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f-State luminescence of trivalent lanthanide and actinide ions in solution

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Abstract

Detailed studies of the luminescence of aquated Am^{3+} are presented in the context of prior work on lanthanide and actinide ions. The luminescing state of aquated Am^{3+} is confirmed to be $^5D_1$ based on observed emission and excitation spectra. The luminescence lifetime of Am^{3+} in H_2O solution is (22 ± 3) ns and (155 ± 4) ns in D_2O solution at 295 K. Judd–Ofelt transition intensity theory qualitatively describes the observed Am^{3+} relative integrated fluorescence intensities. Recent luminescence studies on complexed trivalent f-element ions in solution are reviewed as to the similarities and differences between the lanthanide ion 4f state and the actinide ion 5f state properties.

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1. Introduction

Optical luminescence from f-element ions in solution provides a variety of experimentally convenient and theoretically challenging features. Experimental studies of f-element solution luminescence are diverse. Examples of such work include determination of f-element concentration, speciation of metal ion complexes, elucidation of factors influencing non-radiative decay, and measurement of binding in fluorescence immunoassays. Theoretical efforts stem from the need to understand the energy level structure, ligand field splitting, band intensities and photodynamics of f-electron states. Studies of aquated 3+ f-element ions have provided benchmark experimental data and tests of theoretical models. Early work on aquated lanthanide ion fluorescence was reviewed by Carnall [1]. Beitz has reviewed the similarities and differences between aquated 3+ lanthanide and actinide ion spectroscopy and photodynamics [2]. This paper presents experimental data on luminescence from laser-excited aquated Am^{3+} in the context of prior f-element studies and reviews some recent solution luminescence studies of complexed trivalent f-element ions.

2. Prior Am^{3+} luminescence work

Relatively few reports of fluorescence from Am^{3+} have been published. This might seem surprising in that Am^{3+} is the 5f analog of Eu^{3+} (both Am^{3+} and Eu^{3+} contain six formally non-bonding f electrons) and Eu^{3+} has been the subject of numerous fluorescence studies that have been reviewed (see, *e.g.* [1–8]). Alteration in the ordering of f-electron states and their splittings in Am^{3+}, in comparison with Eu^{3+}, undoubtedly is a contributing factor (see Fig. 1). In consequence, non-radiative decay of Am^{3+} is significantly enhanced with a resulting substantial reduction in fluorescence quantum yield.

A low temperature study of Am^{3+} doped into $LaCl_3$ was the first detailed report of fluorescence from Am^{3+} [9]. Attempts to observe optical gain from Am^{3+} in liquid $POCl_3$ [10] and solid $CaWO_4$ [11] failed, but luminescence attributable to Am^{3+} was reported [11]. Subsequent solid state work has included detailed investigation of Am^{3+} luminescence in a heavy metal fluoride glass by Brundage and co-workers [12–15] and Am^{3+} (and Eu^{3+}) in ThO_2 by Hubert and Thouvenot [16].

Fluorescence from aquated Am^{3+} was first reported by Beitz *et al.* [17] who assigned the four observed emission bands as arising from the $^5D_1$ state of Am^{3+} (throughout this paper, f-electron states are identified for convenience by term symbols, such as $^5D_1$, but these states are of mixed parentage). Subsequent work by Yusov [18] reported fluorescence lifetimes with substantial uncertainties for Am^{3+} in D_2O and several protiated and deuterated organic solvents and a limit for the lifetime of Am^{3+} in H_2O. He adopted the

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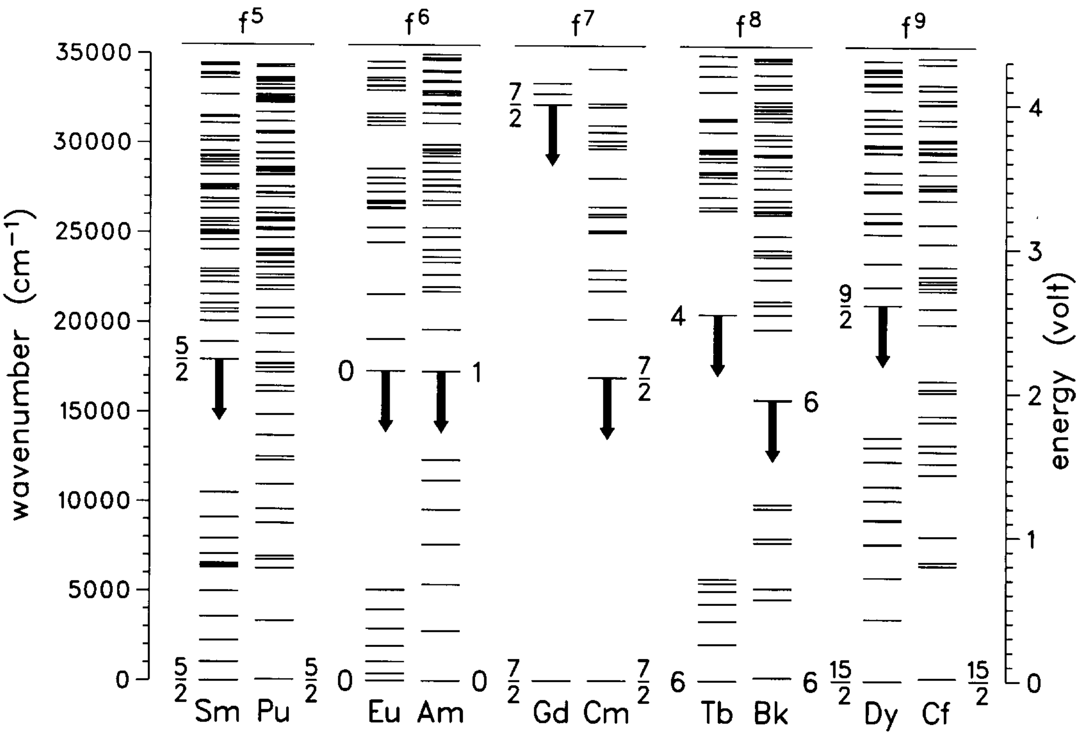

Fig. 1. Comparison of calculated "free-ion" f-state energies of 3+ lanthanide [22] and actinide [23] ions having the same number of f-electrons. Downward-pointing arrows denote the predominant emitting state for those ions that have been observed to luminesce as aquated ions in aqueous solution. The *J* value of the ground and predominant emitting f state is shown.

emission spectra assignment of Beitz *et al.*, but reported no spectra of the $^5D_1 \rightarrow {}^7F_0$ transition, evidently due to low spectral resolution and diminished detection system sensitivity near 580 nm.

Yusov reported that Am^{3+} solution fluorescence lifetimes increased by a factor of 2.3 on changing the solvent from CH_3OD to CD_3OD [18]. On changing the solvent from CH_3SO_2 to CD_3SO_2, the observed Am^{3+} lifetime increased from 800 ns to 3500 ns (*i.e.* a factor of 4.3). This provides evidence that high frequency C–H vibrational modes in close proximity to Am^{3+} are a significant source of non-radiative decay. He also observed sensitized luminescence (*i.e.* ligand-to-metal ion energy transfer) using several organic chelates and polytungstate. Some uncertainty may remain as to the identity of the emitting state because emission from $^5L_6$ (the Am^{3+} state at 19 602 cm^{-1}) could occur at many of the same wavelengths as emission from $^5D_1$. Thouvenot *et al.* [19] reported fluorescence lifetimes (20% stated accuracy) for Am^{3+} in H_2O and D_2O solutions containing an unstated concentration of $HClO_4$. The present experimental work was carried out to confirm the identity of the emitting state, improve the accuracy of the fluorescence lifetime of aquated Am^{3+} in H_2O, compare the observed fluorescence band positions to energy level structure calculations, and explore the application of Judd–Ofelt transition intensity theory to aquated Am^{3+} fluorescence branching ratios.

3. Experimental details

The samples were prepared using ^{243}Am that had been produced at Oak Ridge National Laboratory under the transplutonium production program of the US Department of Energy. The Am was precipitated as the hydroxide, washed and dissolved in 0.1 M $HClO_4$ in triply distilled H_2O. Triply distilled D_2O (99% D atom) and concentrated $DClO_4$ (Aldrich) were used to prepare an 0.1 M $DClO_4$ stock solution. The most concentrated Am^{3+} in D_2O solution was prepared by taking Am^{3+} in $HClO_4$ to dryness using a hot plate and a stream of dry nitrogen gas and then adding 0.1 M $DClO_4$. This solution was taken to dryness twice more using stock $DClO_4$ to bring the Am^{3+} back into solution each time before the final aliquot of 0.1 M $DClO_4$ was added and the solution transferred to a 3×9 mm cuvette which was sealed. Lower concentration solutions of Am^{3+} in D_2O were prepared by dilution using stock 0.1 M $DClO_4$. The sample cuvettes were made from mandrel shrunk Suprasil fused silica. All experiments were carried out at 295±1 K.

A tunable dye laser (Molectron DL-16) equipped with a post-amplifier was used as the excitation source. The dye laser was pumped by a Nd:YAG laser (Quanta-Ray DCR-2A) and provided approximately 5 ns full width at half maximum (FWHM) pulses with typically 0.1 mJ per pulse energy. Use of higher laser energy resulted in saturation of the Am^{3+} fluorescence signal under the focusing conditions used. Fluorescence emission spectra were recorded using an f/4 20-cm focal length grating monochromator (ISA H20) equipped with a 1200 groove/mm grating and a photomultiplier (RCA C31034). This system was useful to about 860 nm. More efficient light collection (f/1.4) together with use of a circular variable bandpass interference filter (OCLI model CV-680/1200) and a cooled S-1 photomultiplier (RCA 7102) extended the wavelength range to 1200 nm. Long pass optical filters (Schott KV and RG series) were used to minimize the effect of scattered laser light. Fluorescence emission spectra were recorded using a boxcar integrator (PAR 162/164) and were normalized to the dye laser intensity using a pyroelectric detector (Molectron Joulemeter) and a second boxcar. The boxcar signals were digitized and recorded on a DEC 11/23+ minicomputer. Fluorescence lifetimes were measured using a variable input resistance buffer amplifier and a 512 channel, 500 MHz bandwidth transient recorder (Tektronix 7912AD) interfaced to a DEC 11/23+ minicomputer. The measured detection system response time (1/e) was 12 ns when using the C31034 tube and 55 ns when using the 7102 tube. The lifetime data were analyzed using a non-linear least squares fitting procedure.

4. Aquated Am^{3+} spectroscopy and photophysics

4.1. Fluorescence spectra

The fluorescence emission spectra of 2×10^{-2} M Am^{3+} in 0.1 M $DClO_4$ are shown in Fig. 2. The data were recorded using 428.3 nm excitation and a 200 ns wide boxcar gate, delayed by 50 ns. The observed width of the 580.3 nm band is little larger than the best usable spectral bandpass achieved (1 nm FWHM) which indicates that the actual width of this band is less than 1 nm. Only weak emission was observed near 1 μm. For this reason, the data for longest wavelength band were recorded using f/1.4 fluorescence light collection, a circular variable bandpass interference filter, and a cooled S-1 photomultiplier to improve detection sensitivity. The half width of the observed 1033 nm band is little larger than the measured FWHM bandpass of the circular variable filter. Even when using excitation wavelengths as short as 355 nm, no fluorescence attributable to Am^{3+} was observed near 503 nm. The emission spectra shown in Fig. 2 have been converted to the traditional spectroscopy unit of energy, the vacuum wavenumber ($1\ cm^{-1}=1.23980\times10^{-4}$ eV).

The fluorescence excitation spectrum of 1×10^{-6} M Am^{3+} in 0.1 M $DClO_4$ in D_2O is shown in Fig. 3 and is in excellent agreement with a published absorption spectrum of Am^{3+} in 0.1 M NH_4ClO_4 at pH 0.8 [20]. The excitation spectrum was recorded by monitoring the 837 nm emission band using f/1.4 light collection and a series of long pass optical filters whose 50% transmission point was 780 nm. Interference from scattered laser light was minimized by use of a 400 ns boxcar gate, delayed by 200 ns from the laser pulse. The excitation spectrum shown in Fig. 3 has been normalized to the recorded dye laser energy.

4.2. Relative banal intensities

The emission spectrum of 4×10^{-2} M Am^{3+} in 0.1 M $DClO_4$ from 655 nm to 1200 nm was recorded using a circular variable filter and a cooled S-1 photomultiplier to enable determination of the relative emission band intensities. The relative spectral responsivity of this detection system was obtained using a tungsten filament lamp whose filament temperature was measured with an optical pyrometer. The observed emission spectra were corrected for the wavelength-dependent response of the detection system using the known emissivity of tungsten [21] as a function of temperature. The resulting band areas were determined by digital integration and have been normalized to the area of the 692.3 nm band. These values are listed in Table 1. The band area shown for the 580.3 nm band is based on a spectrum recorded using a C31034 photomultiplier and the 20 cm monochromator.

4.3. Fluorescence lifetime measurements

Table 1 shows the measured fluorescence lifetimes of the emission bands peaking at 580.3 nm, 692.3 nm and 837 nm using 424 nm excitation and 2×10^{-2} M Am^{3+} in 0.1 M $DClO_4$. The same lifetimes were observed when using 355 nm excitation (355 nm was generated by frequency tripling the 1064 nm output of the Nd:YAG laser). The much lower quantum efficiency and slower response of the S-1 photomultiplier prevented accurate measurement of the lifetime of the 1033 nm band. The lifetimes of the 692.3 nm and 837 nm bands of 2×10^{-2} M Am^{3+} in 0.1 M $HClO_4$ were measured and are shown in Table 1. In all cases, the observed fluorescence decays were well fit by a single exponential decay model. The measured lifetime of Am^{3+} in H_2O solution was so short as to require deconvolution of the detection system response time. The Am^{3+} in H_2O values shown in Table 1 have been corrected for the finite detection system response time.

5. Analysis

Carnall and co-workers (see references contained in [1,2]) have shown that the centers of gravity of many observed f–f absorption bands of aquated 3+ lanthanide and actinide ions correspond typically to within a few

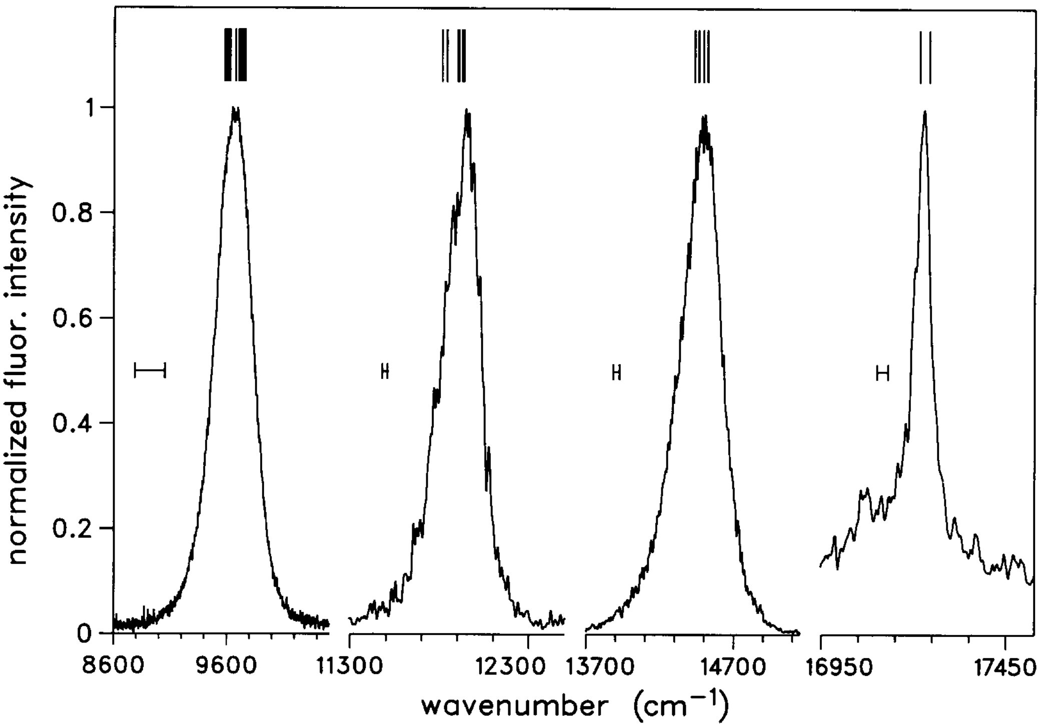

Fig. 2. Observed emission bands, normalized to unit intensity, of Am^{3+} in 0.1 M $DClO_4$ in D_2O solution at 295 K compared to the positions of all possible zero phonon emission lines (short vertical lines) of the $^5D_1$ state of Am^{3+} in $LaCl_3$ based on the calculations of Carnall [23]. The spectral bandpass for each emission band is shown.

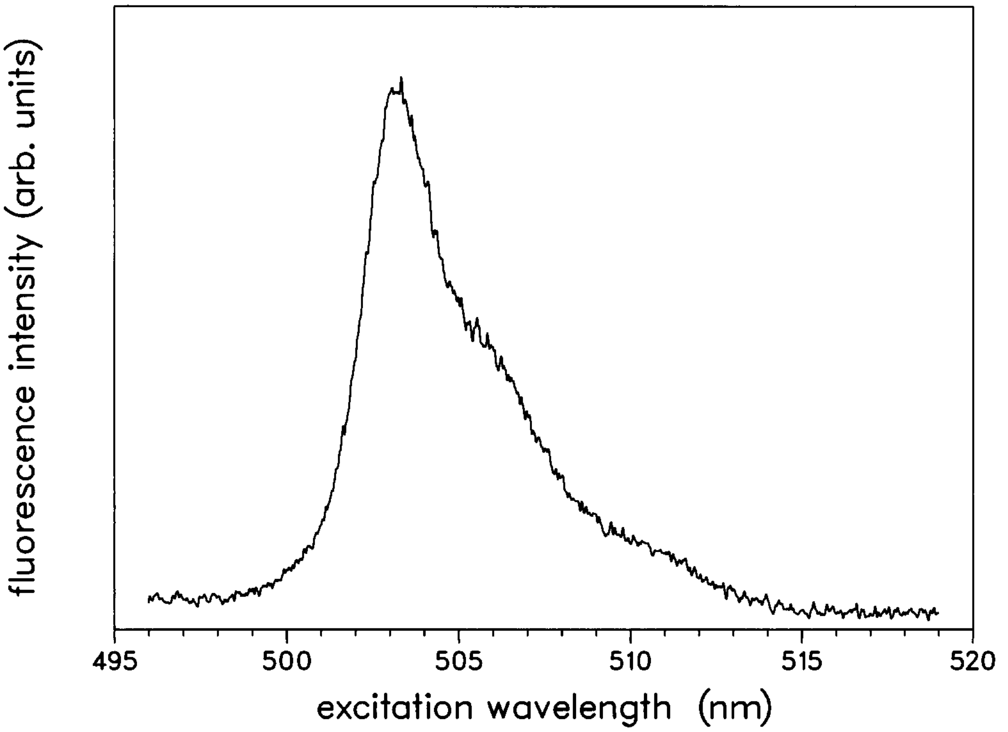

Fig. 3. Excitation spectrum of 1×10^{-6} M Am^{3+} in 0.1 M $DClO_4$ in D_2O solution at 295 K ($^5D_1 \rightarrow {}^7F_2$ emission band monitored).

tens of wavenumbers to the difference in energy between the calculated "free-ion" f-state energy levels. These workers assumed a combined Gaussian–Lorentzian line shape for a given f–f transition. No detailed theoretical interpretation of the observed line shapes of f–f transitions in solution is available. Systematic analysis of the available experimental data on the f-state energy level structure of 3+ lanthanide ions doped into LaF_3

TABLE 1. Fluorescence properties of aquated Am^{3+} at 295 K

Observed band maximum (nm)	Band assignment	Calculated free ion transition[a] (nm)	Observed fluorescence lifetime[b]		Observed relative integrated band intensity	Judd–Ofelt theory calculated relative branching ratio	
			D_2O (ns)	H_2O (ns)		Interpolated parameters[c] (cm^2)	Ω_2 only varied[d] (cm^2)
580.3	$^5D_1 \rightarrow {}^7F_0$	580.7	155 ± 5	[e]	(0.005)[f]	1.7×10^{-4}	5.1×10^{-5}
692.3	$^5D_1 \rightarrow {}^7F_1$	689.1	152 ± 2	23 ± 2	1.0	0.40	1.0
837.0	$^5D_1 \rightarrow {}^7F_2$	841.3	159 ± 4	21 ± 4	0.49	1.0	0.49
1033	$^5D_1 \rightarrow {}^7F_3$	1039.6	[e]	[e]	(0.11)[f]	0.53	0.50

[a] Free ion parameters from systematic studies of the energy level structure of 3+ actinide ions doped into $LaCl_3$ [23].

[b] In previous work, Yusov [18] reported the fluorescence lifetime of $Am(ClO_4)_3$ dissolved in H_2O as less than 40 ns and as (200 ± 50) ns in D_2O. Thuovenot *et al.* [19] reported 0.03 μs for Am^{3+} in $HClO_4$ in H_2O and 0.2 μs for Am^{3+} in D_2O containing $HClO_4$ (20% stated accuracy).

[c] Parameter values used in calculation: $\Omega_2 = 1 \times 10^{-20}$ cm^2, $\Omega_4 = 7.6 \times 10^{-20}$ cm^2, $\Omega_6 = 4.8 \times 10^{-19}$ cm^2.

[d] Parameter values used in calculation: $\Omega_2 = 7.1 \times 10^{-20}$ cm^2, $\Omega_4 = 7.6 \times 10^{-20}$ cm^2, $\Omega_6 = 4.8 \times 10^{-19}$ cm^2.

[e] Not measured due to very weak fluorescence intensity.

[f] Upper limit due to finite spectral resolution. Actual relative integrated band intensity is smaller than the value shown.

[22] and actinide ions doped into $LaCl_3$ [23] has resulted in "free-ion" values across the both the lanthanide and actinide series of elements. Figure 1 compares the calculated "free-ion" energy level structure of mid-series trivalent lanthanide [1] and actinide ions [23]. The data are arranged according to the number of f-electrons (4f or 5f) that the ion possesses.

Several aspects of the comparison shown in Fig. 1 merit comment. Consider pairs of ions having the same number of f-electrons. The larger spin-orbit coupling and configuration interaction characteristic of the actinide elements results in a comparatively open energy level structure near the ground state, with some alteration in the relative energies of states of different parentage. Using Tb^{3+} and Bk^{3+} for comparison, the consequence is that the most commonly observed emitting state of Tb^{3+} in solution is $^5D_4$ whereas Bk^{3+} fluoresces from its $^7F_6$ state in aqueous solution [24]. For each pair of lanthanide and actinide ions shown in Fig. 1, in which both ions emit as aquated ions, a smaller difference exists between the energy of the observed emitting free ion state and the next lower-lying free ion state for the actinide ion in comparison with its corresponding lanthanide ion. Such energy differences usually are referred to as energy gaps. The strong dependence of the non-radiative decay rate of aquated 3+ lanthanide ions [1] and actinide ions [2] on energy gap results in considerably reduced luminescence from an aquated 5f actinide ion in comparison with its aquated 4f lanthanide ion counterpart.

In Fig. 2, the observed fluorescence bands of aquated Am^{3+} are compared to the transition energies expected for emission from the $^5D_1$ state of Am^{3+} in $LaCl_3$ based on the energy level structure calculations of Carnall [23]. Good agreement is found between the centers of gravity of Am^{3+} 5f state emission bands and the transition energies of Am^{3+} in $LaCl_3$. The data shown in Fig. 2 also conform to another trend. The reported 5f state emission bands for aquated Cm^{3+} [25], Bk^{3+} [24] and Es^{3+} ions [26] have widths that do not exceed the sum of the total crystal field splitting for the same transition of the An^{3+} ion doped into $LaCl_3$ and the average thermal energy of the solution. A similar comparison can be made for the observed fluorescence bands of the $^5D_0$ state of aquated Eu^{3+} [27] and the transition energies expected for $^5D_0$ emission from Eu^{3+} in $LaCl_3$ [28]. The centers of gravity of the Eu^{3+} in $LaCl_3$ transitions and those of the aquated Eu^{3+} emission bands are quite similar. However, the widths of the aquated Eu^{3+} emission bands do not correlate as well with the energy spanned by the corresponding Eu^{3+} in $LaCl_3$ transitions.

The purely radiative rate of relaxation of an excited state, (ΨJ), to a particular lower state, $(\Psi' J')$, is the Einstein A coefficient, which, following Axe [29], can be expressed as

$$A(\Psi J, \Psi' J') = \frac{65\pi^4\sigma^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} \bar{F}^2 + n^3\bar{M}^2$$

where m is the mass of the electron, c is the speed of light, σ is the energy of the transition, h is Planck's constant, e is the charge of the electron, $\bar{F}$ and $\bar{M}$ are the electric dipole and magnetic dipole matrix elements, respectively, that connect the initial state, J, to the final state, J', and n is the index of refraction of the medium. The fluorescence branching ratio for a particular emission transition is obtained by dividing the A value for that transition by the sum of the A values for all transitions from the emitting state to lower-lying states.

For most observed transitions of 3+ lanthanides and actinides, the magnetic dipole contribution is negligible. When the magnetic dipole contribution needs to be considered, calculations of $\bar{M}^2$ for 3+ lanthanide ions [30] and 3+ actinides ions [31] are available. Using a theory independently developed by Judd [32] and Ofelt [33], the electric dipole contribution can be parameterized as follows:

$$\bar{F}^2 = e^2 \sum_{k=2,4,6} \Omega_k (\Psi J \| U^{(k)} \| \Psi' J')^2$$

where $U^{(k)}$ is a unit tensor operator of rank k and Ω_k are three parameters that, in practice, are evaluated from measured band intensities. Analyses of solution absorption spectra of aquated ions have resulted in values of Ω_k for all aquated trivalent lanthanides and many aquated trivalent actinides. The Ω_k values for trivalent lanthanides become nearly constant for elements heavier than Nd [1]. A similar effect evidently occurs in the actinide series beginning at Cf if one fixes the value of Ω_2 at 1×10^{-20} cm^2 [34]. A fixed value of Ω_2 was adopted because Ω_2 is poorly established in absorption studies of aquated 3+ actinide ions.

Emission from Am^{3+} provides an unusual opportunity to establish a value for Ω_2 because the reduced matrix elements involved are such that Ω_2 dominates the calculated fluorescence branching ratios for the $^5D_1$ state. Table 1 compares the observed and calculated integrated fluorescence band intensities (relative to the most intense band) for aquated Am^{3+}. One set of values was calculated using Judd–Ofelt parameters obtained by interpolation between those reported for Pu^{3+} and Cm^{3+} [34]. In the other, the value of Ω_2 was varied while holding Ω_4 and Ω_6 fixed at their interpolated values (due to the sparse distribution of non-zero reduced matrix elements, varying Ω_4 and Ω_6 as well resulted in little additional improvement). It is evident that Judd–Ofelt theory provides a qualitative understanding of the observed fluorescence band intensities of aquated Am^{3+}, but fails to quantitatively account for the experimental observations.

Although Judd–Ofelt theory generally has been successful in accounting for the observed f–f transitions of most trivalent lanthanide and actinide ions, its does not account for observed $J=0$ to odd-J transitions in the absorption spectrum of aquated Eu^{3+} and Am^{3+}. In the case of Am^{3+}, such failure has been attributed, qualitatively, to simplifications employed in development of the theory [35]. Burdick and Downer [36] have argued that higher order perturbations than those considered in Judd–Ofelt theory are needed to account for some Eu^{3+} transitions. In a recent study of the f–f absorption bands and luminescence lifetimes of Am^{3+} doped into a heavy metal fluoride glass, Williams and Brundage [13] concluded that Judd–Ofelt theory was unable to account for the observed fluorescence transition rates and suggested that the inconsistency may be due to third order contributions of spin-orbit interaction to the transition rate. If one assumes that the observed emission decay rate of the $^5D_1$ state of Am^{3+} at 15 K in a glass [13] is purely radiative, then the spontaneous emission rate of the $^5D_1$ state is 660 s^{-1}. Using this value and the observed lifetimes shown in Table 1 results in calculated fluorescence quantum yields for aquated Am^{3+} of 1.4×10^{-5} in H_2O solution and 1×10^{-4} in D_2O solution.

The observed aquated Am^{3+} ion luminescence is assigned as arising from the $^5D_1$ state of Am^{3+} based on the good agreement between the observed emission band positions and those calculated from "free-ion" energy levels, the essentially identical observed fluorescence lifetimes for the bands, and the absence of any observable $^5L_6 \rightarrow {}^7F_0$ emission. In addition, the $^5D_1$ state of Am^{3+} has the largest energy gap of any 5f state of Am^{3+}. Past studies of 5f state fluorescence from aquated Cm^{3+} [25], Bk^{3+} [24] and Es^{3+} [26] ions identified the emitting state as the state having the largest energy gap for a given ion. While both Eu^{3+} and Am^{3+} are f^6 ions whose emitting states as aquated ions are dominated by non-radiative decay [1], the much smaller energy gap of Am^{3+} reduces its observed luminescent lifetime to 22 ns in comparison with the 110 μs lifetime of aquated Eu^{3+} [37].

6. Comparison of some recent lanthanide and actinide solution luminescence studies

In this section, we review some recent complexed f-element ion fluorescence studies in solution that involve luminescence enhancement *via* complexation and encapsulation, speciation of metal ion complexes, studies on the influence of dissolved oxygen on f-state non-radiative decay, time-resolved excited state racemization, electrogenerated f-state luminescence, and quantum electrodynamics effects on f-state spectra and dynamics.

6.1. Luminescence enhancement via complexation and encapsulation

Some recent fundamental luminescence studies have focused on lanthanide or actinide β-diketone complexes in aqueous solutions containing surfactants [38,39] while others have involved correlation of ligand properties and luminescence of the complexes [40,41]. The use of β-diketones to enhance f-element luminescence is not novel, but most past studies that sought to achieve high sensitivity using such complexes were carried out in organic solvents. For example, Yamada *et al.* [42] reported in 1982 that they had achieved a detection limit of 5×10^{-16} M for a europium β-diketone complex dissolved in ethanol.

The underlying concept of the recent work in aqueous solutions is reduction of non-radiative decay by sequestering the f-element ion within the interior of a micelle, forming a cage structure *via* coordinated ligands, or solubilizing a suspension of aggregated metal ion complexes while enhancing f-state emission by energy transfer from ligand excited states to the metal ion. For example, Aleksandruk *et al.* [39] reported a detection limit of 4×10^{-13} M for curium present in an aqueous suspension formed from a gadolinium β-diketone phenanthroline complex and a surfactant. Enhancement of curium fluorescence was attributed to energy transfer from excitation initially localized on the organic ligands coordinated to Gd^{3+}. This method of enhancing f-state luminescence has been termed co-fluorescence.

Variants of the co-fluorescence method have been the basis for improvements in luminescence determination of lanthanide ions including a demonstration of simultaneous determination of samarium, europium, terbium and dysprosium [43]. The co-fluorescence effect also has been employed in fluorescence immunoassay (FIA) methods that rely on detection of lanthanide f-state luminescence. The highest reported sensitivities have been achieved in FIA using surfactant concentrations below the critical micelle concentration with luminescence determinations carried out in a fixed time period after solution preparation. The time period is selected such that some aggregation of metal ion complexes has occurred but precipitation has not commenced. A recent review by Xu *et al.* [44] should be consulted for additional details as well as an update published by Hemmilä [45]. In a further development of lanthanide FIA, Christopoulos and Diamandis [46] have reported achieving detection of 1.5×10^5 molecules of a monoclonal anti-α-fetoprotein antibody by enzymatic amplification of FIA using terbium chelates.

Progress in achieving improved luminescence properties from encapsulated lanthanide ions in aqueous solution has been reported by Sabbatini and Guardigli [47]. These workers have achieved a Eu^{3+} $^5D_0$ state observed fluorescence decay rate of $670\ s^{-1}$ for an aqueous solution of Eu^{3+} encapsulated by macrocyclic ligands containing 2,2-bipyridine units. The calculated purely radiative rate of the $^5D_0$ state of aquated Eu^{3+} is $103\ s^{-1}$ [1]. If this value holds in the work of Sabbatini and Guardigli, then non-radiative decay dominates the observed luminescence lifetime of the encapsulated Eu^{3+} and further improvement in fluorescence quantum yield may be obtainable. Such improvement might be achieved by removing high frequency ligand vibrational modes, such as C–H stretches, from close proximity to the luminescing metal ion.

In addition to luminescence studies that focus on the properties of the complexed metal ion, such as the influence of simple inorganic anions on Eu^{3+} lifetimes [48], analytical application can be made of the influence of solution constituents on metal ion luminescence. Recently reported examples include employment of 3+ europium fluorescence as the basis for analytical determination of nitric acid concentration [49] and of water in two organic solvents [50].

It is evident that enhancement of 3+ lanthanide and actinide ion luminescence can be achieved via co-fluorescence and related methods such as encapsulation. It seems likely that further significant improvement will be achieved. The degree to which these methods can provide high sensitivity in luminescence determination of ions such as Nd^{3+} or Am^{3+} that fluoresce very weakly in aqueous solution has not been established.

6.2. Speciation of metal ion complexes via luminescence

Many recent studies of the luminescence of f-element ions in solution have focused on speciation of the metal ion complexes. In this context, speciation refers to determination of the chemical identity and concentration of metal ion complexes. Lanthanide and actinide ion binding to humic acid [51–53] and fulvic acid [54,55] has been probed *via* f-state luminescence. Studies of the interaction of europium ion with extractants [56], and as a complexed ion in organic phases [57], have been reported in which luminescence from Eu^{3+} was used to probe metal ion coordination. The speciation of Cm^{3+} in natural water [58] and as an ion undergoing hydrolysis [59] has been accomplished by exploiting the very high sensitivity afforded by time- and wavelength-resolved laser-induced fluorescence methods. Past work on Cm^{3+} luminescence in solution has been reviewed by Beitz [60] and Kim *et al.* [61].

6.3. Effect of dissolved oxygen gas on excited f-states

Frequently, lanthanide ion f-state luminescence in solution is considered to be free of quenching by dissolved oxygen gas. However, two recent studies provide evidence that control of oxygen partial pressure is necessary in high accuracy studies of Eu^{3+} species with long emission lifetimes. Beitz and Sullivan [62] reported a 12% reduction in the observed luminescence decay rate of an Eu^{3+} extractant complex in toluene solution when the solution was sparged with helium gas instead of oxygen gas. These workers speculated that the $^1\Sigma_g^+$ state of O_2 might be produced, based on energetic considerations. Subsequent work by Darmanyan *et al.* [63] involved time-resolved luminescence of a Eu^{3+} β-diketone-phenanthroline complex dissolved in carbon tetrachloride. Quenching of the $^5D_0$ state of the complexed Eu^{3+} species by dissolved O_2 gas was observed to occur with a rate constant of 4.7×10^4 M^{-1} s^{-1} at 293 K. These workers identified the O_2 excited electronic state produced, $^1\Delta_g$, by its characteristic near-infrared emission at 1.27 μm. The precise mechanism by which the $^5D_0$ state of Eu^{3+} is quenched is not known. Conservation of energy suggests that the initial quenching step is $Eu^{3+}(^5D_0)+O_2(^3\Sigma_g^-) \rightarrow Eu^{3+}(^7F_5)+O_2(^1\Sigma_g^+)$ in which the energy excess is about 300 cm^{-1}. However, no direct evidence of formation of $O_2(^1\Sigma_g^+)$ has been reported. Direct production of $O_2(^1\Delta_g)$ *via* the minimum energy process, $Eu^{3+}(^5D_0)+O_2(^3\Sigma_g^-) \rightarrow Eu^{3+}(^7F_6)+O_2(^1\Delta_g)$, requires that about 4400 cm^{-1} of energy be converted into vibrational, rotational or translational energy. All of the emitting states shown in Fig. 1 occur at energies in excess of that required to produce either $O_2(^1\Sigma_g^+)$ or $O_2(^1\Delta_g)$. In consequence, quenching of these states by dissolved O_2 cannot be ruled out *a priori*.

6.4. Time-resolved excited state racemization

Metcalf *et al.* [64] and Wu *et al.* [65] have reported studies of time-resolved chiroptical luminescence. They have shown that excitation of a racemic excited-state population followed by interaction with a chiral quencher molecule can lead to differential quenching of enantiomers. Time resolution of total and circularly polarized luminescence with subsequent calculation of the resulting emission dissymmetry enabled studies of racemization kinetics and intermolecular chiral discrimination of Eu^{3+} and Tb^{3+} complexes in solution [64]. Similar studies on 3+ actinides have not been reported but seem technically feasible for good emitters such as Cm^{3+}.

6.5. Electrogenerated luminescence in solution

Most high sensitivity luminescence studies of f-element ions have employed a laser as the excitation light source. Kankare *et al.* [66] recently accomplished subpicomolar detection of Tb^{3+} *via* luminescence without utilizing an excitation light source. These workers have developed a simple electroluminometer in which electrogenerated luminescence occurs at disposable oxide-covered aluminum electrodes. They report observation of electrogenerated luminescence from Sm^{3+}, Eu^{3+} and Tb^{3+} in aqueous solution and used pulsed current flow in time-resolved luminescence studies. They observed a 2.1 ms luminescence lifetime for Tb^{3+} complexed by a carboxymethylaminomethylbenzoylphenol ligand in 0.3 M sodium sulfate solution at pH 10 containing 1 mM potassium peroxodisulphate. Their reported detection limit for electroluminescence determination of this Tb^{3+} complex is 10^{-13} M. The detailed mechanism of the cathodically induced electroluminescence is under investigation. Chemiluminescence of Tb^{3+} [67], Cm^{3+} [67,68] and Am^{3+} [68] in solution has been reported by Yusov *et al.* This raises the possibility that high sensitivity determination of Am^{3+} and Cm^{3+} can be achieved *via* electrogenerated luminescence.

6.6. Quantum electrodynamics effects on f-state luminescence

The effect of cavity quantum electrodynamics (QED) on the luminescence of Eu^{3+} in solution has been reported by Lin *et al.* [69]. Individual droplets (typically 10 μm or 24 μm in diameter) of a dimethylformamide/methanol/ethanol solution containing a dissolved Eu^{3+} β-diketone complex were photoexcited. In accord with QED theory, evidence of both enhanced and diminished spontaneous emission rates as well as alteration of the shape and number of observed emission peaks was obtained. In effect, a droplet can act as a resonant optical cavity with a Q as large as 10^8! In comparison with bulk solution measurements, Eu^{3+} luminescence lifetime lengthening by a factor of >1.5 and lifetime shortening by a factor of >2.5 were observed in the droplets. The work of Lin *et al.* provides a note of caution to those striving to improve sensitivity *via* reduction of sample size to micrometer dimensions in f-state luminescence studies.

7. Conclusions

Calculated "free-ion" f-state energy levels continue to be a reliable guide in interpreting the observed emission bands of f-element ions in solution. Line shapes and underlying ligand field splitting of f-state emission bands of 3+ lanthanide and actinide ions in solution remain areas for future investigation. Demonstrated methods of enhancing lanthanide and actinide f-state luminescence in solution include energy transfer from ligand excited states, exclusion of water from the primary coordination sphere, and reduction in the number of high frequency vibrational modes in close proximity to the luminescing metal ion. Energy gap considerations dominant non-radiative decay of most emitting f-states in solution, but complete exclusion of inner coordination sphere water molecules does not necessarily eliminate non-radiative decay as the primary factor influencing observed luminescence lifetimes. Future non-linear optical studies on solution luminescence may include anti-Stokes work on actinide ions, based on the observations of Murray and co-workers concerning anti-Stokes luminescence from Cm^{3+} and Cf^{3+} in solid halide phases [70].

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