in  $\text{D}_2\text{O}$  ( $940 \mu\text{s}$ ). Solvent deuteration increased the observed lifetime in all cases studied. This provides evidence that high frequency fundamental vibrational modes of coordinated  $\text{H}_2\text{O}$  are the dominant factor in nonradiative decay of complexed  $\text{Cm}^{3+}$  in aqueous solution and that the nonradiative decay path is electronic-to-vibrational energy transfer.



The observed luminescence lifetime,  $\tau_{\text{obs}}$ , of a  $\text{Cm}^{3+}$  species is simply related to its luminescence rate,  $k_{\text{obs}}$ :

$$k_{\text{obs}} = \frac{1}{\tau_{\text{obs}}} \quad (1).$$

When the observed luminescence decay of a given species is well-fit by a single exponential decay model,  $k_{\text{obs}}$  is sum of the purely radiative rate,  $k_r$ , and the total nonradiative decay rate,  $k_{\text{nr}}$ :

$$k_{\text{obs}} = k_r + k_{\text{nr}} \quad (2).$$

Experimentally,  $k_{\text{obs}}$  is measured directly by time resolving the luminescence decay, but this does not, in general, result in values for  $k_r$  and  $k_{\text{nr}}$ . An exception is evident from eqn. 2: when  $k_{\text{nr}} \gg k_r$ ,  $k_{\text{nr}} = k_{\text{obs}}$ .

A value of  $k_r$  for the A state of aquo  $\text{Cm}^{3+}$ ,  $7.7 \times 10^2 \text{ s}^{-1}$ , is available from the work of CARNALL and CROSSWHITE[8], based on Judd-Ofelt theory[4,5] and the earlier work of CARNALL and RAJNAK[3]. It is known that the integrated band strength of nonhypersensitive f-electron transitions (and therefore  $k_r$ ) of  $\text{Ln}^{3+}$  ions are comparatively insensitive to the ligands surrounding the metal ion[17]. Much less data are available for f-f transitions of actinide ions, but similar behavior is expected, if the site symmetry at the metal remains constant, for heavy 3+ actinide ions whose spectroscopy is similar to that of 3+ lanthanide ions [18,19]. If we assume that  $k_r$  is  $7.7 \times 10^2 \text{ s}^{-1}$  for all the complexes of  $\text{Cm}^{3+}$  observed in the present work, we arrive at the  $k_{\text{nr}}$  values listed in Table 1.

The 0.82 ms observed lifetime for  $\text{Cm}^{3+}$  in  $(\text{CH}_3)_2\text{SO}$  solution in the present work is significantly longer than the 0.235 ms lifetime reported by Yusov and co-workers[9] for  $\text{Cm}^{3+}$  in the same solvent. The difference in observed lifetimes likely arises from the presence of inner coordination sphere water in the work of Yusov and co-workers who extracted  $\text{Cm}^{3+}$  from an aqueous solution as a complex with thenoyltrifluoroacetate[9]. The shape of emission spectrum of  $\text{Cm}^{3+}$  in methyl sulfoxide in the present work (Figure 2, panel a) is essentially the same as that reported by YUSOV and co-workers[9], but the band as a whole is shifted to shorter wavelengths by approximately 7 nm.

HORROCKS and co-workers have established a correlation between the number of inner coordination sphere water molecules and the observed luminescence lifetime for complexed  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$  in aqueous solutions (see [20] for a review of this method and related topics). The method of HORROCKS and co-workers relies on knowledge of the number of coordinated water molecules for the aquo  $\text{Ln}^{3+}$  ion and measurement of the luminescence lifetimes of the aquo ion in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solutions and the complexed  $\text{Ln}^{3+}$  ion in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solutions. The method relies on each coordinated water molecule *independently contributing separately to the total nonradiative decay rate as well as the large quenching effect of high frequency O-H stretch vibrational modes in comparison with quenching due to O-D modes*. The method is stated to be accurate to circa  $\pm 0.5$  coordinated water molecules for complexes of  $\text{Eu}^{3+}$  and  $\text{Tb}^{3+}$ [20]. Since the method relies on excited state measurements, the values for coordinated water refer to the metal ion its emitting state. There is, however, evidence that  $\text{Eu}^{3+}$ -ligand association and dissociation kinetics, monitored via  $\text{Eu}^{3+}$  4f-state luminescence, reflect the kinetics in a ground-state equilibrium system[21].

If one assumes that aquo  $\text{Cm}^{3+}$  has 9  $\text{H}_2\text{O}$  molecules in its inner coordination sphere and uses the lifetimes reported by BEITZ and HESSLER[2] for aquo  $\text{Cm}^{3+}$  in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  solutions together with the data shown in Table 1, then the number of coordinated water molecules, calculated using the method of HORROCKS and co-workers, is 2.8 for  $\text{Cm}^{3+}$  in 1 mol/dm<sup>3</sup>  $\text{Na}_2\text{CO}_3$ , 3.8 for  $\text{Cm}^{3+}$  in 0.1 mol/dm<sup>3</sup> DCTA, and 1.5 for  $\text{Cm}^{3+}$  in 0.1 mol/dm<sup>3</sup> DTPA. If one assumes that aquo  $\text{Cm}^{3+}$  has 8 coordinated water molecules, then the values become 2.5, 3.4, and 1.3, respectively. These calculated values for inner coordination sphere water are chemically plausible. For example, DELLE SITE and BAYBARZ[22], using absorption spectroscopy, concluded that DTPA, in complexing  $\text{Am}^{3+}$ , forms a 1:1 complex and acts as at most an octadenate ligand. From the work of BAYBARZ, it is known that DCTA forms a 1:1 complex with  $\text{Cm}^{3+}$ [23] and a lesser ligand coordination number would be expected for DCTA in comparison with DTPA. If  $\text{CO}_3^{2-}$  acts as a bidentate ligand and triscarbonato  $\text{Cm}^{3+}$  is the predominant  $\text{Cm}^{3+}$  species in 1 mol/dm<sup>3</sup>  $\text{Na}_2\text{CO}_3$ , then 2 or 3 coordinated water molecules are expected. Considerable additional evidence, however, will be needed to establish that HORROCKS and co-workers correlation reliably determines the number of inner coordination sphere water molecules for complexed  $\text{Cm}^{3+}$ . Studies of the photophysics of complexed  $\text{Cm}^{3+}$  in well-characterized crystalline solids where the number of water molecules is known from X-ray crystallography would be particularly helpful.

The emission spectra shown in Figure 2 provide renewed evidence that complexation of  $\text{Cm}^{3+}$  results in readily observable changes in luminescence emission spectra. It is of interest that complexation of  $\text{Cm}^{3+}$  results in a nephelauxetic effect (shifts the emission peak to longer wavelengths) in

comparison with luminescence from aquo  $\text{Cm}^{3+}$ . However, in none of the cases shown in Figure 2, or in other reported emission spectra of complexed  $\text{Cm}^{3+}$  in solution[1,7,,9,11,14,15], does the  $\text{Cm}^{3+}$  emission peak at as long a wavelength as the from solid  $\text{Cm}(\text{C}_5\text{H}_5)$ [24]. Based on the conclusion of NUGENT and co-workers[23] that the nephelauxetic parameter for  $\text{Cm}(\text{C}_5\text{H}_5)$  is small and corresponds to little covalency in its curium-cyclopentadienide bonds, the emission spectra shown in Figure 2, and previously reported emission spectra[1,7,9,11,14,15], provide evidence for primarily ionic bonding in the luminescent complexes of  $\text{Cm}^{3+}$  in solution.

## **Conclusions**

Photophysical studies have probed the interaction of an f-state of  $\text{Cm}^{3+}$  with inner coordination sphere ligands. Luminescence lifetime data provide evidence that high frequency vibrational modes of directly coordinated ligands (notably the O-H stretch of water) provide facile pathways for nonradiative loss of excited 5f-state energy. The distinct patterns of 5f-state emission from  $\text{Cm}^{3+}$  complexed by inorganic and organic ligands provide a basis for speciating  $\text{Cm}^{3+}$  in aqueous solution at high sensitivity using laser-induced fluorescence.

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**Table 1.** Observed luminescence lifetimes and calculated nonradiative decay rates of the A state of complexed Cm<sup>3+</sup> in solution.

solvent composition	observed Cm <sup>3+</sup> lifetime ( $\mu$ s)[a]	calculated Cm <sup>3+</sup> nonradiative decay rate ( $s^{-1}$ )[b]
1.0 mol/dm <sup>3</sup> Na <sub>2</sub> CO <sub>3</sub> in H <sub>2</sub> O	160	5.5x 10 <sup>3</sup>
1.0 mol/dm <sup>3</sup> Na <sub>2</sub> CO <sub>3</sub> in D <sub>2</sub> O	560	1.0x 10 <sup>3</sup>
16 mol/dm <sup>3</sup> HNO <sub>3</sub> in H <sub>2</sub> O	107	8.6x 10 <sup>3</sup>
0.1 mol/dm <sup>3</sup> DCTA in H <sub>2</sub> O	66	1.4x 10 <sup>4</sup>
0.1 mol/dm <sup>3</sup> DCTA in D <sub>2</sub> O	115	7.9x 10 <sup>3</sup>
0.1 mol/dm <sup>3</sup> DTPA in H <sub>2</sub> O	271	2.9x 10 <sup>3</sup>
0.1 mol/dm <sup>3</sup> DTPA in D <sub>2</sub> O	764	5.5x 10 <sup>2</sup>
(CH <sub>3</sub> ) <sub>2</sub> SO	823	4.5x 10 <sup>2</sup>
(CD <sub>3</sub> ) <sub>2</sub> SO	935	2.9x 10 <sup>2</sup>

a. Mean of replicate determinations ( $\pm 3\%$  estimated uncertainty).

b. Based on assumption of  $k_r = 7.7 \times 10^2 s^{-1}$  for all Cm<sup>3+</sup> species.

## FIGURE CAPTIONS

**Fig. 1.** Comparison of the optical absorption spectrum of  $\text{Cm}^{3+}$  in dilute  $\text{HClO}_4$ [3] (shown at the left) and the free-ion states of  $\text{Cm}^{3+}$  (shown as horizontal lines)[3] to the pump laser energy (vertical pointing arrow), nonradiative decay (wavy arrow) and  $\text{Cm}^{3+}$  luminescence energy (downward pointing arrow) typical of the present study. The conventional alphabetic labels (Z, A, and G) are shown for 3 of the absorption bands of  $\text{Cm}^{3+}$  as are the J values for its ground and emitting free-ion states.

**Fig. 2.** Luminescence emission spectra of  $\text{Cm}^{3+}$  in solution. Panel **a** shows the emission spectrum of aquo  $\text{Cm}^{3+}$ [2] (dashed curve) and  $\text{Cm}(\text{ClO}_4)_3$  dissolved in  $(\text{CD}_3)_2\text{SO}$  (solid curve). The four vertical lines denote the wavelengths of the crystal field components of the first excited  $J=7/2$  state of  $\text{Cm}^{3+}$  in  $\text{LaCl}_3$ [6]. Panel **b** shows the emission spectrum of  $\text{Cm}^{3+}$  in 0.1 mol/dm<sup>3</sup> DCTA in  $\text{D}_2\text{O}$  (dashed curve) and in 0.1 mol/dm<sup>3</sup> DTPA in  $\text{D}_2\text{O}$  (solid curve). Panel **c** shows the emission spectrum of  $\text{Cm}^{3+}$  in 16 mol/dm<sup>3</sup>  $\text{HNO}_3$  (dashed curve) and in 1 mol/dm<sup>3</sup>  $\text{Na}_2\text{CO}_3$  in  $\text{D}_2\text{O}$  (solid curve).

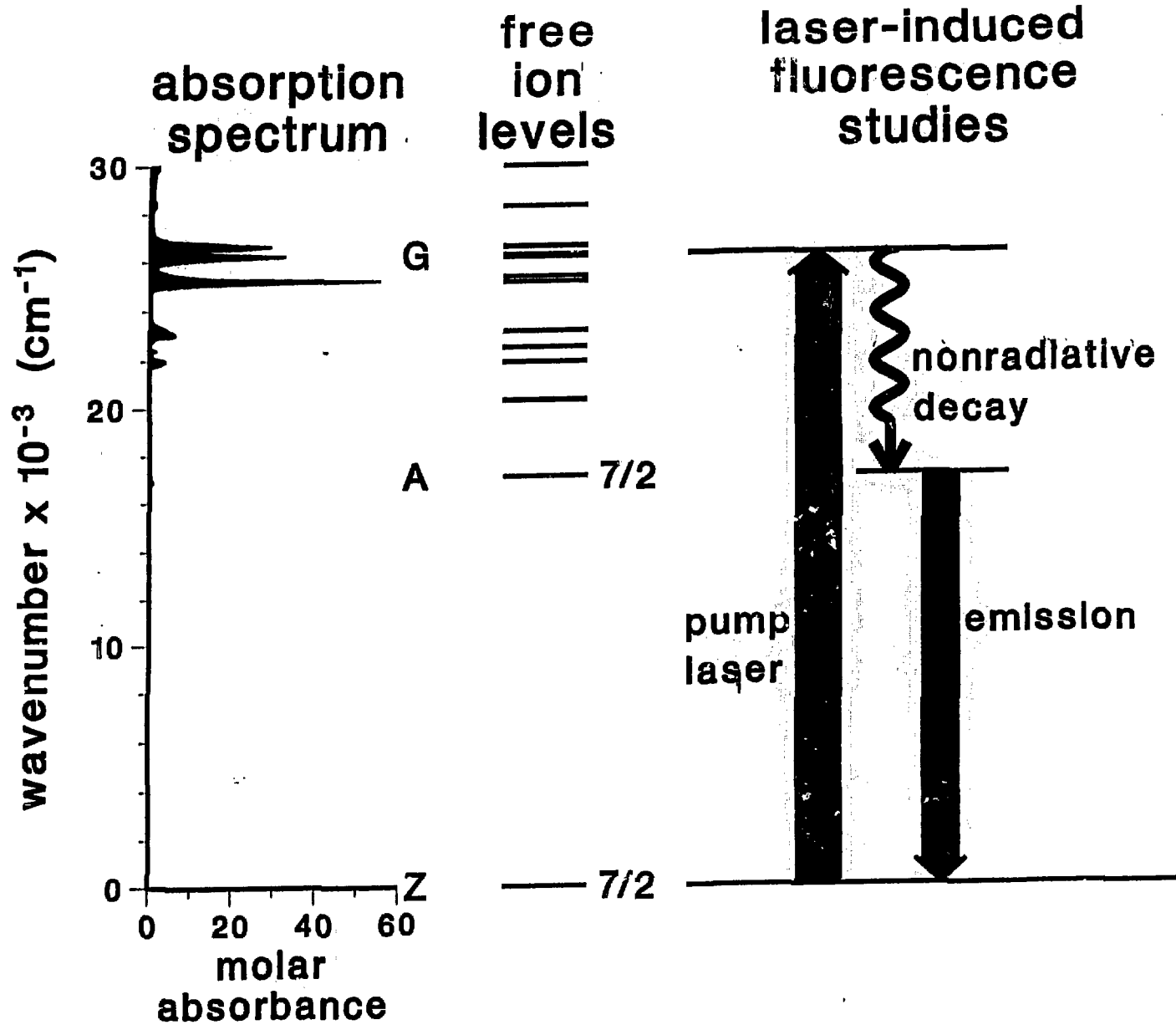


Figure 1. Beitz "Laser-induced Fluorescence Studies of  $\text{Cm}^{3+}$  Complexes in Solution"

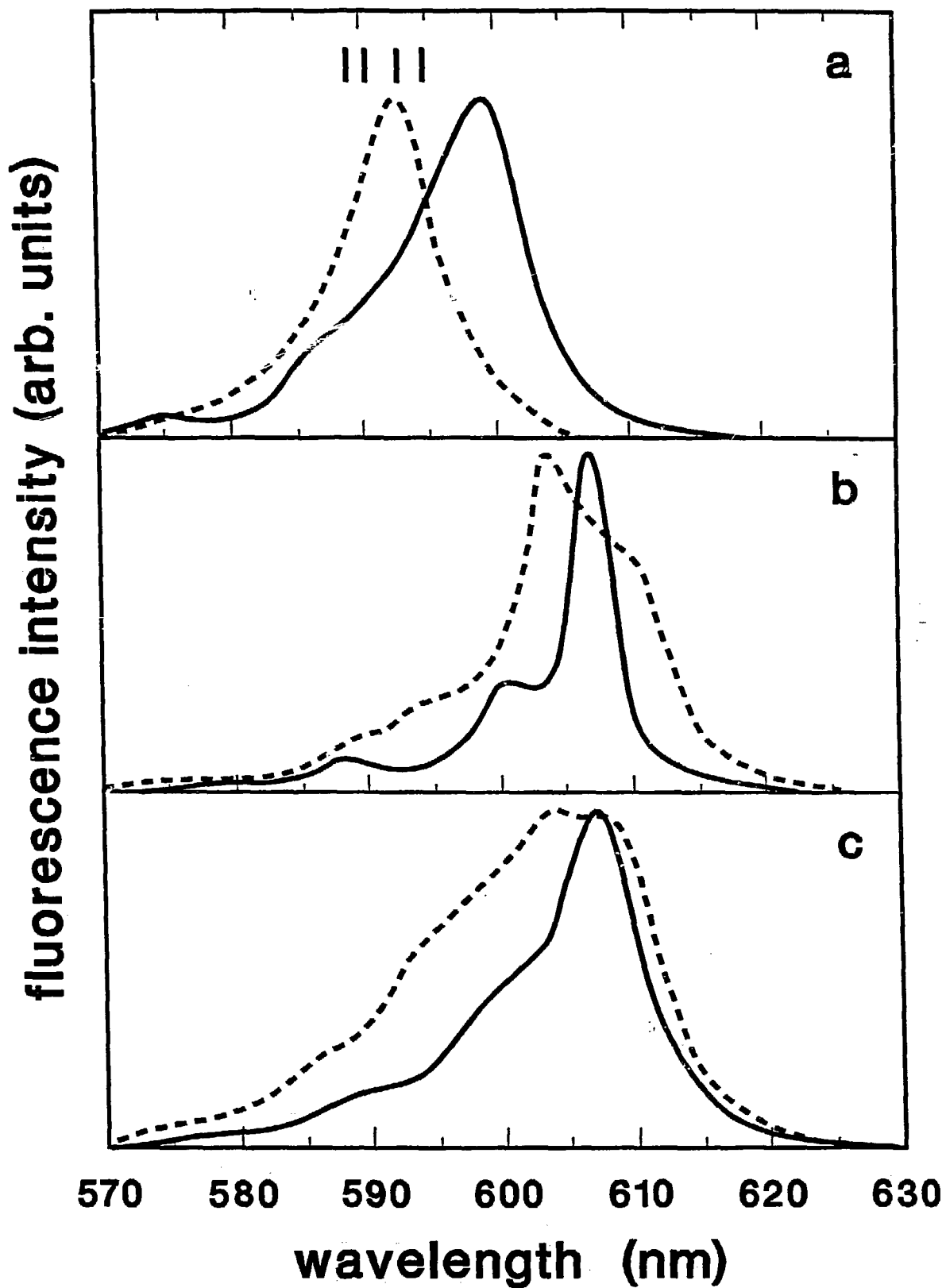


Figure 2. Beitz "Laser-induced Fluorescence Studies of  $\text{Cm}^{3+}$  Complexes in Solution"