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QUENCHING OF EXCITED STATES BY LANTHANIDE IONS AND CHELATES IN SOLUTION

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ABBREVIATIONS

acac	acetylacetonate anion
acacH	acetylacetone
dbm	dibenzoylmethide anion
DMSO	dimethyl sulphoxide
EDTA	ethylenediaminetetraacetate
hfac	1,1,1,5,5,5-hexafluoroacetylacetonate anion
8-hq	8-hydroxyquinolate anion
thd	2,2,6,6-tetramethyl-3,5-heptanedionate anion

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A. INTRODUCTION

The lanthanides from cerium to lutetium (atomic number 58–71) are 14 elements that follow lanthanum in the Periodic Table, in which the 14 $4f$ electrons are successively added to the lanthanum configuration. The $4f$ electrons are shielded from the environment by an outer core of $5s$ and $5p$ electrons. Therefore in general, the atomic properties of rare earth metal ions are almost always retained after formation of complexes with different ligands. Most metal ion complexes absorb visible and/or UV radiation but only a few re-emit the absorption energy in the form of visible or UV photons. However, the tervalent lanthanide ions and their complexes are known to luminesce, giving sharp atomic bands corresponding to f–f transitions in the central metal atom.

The interest in sensitized emission in lanthanide chelates started in 1942 when Weissman noticed that the absorption of UV light by a variety of β-diketonate complexes resulted in a line-like emission characteristic of the europium(III) ion [1]. For two decades after this initial work, very little research was done until the advent of laser spectroscopy began a renewed interest in lanthanide emission. Since then, a large number of papers have been published on lanthanide luminescence in various areas. Crosby in 1966 presented a review on the luminescence of organic complexes of lanthanides [2]. At about the same time, Sinha published a monograph covering luminescence studies of europium and later, in 1971, a review on luminescence and laser action in chelates [3,4]. More recently, the absorption and luminescence properties of rare earth ions in solution have been reviewed by Carnall [5]. Several monographs on various aspects of the excited state properties of lanthanide ions have been published [6–8]. In 1984 Horrocks and Albin published an excellent review on lanthanide ion luminescence in coordination chemistry and biochemistry, describing the applications to biomolecular systems [9].

The great interest in studies of the luminescence properties of lanthanide ions and chelates is mainly due to their potential practical applications. Firstly, lanthanide ions and chelates are used as laser materials [8,10]. Secondly, the analytical application of luminescence methods to determine traces of tervalent lanthanide ions in solution is well known [11]. Fluorescence methods are also used to obtain information about the structure of rare earth complexes, their formation constants, symmetry etc. [9,12–14]. Rare earth elements can thus be used as luminophores [15]. Recently, the trend has been for interest to extend to applications in biochemistry [9]. Thus tervalent ions of europium and terbium are being used as very sensitive luminescent probes [16].

In this paper, after general concepts concerning absorption, emission and photophysical properties, the quenching of excited states by lanthanide ions and chelates in solution is reviewed. Because of the great interest in the applications of the luminescence properties of rare earth elements, it becomes important to review and clarify the problems concerning energy transfer processes between lanthanide ions and chelates. The purpose of this paper is also to inspire researchers to study mechanisms of interactions between excited states of organic molecules and lanthanide complexes.

All lanthanide(III) ions are known to luminesce, particularly in the solid state under anhydrous conditions. The literature about lanthanide(III) luminescence in phosphors, doped glasses, single crystals and solid state materials is vast [17]. Therefore neither these topics nor the lanthanide(III) emission studies in biochemically related research will be covered here.

B. SPECTRAL PROPERTIES OF LANTHANIDES

(i) Electronic energy states

The electronic configurations of lanthanides are not known with complete certainty owing to the great complexity of their electronic spectra. Table 1 shows the electronic configurations of lanthanide atoms and ions generally accepted in the literature. Since the +3 oxidation state is characteristic for

TABLE 1

Electronic configuration of lanthanide atoms and ions [a]

Atomic number	Name	Symbol	Atom	M^{2+}	M^{3+}	M^{4+}
57	Lanthanum	La	$5d^1 6s^2$	$5d^1$	[Xe]	–
58	Cerium	Ce	$4f^1 5d^1 6s^2$	$4f^2$	$4f$	[Xe]
59	Praseodymium	Pr	$4f^3 6s^2$	$4f^3$	$4f^2$	$4f$
60	Neodymium	Nd	$4f^4 6s^2$	$4f^4$	$4f^3$	$4f^2$
61	Promethium	Pm	$4f^5 6s^2$	–	$4f^4$	–
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^5$	–
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^6$	–
64	Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7 5d^1$	$4f^7$	–
65	Terbium	Tb	$4f^9 6s^2$	$4f^9$	$4f^8$	$4f^7$
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$	$4f^8$
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$	–
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$	–
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$	–
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$	–
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	–	$4f^{14}$	–

[a] Only the valence shell electrons (those outside the [Xe] shell) are given.

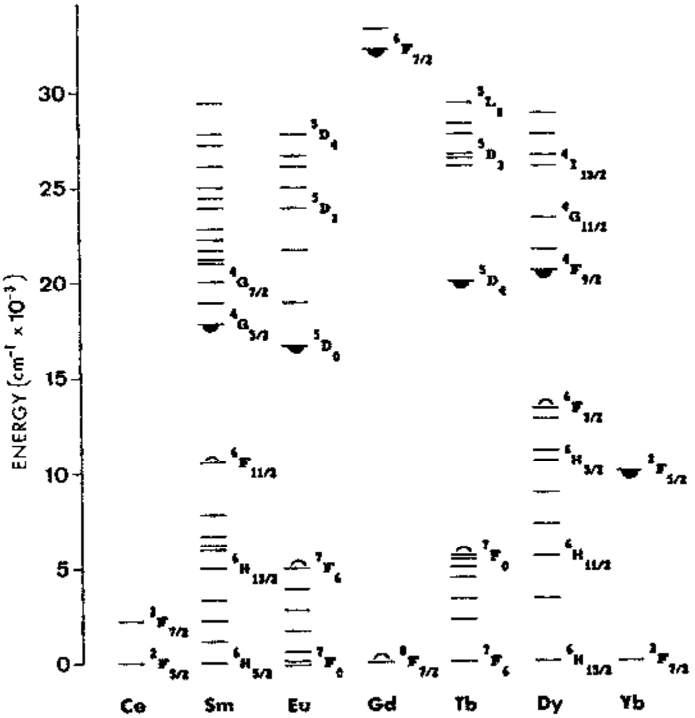

Fig. 1. Comparison of electronic energy levels for triply charged lanthanide ions (Ln^{3+}). Filled semicircles indicate the lowest luminescent level whereas unfilled semicircles indicate the highest level of the ground state manifold.

all lanthanides, this review will focus mainly on the tervalent lanthanide(III) ions and their compounds.

The electronic energy states of the lanthanide $4f^n$ configurations are only minimally affected by their surroundings owing to the effective shielding of the $4f$ electrons from the external field by the $5s^2 5p^6$ arrangement. Therefore these energy states remain practically invariant for a given ion in all its compounds and in different environments.

The absorption and emission spectra of lanthanide(III) ions give sharp, spectrally narrow bands. Their variety and complex character are due to the large number of electronic levels (Fig. 1). The energy states derive from the splitting of the $4f^n$ electronic configuration owing to electrostatic interaction and spin–orbit coupling. The comparatively large values of spin–orbit coupling constants (ca. 1000 cm^{-1} (2.9 kcal mol^{-1})) cause the individual J levels to be well separated. Thus nearly every tervalent lanthanide ion is characterized by a ground state with a single value of total orbital momentum J and by a first excited state at an energy many times kT (ca. 0.57 kcal

mol^{-1} at room temperature) above the ground state. Thus the first excited state is essentially unpopulated by electrons except at very high temperatures. However, samarium(III) and europium(III) ions are two exceptions, their first excited states lying close enough to the ground state so that they are populated by electrons even at ambient temperatures (Fig. 1). Theoretical calculations have given results which are, in most cases, in excellent agreement with the experimental observations [5,18].

(ii) Absorption spectra

The lanthanide(III) ions with incompletely filled $4f$ orbitals absorb electromagnetic radiation in the near-UV, visible and near-IR regions (ca. 300–900 nm) [19]. These spectral areas are easily accessible experimentally. The transitions taking place in these regions are caused by, or result from, the incomplete $4f$ subshells. Generally, there are three types of transitions: intra-$4f^n$, $4f^n \rightarrow 4f^{n-1}5d$, and charge transfer between the lanthanide ion and the ligands.

The $4f^n \rightarrow 4f^{n-1}5d$ transitions occur in the near-UV region for cerium(III), praseodymium(III) and terbium(III) compounds. These transitions tend to be broad and the upper $5d$ level is split by the ligand field surrounding the ion.

Charge transfer bands result whenever an easily oxidized ligand is bound to a tervalent lanthanide(III) ion which can be reduced to the divalent state, or when a ligand is bound to a tetravalent ion [20]. Such transitions are commonly observed in the spectra of samarium(IV), europium(III), thulium(III), ytterbium(III) and cerium(IV) complexes. The positions of these bands in the spectra are markedly dependent on the properties of ligands and metal ions.

By far the most interesting and useful transitions in the spectra of lanthanide complexes are the intra-$4f^n$ transitions [21]. Splittings of the various states in the $4f^n$ configurations by external fields (ligand field) are very small, ca. 100 cm^{-1} (286 cal mol^{-1}). This is due to the effective shielding of these orbitals from their surroundings (vide supra). Thus, when an f–f transition occurs from one spectroscopic term of a $4f^n$ configuration to another term of the same configuration, the absorption band is extremely sharp. The bands are similar to those of free atoms and are quite unlike the broad d–d bands in transition metal complexes. Virtually all the absorption bands found in the visible and UV spectra of lanthanide(III) ions have this line-like character.

The simplest structure of absorption spectra is observed for Ce^{3+} and Yb^{3+} ions because, as shown in Fig. 1, there are only two electronic levels for these ions. In the case of other lanthanide ions the spectra are much more complex due to the presence of a large number of electronic levels. The absorption spectra of all lanthanide(III) ions are characterized by small values of molar absorption coefficients in the visible range ($\epsilon < 10$). The problems concerning the absorption spectra of rare earth ions in solutions, including the historical development and theoretical interpretation, have been reviewed by Carnall [5].

Recently, several research groups have concentrated on the spectrophotometric studies of rare earth complexes, e.g. the influence of different ligands and solvents on the absorption spectra of lanthanide ions in solution [5,22–25]. When the spectrum of a complexed lanthanide(III) ion is compared with that of an aquated ion (the spectra of "free" ions are generally unknown), three effects on the absorption bands are observed: (1) small displacements usually towards longer wavelengths; (2) the development of fine structure, but only in certain bands; and (3) changes in intensities, again only in certain bands. However, in no instance does complexation alter the spectrum of a given lanthanide(III) ion profoundly. The transitions within the 4*f* arrangements of lanthanide complexes are affected but not obviated.

(iii) *Emission spectra*

The emission spectra of rare earth ions in solutions and in solid state have been extensively studied since the early 1930s. The historical development, theoretical aspects and discussions of steady state and lifetime measurements have been reviewed by Carnall [5] and Horrocks, Jr. [9]. The fluorescence of tervalent ions consists of sharp emission bands corresponding to the *f*–*f* transitions (Fig. 1). This line-like emission is attributed to the shielding of 4*f* electrons from the environment by an outer core of 5*s* and 5*p* electrons. However, not all the possible transitions result in fluorescence, emphasizing again the importance of environmental and consequent symmetry effects. The lanthanide(III) ions, particularly those in the middle of the series, such as samarium, europium, terbium and dysprosium, form complexes that often emit visible radiation corresponding to the *f*–*f* transitions in the central metal ion when excited in the near-UV. Generally, the emission may occur (1) from the excited ligand perturbated by the cation, (2) from the excited cation perturbated by the ligand, and (3) as a consequence of a non-radiative intramolecular energy transfer from the excited ligand to the cation, followed by emission from the latter. These various types of emission are the consequence of different energy diagrams for the lowest excited states for the rare earth complexes. Schematic energy level diagrams for three typical types of lanthanide(III) complexes are illustrated in Fig. 2 [26].

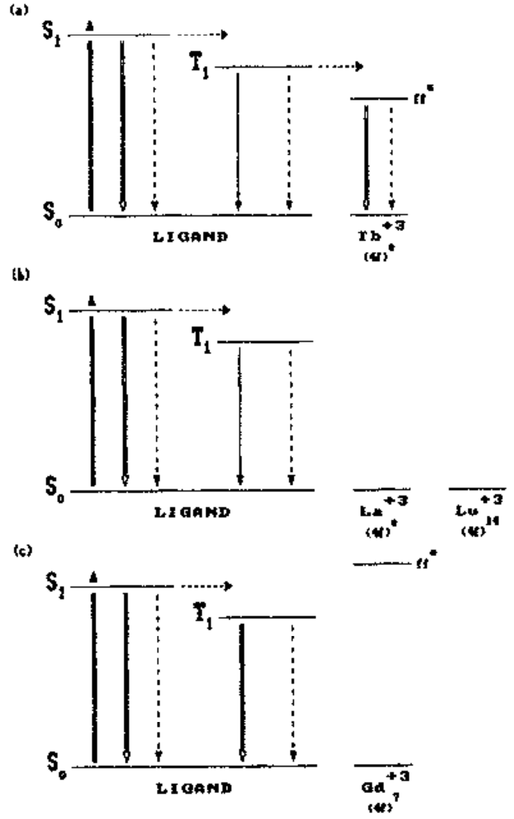

Fig. 2. Schematic energy level diagrams for three typical types of rare earth complexes. The lowest *ff* * levels of the central metal ion are located at energetically lower (a) or higher (c) states than the lowest triplet level (T_1) of a ligand. There are no *ff* * levels in La^{3+} and Lu^{3+} complexes (b). Radiative, very low efficient radiative, and non-radiative processes are represented by $\Rightarrow$, $\rightarrow$ and ⇢ respectively [26].

When the *ff* * levels of the central metal ion are energetically higher than the lowest triplet (T_1) of the ligand (case (c)) or there are no *ff* * levels as in the case of La^{3+} and Lu^{3+} (case (b)), the ligand-localized emission (fluorescence and phosphorescence) can be observed. However, in the case of complexes with low-lying radiative *ff* * levels (case (a)), an intramolecular energy transfer from the ligand excited T_1 state to the *ff* * level of the lanthanide(III) ion may occur. In this case, lanthanide(III) ion fluorescence is observed. In order to observe fluorescence from lanthanide chelates under such indirect excitation, at least one acceptor level should lie below the lowest triplet level of the ligand.

From the point of view of metal ion luminescence, the chelated lanthanide(III) ions can be classified into three groups:

(1) Those ions that show no fluorescence such as La^{3+} ($4f^0$) and Lu^{3+} ($4f^{14}$), and those for which luminescence is seldom observed such as Gd^{3+} ($4f^7$). Intra-$4f^n$ transitions are of course forbidden in lanthanum(III) and lutetium(III) complexes. However, the lowest lying excited level of gadolinium(III) is too high (92.3 kcal mol^{-1}) to accept energy from a typical ligand T_1 state.

(2) Those ions, such as Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+}, that exhibit strong fluorescence due to the fact that in each instance an excited energy state lies just below the ligand triplet state, and relatively large energy gaps exist between excited and ground state (Fig. 1).

(3) Those ions, such as Pr^{3+}, Nd^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+}, that show only weak fluorescence because of the small differences between energy states which increase the probability of non-radiative transitions.

The line-like structure of the emission spectra of some β-diketonates of samarium(III), europium(III), terbium(III) and dysprosium(III) ions indicates that the lines arise from radiative f–f transitions (Fig. 1) [27]. Since emissions of samarium(III), terbium(III) and dysprosium(III) ions originate from radiative transitions at a unique resonance level for each ion, it is possible to assign most groups of lines unambiguously to transitions between particular terms on the basis of energy gaps only. This kind of assignment, however, is not so simple for europium(III) complexes since spectral lines in this ion originate from two excited states, $^5D_1$ and $^5D_0$, both of them populated by energy transfer. However, the recording of spectra through a special phosphoroscope, which effectively eliminates lines originating from the short-lived $^5D_1$ resonance level allows for the assignment of the $^5D_0$–^7F transitions. A more detailed discussion is presented in the next sections.

It should be noted that, besides the small shifts in band energy and changes in band intensities, fluorescence techniques can give more information about the excited states of lanthanide complexes, namely their lifetimes. Fluorescence decay measurements can be used as excellent and sensitive tools for the study of the changing environment of lanthanide(III) ions.

Since Carnall's review [5] about the effect of changing environments on the emission properties of tervalent lanthanide ions, a large number of papers have been published on that subject. For example, Bilal and coworkers [14,28,29] determined the formation constants of lanthanide(III) complexes in solution using luminescence intensity and lifetime measurements. The influence of pH, excess of complexing agent, size and charge of ligand molecules, and temperature on the fluorescence intensity of lanthanide complexes with amino-polyacetic acids in solution has also been carefully studied [30,31]. The experimental results have been explained using a simple theoretical model connecting the intensity of transition for the lanthanide(III) ion with the resultant transition dipole moment of the system [30].

Fluorescence techniques also allow the study of the structure, symmetry and stability of rare earth complexes, the presence of covalent interactions, the structure of first and second coordination spheres of lanthanide(III) ions, the exchange of ligands between the complexes etc. [22,32–39]. Widely used for these types of study is the investigation of the effect of changes in the environment of lanthanide(III) ions on the so-called "hypersensitive transitions" [5,22,30–36]. The reader is referred to recent reviews [9,39] for experimental and theoretical details concerning environmental effect on lanthanide(III) ion luminescence.

A great enhancement of the lanthanide(III) ion emission can be achieved by introducing a triplet sensitizer with its triplet level above that of the chelate. Thus when a system containing benzophenone and $Eu(hfac)_3$ is excited at 380 nm, where the chelate has no absorption, a tenfold increase in the intensity of europium(III) fluorescence is observed [40]. This is due to intermolecular and intramolecular energy transfer processes which will be discussed in the next sections.

C. INTRAMOLECULAR ENERGY TRANSFER

Intramolecular energy transfer after near-UV light excitation has been the subject of numerous studies for almost 30 years [11]. It was Weissman who first indicated that after irradiation of the organic part of a europium complex, the atomic line emission of the Eu^{3+} ion was observed [1]. It was proposed that the direct excitation of lanthanide(III) was not responsible for the observed emission, and that it was due to an internal energy transfer from the ligand to the 4*f* subshells of the central metal ion. The similarity in the chemical properties of the lanthanides combined with the insensitivity of the 4*f* electrons to the ion environment make these chelates ideal systems for the study of the problem of intramolecular energy transfer from the ligand to the complexes metal ion.

Three mechanisms by which excitation energy can be transferred from ligands to lanthanide(III) ions have been proposed (Fig. 3) [41–45]:

Mechanism I. After an efficient intersystem crossing between the lowest singlet and triplet excited states of the ligand, energy transfer occurs from T_1 to a lower energy state (En) of the lanthanide(III) ion:

$S_1 \rightarrow T_1 \rightarrow \mathrm{En}$ (of Ln) → emission

Mechanism II. There is a direct energy transfer from S_1 to a lower energy state (En) of the lanthanide(III) ion:

$S_1 \rightarrow \mathrm{En}$ (of Ln) → emission

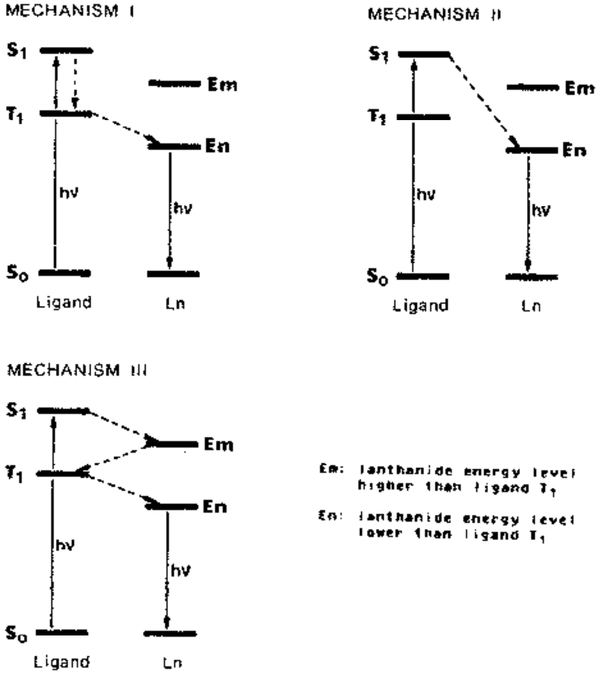

Fig. 3. Three different mechanisms for intramolecular energy transfer in lanthanide chelates.

Mechanism III. There is an energy transfer from S_1 to an upper intermediate level (Em) of the lanthanide(III) ion, then back to T_1 to return finally to a lower energy level (En) of the lanthanide(III) ion before emitting:

$$S_1 \rightarrow \text{Em (of Ln)} \rightarrow T_1 \rightarrow \text{En (of Ln)} \rightarrow \text{emission}$$

Mechanism I seems to agree with most of the experimental results obtained by various research groups. In order to clarify whether intramolecular energy transfer in europium chelates takes place via the triplet states of ligands [45], the T_1 state of europium dibenzoylmethide, $Eu(dbm)_3$, was generated by exciting lanthanum dibenzoylmethide, $La(dbm)_3$, at 365 nm in a mixed solution of both complexes. When the mole fraction of $Eu(dbm)_3$ increases, $La(dbm)_3$ ligand phosphorescence intensity decreases while $Eu(dbm)_3$ emission intensity increases nearly in the same proportion. Intermolecular energy transfer does occur from the $La(dbm)_3$ triplet to the $Eu(dbm)_3$ triplet (Fig. 4).

A direct energy transfer from triplet $La(dbm)_3$ to europium(III) ion is rejected since in a mixed solution of free Eu^{3+} and free ligand, no energy transfer was observed. A comparison of the emission intensities obtained by

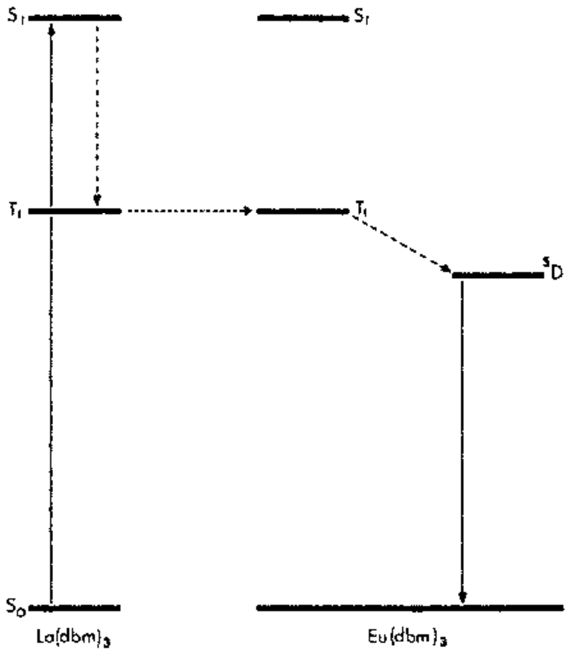

Fig. 4. Intermolecular and intramolecular energy transfer of La(dbm)$_3$ and Eu(dbm)$_3$.

direct excitation of europium ion (546 nm) and that obtained from excitation of the ligand (365 nm) confirmed the occurrence of an intermolecular energy transfer from La(dbm)$_3$ to Eu(dbm)$_3$. This fact is also taken as clear evidence that intramolecular energy transfer takes place via the triplet state (Fig. 4). As shown by Dawson et al. [46], the efficiency of this intramolecular energy transfer process ranged from a few per cent to over 50% depending on the 1,3-diketonate ligand used for terbium(III) and europium(III). Those values were calculated on the basis of the fluorescence quantum yield measurements upon excitation to the ligand absorption band (to S_1, Fig. 3) and selective excitation to an emitting level of the lanthanide ion (to En, Fig. 3). Thus they represent the efficiencies of all possible modes of deactivation of the S_1 state of the ligand to the emitting level of the lanthanide(III) ion (En).

Most of the qualitative conclusions reached in the early work concerned with the intramolecular energy transfer processes, and more generally, with the photophysical properties of lanthanide chelates have been confirmed by more recent and often more sophisticated studies. As shown earlier, from an energetic point of view there are three typical types of rare earth complexes (Fig. 2). If at least one *ff** level of the central metal ion lies below the lowest triplet state of the ligand, intramolecular energy transfer can be

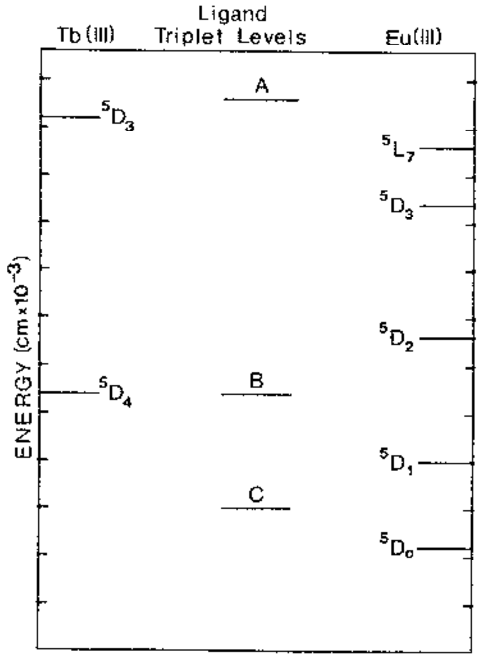

Fig. 5. Schematic energy level diagram showing relative positions of excited europium(III), terbium(III), and β-diketonate triplet levels.

observed (case (a)). Because of the large number of *ff* * levels the schematic energy level diagram of the chelates is much more complicated. Taking the terbium(III) and europium(III) complexes as examples, their photophysical processes can be understood with the aid of the diagram shown in Fig. 5.

Watson et al. [47] reported the time-resolved and spectrally resolved luminescence of several europium(III) and terbium(III) chelates in glass-forming solvents using pulsed laser excitation (to ligand-localized singlet states). For europium(III) 8-hydroxyquinolate, Eu(8-hq)$_3$, in which the ligand triplet state lies below the $^5D_1$ level (Fig. 5, triplet level C), luminescence from $^5D_0$ was observed and shown to increase rapidly within the time resolution of the apparatus (ca. 10^{-8} s) followed by a slow decay characteristic of the $^5D_0$ emission. No short-lived emission typical of $^5D_1$ luminescence was detected. In contrast, europium(III) tris(dibenzoylmethide), Eu(dbm)$_3$, in which the ligand T_1 state lies above the $^5D_1$ level (Fig. 5, triplet level B), showed luminescence from both $^5D_1$ and $^5D_0$. The emission from the $^5D_1$ level exhibits a rapid initial rise and decays in ca. 2×10^{-6} s. Concurrently, the $^5D_0$ emission exhibits a rapid initial rise followed by a slow rise in 2×10^{-6} s, then by a characteristic slow decay (ca. 5×10^{-4} s). Chelates with T_1 levels above $^5D_2$ and $^5D_3$, e.g. Eu(acac)$_3$ (Fig. 5, triplet level A) did not show

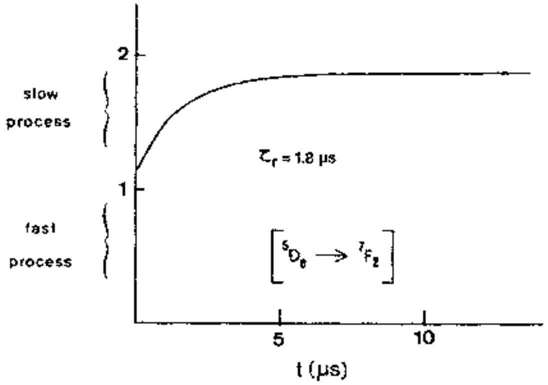

Fig. 6. Typical plot of intensity against time for luminescence from $^5D_0$ levels of certain complexes on a microsecond time scale [17].

any emission from these levels, but did show luminescence from $^5D_1$ and $^5D_0$. The rise and decay times were similar to those of Eu(dbm)$_3$. Thus the $^5D_0$ level is populated by both "fast" and "slow" processes (Fig. 6). By systematically correlating $^5D_1$ decay times and $^5D_0$ rise times, the "slow" process has been identified as an internal conversion $^5D_1 \rightarrow {}^5D_0$ (which determines the lifetime of the $^5D_1$ level). The "fast" process is predicted to be an intramolecular energy transfer via the ligand-localized triplet state $T_1 \rightarrow {}^5D_0$. A similar energy transfer process is responsible for the population of the $^5D_1$ level, $T_1 \rightarrow {}^5D_1$. In the case of Tb(acac)$_3$, even though the ligand T_1 level is sufficiently high (Fig. 5, triplet level A) to populate $^5D_3$, only emission from the $^3D_4$ level is observed with a rise time of 10^{-8} s or less and a slow decay of about 10^{-3} s.

On the basis of their results and the literature data, Watson et al. [47] concluded that the predominant intramolecular energy transfer pathway goes through a triplet state: $S_1 \rightarrow T_1$, and then $T_1 \rightarrow$ rare earth (mechanism I). However, they also proposed a spin-allowed enhanced intersystem crossing mechanism for relaxation of the ligand-localized S_1 state involving ^7F_j electronic levels of the rare earth complexes of terbium(III) and europium(III). The results of Watson et al. are in good agreement with those previously obtained by Tanaka et al. [48] using the stroboscopic technique to study the time-resolved emission spectra of europium(III) and terbium(III) β-diketonate chelates. Additional arguments for the participation of the ligand-localized triplet state in the migration of electronic energy in those complexes come from the study of the effects of changing the triplet energies on the energy transfer process [49,50]. Sato and Wada [49] studied a series of terbium(III) and europium(III) β-diketonates with ligands of different triplet energies. To explain such experimental results as a relation between fluorescence yields and triplet energies, and temperature dependence of fluorescence lifetimes, they proposed that the energy transfer through the triplet state of the ligand takes place via an exchange interaction and an additional thermal deactivation process (via the triplet state) from emitting levels of lanthanide ions.

Hayes and Drickamer [50] recently described an excellent method for the investigation of energy transfer in rare earth chelates, the high pressure luminescence technique. The organic-ligand-localized excited states are extremely sensitive to pressure, which results in large energy shifts. However, owing to the shielding by an outer core of 5*s* and 5*p* electrons, the lanthanide ion 4*f* levels are not sensitive to pressure. Thus an increase in pressure can tune in a continuous manner the ligand-localized excited states (singlets and triplets) relative to the ion levels. Using this technique, the europium(III) and terbium(III) β-diketonate chelates were studied as crystalline samples and in poly(methyl methacrylate) solutions. Comparing the emission intensity results for the ligand-localized singlet excitation with those obtained when the rare earth ion levels were directly excited, the triplet state was shown to act as (1) a donor of energy to the ion levels (mechanism I of intramolecular energy transfer), (2) an intermediate level for relaxation between the ion levels under proper conditions (as in mechanism III), and (3) a "quencher" of ion levels (thermally activated energy transfer to triplet state from ion level, the so-called "triplet quenching" or "thermal deactivation").

The overall results obtained by high pressure luminescence techniques [50] are similar to those obtained for solutions by Sato and Wada [49] and strongly support the involvement of the ligand triplet state in the intramolecular energy transfer for lanthanide β-diketonate chelates (mechanism I). Energy transfer via the triplet level proceeds most probably by a Dexter exchange mechanism. However, the $S_1 \rightarrow$ rare earth migration of energy (mechanism II) proposed by Kleinerman [43] as a dipole–quadrupole interaction cannot be ignored, at least in some cases. For example, the terbium(III) complexes having a T_1 state below the $^5D_4$ level, the observed $^5D_4$ luminescence can be explained as a direct $S_1 \rightarrow$ rare earth energy transfer.

Further investigations on the energy migration within lanthanide β-diketonate complexes are required. Unfortunately, owing to the lack of emission from the ligand excited states (or in some cases emission too weak to be quantitatively measured) and also owing to the difficulties in determining the ligand-localized triplet–triplet absorption spectra for those chelates, it becomes very difficult to prove directly which state is responsible for the energy transfer process. The ligand-localized triplet–triplet spectra for chelates with low-lying *ff** levels have not been reported so far. However, the kinetic parameters for the lowest excited states have been recently

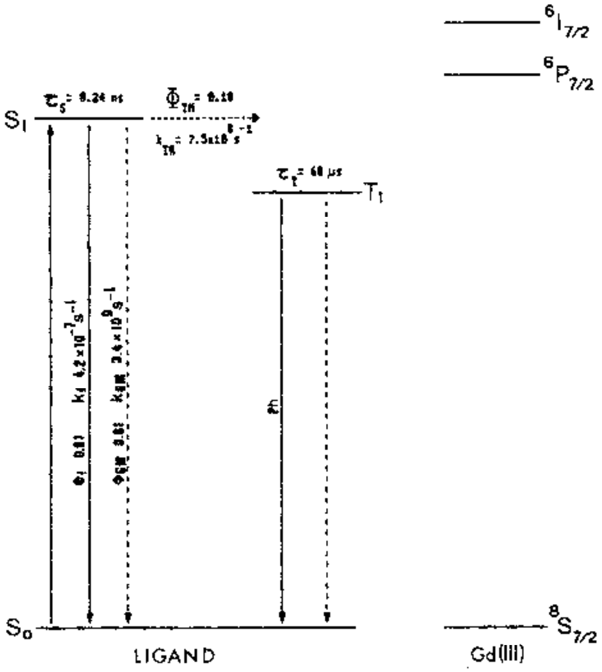

Fig. 7. Energy level diagram and kinetic parameters of the lowest excited state of gadolinium(III) methylsalicylate, at room temperature [26].

determined [26,51] for certain tervalent lanthanide β-diketonate complexes in which the *ff** levels of the central metal ion are either located energetically higher than the lowest triplet state of the ligand (case (c), Fig. 2) or do not exist (case (b), Fig. 2). An energy level diagram including all known kinetic parameters for a gadolinium(III) methylsalicylate complex is presented in Fig. 7. The terbium (III) methylsalicylate complex (case (a), Fig. 2) has a very weak fluorescence from the ligand-localized S_1 state ($\phi_f < 0.01$) and a markedly short fluorescence lifetime, $\tau_f < 10$ ps, which falls beyond the time resolution of the instrument utilized in ref. 51 (Fig. 7). As a comparison, a similar diagram illustrating the photophysical properties of terbium(III) β-diketonate chelates is presented in Fig. 8. It can be visualized how the possibility of intramolecular energy transfer can drastically change the photophysical properties of these complexes. However, additional effects must also be considered. By studying the electronic relaxation processes of rare earth chelates of benzoyltrifluoroacetone and methylsalicylate, Tobita et al. [26,51] came to the conclusion that the paramagnetic properties of the metal ions enhanced significantly both radiative ($T_1 \rightarrow S_0$) and non-radiative ($T_1 \rightarrow S_0$, $S_1 \rightarrow T_1$) rates from ligand-localized singlet and triplet excited states.

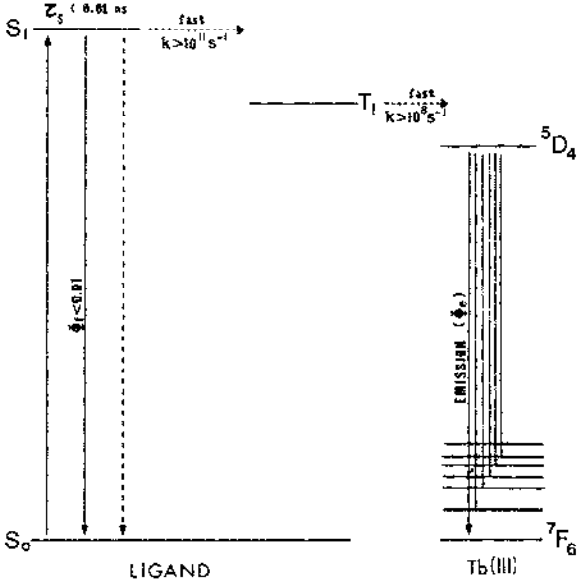

Fig. 8. Energy level diagram and known kinetic parameters for lowest excited states of terbium(III) methylsalicylate at room temperature [26]. (Although the Φ_e and τ values for emitting $^5D_4$ level of terbium(III) methylsalicylate are not reported, appropriate values are known for chelates of the same type, e.g. Tb(acac)$_3$: $\tau = 0.19$ and 0.33 upon excitation to S_1 state of ligand and $^5D_4$ level respectively, in ethanol solution at room temperature [46].)

Generally, the luminescence properties of rare earth β-diketonate chelates are dependent on the ligands, metal ions, solvents, temperature and whether they are of a tris or tetrakis form. Therefore when comparing the photophysical properties of these complexes, the above parameters must be taken into consideration. In the case of europium(III) chelates, owing to the emission from both $^5D_1$ and $^5D_0$ levels, the solvent and temperature effects are even more complex. In most europium chelates the fluorescence lifetime from $^5D_1$ is nearly the same regardless of the media and the nature of the ligands, whereas fluorescence from $^5D_0$ depends on both, the medium and the type of ligand [52].

D. INTERMOLECULAR ENERGY TRANSFER

Intermolecular energy transfer is an important process in photochemistry and photophysics. Its role, possible mechanisms and application to mechanistic and practical problems in coordination chemistry have been recently outlined [53].

Because of their absorption and luminescence properties, lanthanide ions such as Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+} and their chelates are very good model compounds for studying energy transfer processes. This topic has been partially reviewed in some monographs, for example, in refs. 9 and 54–56. In this section, the physical meaning and consequences of energy transfer processes as well as other possible intermolecular quenching processes with the participation of lanthanide ions and chelates will be underlined.

Intermolecular energy transfer in solutions containing lanthanide ions or complexes may occur [54,55] (1) from singlet or triplet excited states of organic molecules to lanthanide ions or chelates, (2) from excited lanthanide(III) ions to organic molecules, or (3) between lanthanide ions or chelates.

In the early 1960s, El-Sayed and Bhaumik [40] showed that the excited triplet state of benzophenone efficiently transferred its energy to the ligand of europium hexafluoroacetylacetonate. The observation of a red emission due to the rare earth ion was taken as direct proof of the involvement of energy transfer in the quenching of benzophenone triplet states.

Energy transfer from T_1 states of ketones and aldehydes to lanthanide ions was demonstrated by measuring the intensities of the acceptor emissions [57]. Heller and Wasserman [58], after an extensive investigation on the direct triplet energy transfer from various organic carbonyl compounds, suggested that a diffusion-controlled collision process was the probable mechanism for excitation of lanthanide(III) ions. By this mechanism, as shown in the next scheme, energy transfer from the lowest triplet state of the donor $D(T_1)$ populates one of the luminescent levels (En) of the lanthanide ion via an intermediate level (Em); this subsequently results in emission from the En level [59]:

$$D(S_0) + h\nu \rightarrow D(S_1) \qquad \text{(absorption)} \qquad (1)$$

$$D(S_1) \rightarrow D(T_1) \qquad \text{(intersystem crossing)} \qquad (2)$$

$$D(T_1) + \mathrm{Ln} \xrightarrow{k_q} D(S_0) + \mathrm{Ln(Em)} \qquad \text{(energy transfer)} \qquad (3)$$

$$\mathrm{Ln(Em)} \rightarrow \mathrm{Ln(En)} \qquad \text{(internal conversion)} \qquad (4)$$

$$\mathrm{Ln(En)} \rightarrow \mathrm{Ln} + h\nu_f \qquad \text{(fluorescence)} \qquad (5)$$

where Ln is a tervalent lanthanide ion in the ground state.

This collisional transfer mechanism was also confirmed by Filipescu and Mushrush [60] when they studied the photoreduction of benzophenone derivatives in 2-propanol in the presence of Tb^{3+} ions. Using steady state kinetic methods they found that energy transfer to the Tb^{3+} acceptor competed with the hydrogen abstraction reaction of the lowest excited triplet state of the ketone [61].

The sensitization of emission of lanthanide(III) ions with aromatic ketones have been systematically investigated by flash photolysis [62]. Quenching rate constants (k_q) were determined from the measurement of the time-dependent decay of the triplet–triplet absorption of the ketones in the presence of lanthanide salts. The k_q values were in the range 10^5–10^7 M^{-1} s^{-1}, values much lower than the diffusion rate constant ($k_d \approx 10^{10}$ M^{-1} s^{-1}), which indicates that approximately one out of 10^3–10^5 encounters of a triplet ketone with a lanthanide ion is effective for quenching. These values, along with a lack of proportionality between k_q and the overlap integral of the spectra, suggest a radiationless energy transfer by an exchange interaction mechanism [62]. The results obtained from measurements at low temperature (77 K) in rigid media using steady state and phosphorescence decay techniques also favour the exchange energy transfer mechanism over the multipolar interactions such as dipole–dipole, dipole–quadrupole and quadrupole–quadrupole [63,64]. The occurrence of the exchange mechanism is also further supported by the work done by Marshall and Pilling [65] on the interaction of triplet states of aromatic hydrocarbons with lanthanide(III) ions. However, in spite of all this evidence, there might be cases in which an electron transfer mechanism could be responsible for the quenching of triplet excited states by lanthanide ions, and this problem will be discussed later.

Although excitation transfer from triplet states of aromatic compounds to lanthanide ions has been well established, only a few studies can be found in the literature involving the quenching of singlet excited states. In 1969, Ermolaev and Shakhverdov [66] reported the quenching of the fluorescence of a number of organic compounds by lanthanide(III) ions. Since some correlation was found between the overlap integral of the emission spectra of the organic donor and the absorption spectra of the acceptor, it was suggested that energy transfer was the cause of the fluorescence quenching. They also observed that Eu^{3+} was a more efficient quencher than other lanthanide ions, which pointed to the involvement of an electron transfer process:

$$D(S_1) + Eu^{3+} \rightarrow D^{\cdot+} + Eu^{2+} \qquad (6)$$

This reaction was later proven by Levin by conventional flash photolysis experiments [67].

More recently, Sabbatini et al. studied the quenching of both S_1 and T_1 states of a series of aromatic hydrocarbons by Eu^{3+} ions in acetonitrile using steady state and laser dynamic spectroscopy [68,69]. A detailed analysis of the transient spectral changes in the visible region after the flash showed the presence of shorter-lived triplets and longer-lived radical cations of the aromatic hydrocarbons. Since these species were formed during the flash (ca. 20 ns), and it was shown earlier that the quenching of triplets by Eu^{3+} is a

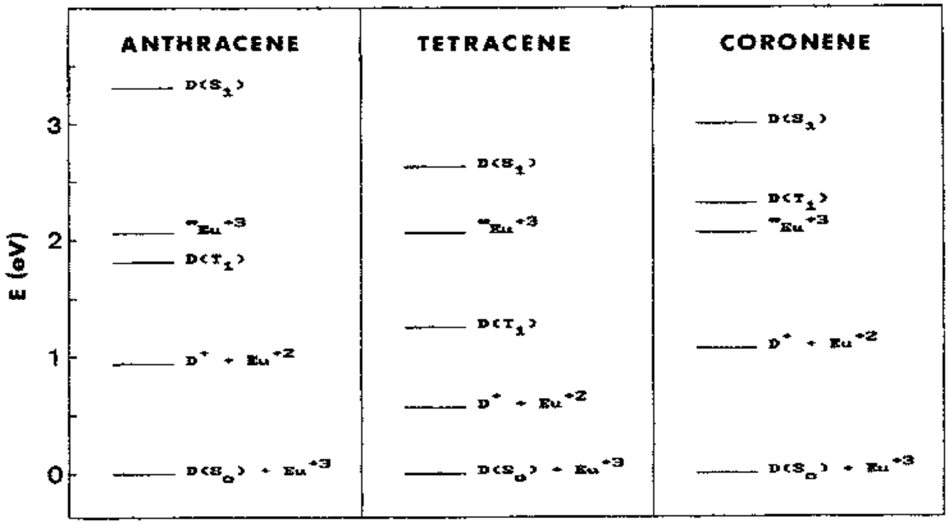

Fig. 9. Relative energetic situation of excited state and redox levels [68].

very slow process, it is reasonable to assume that the radical cations are derived from the singlet excited states.

The quenching of singlet states by Eu^{3+} ions takes place with rate constants close to those for diffusion-controlled processes ($k_q \approx 10^{10}$ M^{-1} s^{-1}). The formation of radical cations and triplet species as the main quenching products showed that the two main processes for quenching of S_1 states are electron transfer and Eu^{3+}-induced intersystem crossing, with the possible involvement of a charge transfer intermediate $[D \cdots Eu^{3+}]^*$:

$$
\begin{array}{llr}
 & \nearrow\ D^{\cdot +} + Eu^{2+} & (7) \\
D(S_1) + Eu^{3+} & \rightarrow\ D(T_1) + Eu^{3+} & (8) \\
 & \searrow\ D(S_0) + Eu^{3+} & (9)
\end{array}
$$

Although energy transfer from the S_1 state of aromatic hydrocarbons to Eu^{3+} ions is energetically allowed and spin allowed (Fig. 9), it does not make an important contribution to the overall quenching constant:

$$D(S_1) + Eu^{3+}(^7F) \rightarrow D(S_0) + Eu^{3+}(^5D) \qquad (10)$$

From the anthracene-sensitized emission of Eu^{3+} ions, an upper limiting value of 1×10^7 M^{-1} s^{-1} was obtained for the rate constant of the electronic energy transfer [69]. When naphthalene was used as the sensitizer, no Eu^{3+} emission was observed, suggesting that the dominant quenching mechanism in these systems is electron transfer.

Triplet excited states of aromatic hydrocarbons are quenched by Eu^{3+} ions with very low rate constants (ca. 10^6 M^{-1} s^{-1}), which is consistent with results previously reported [65,67]. The energy transfer process is endoergonic (for most hydrocarbons used) [69], while the electron transfer pathway is strongly exoergonic for excited triplets and singlets (Fig. 9):

$$D(T_1) + Eu^{3+} \rightarrow D^{\cdot +} + Eu^{2+} \qquad (11)$$

Because of the difficulty in deciding whether the triplet quenching is entirely due to electron transfer, the experimental quenching constants are upper limiting values for the rate of eqn. (11). The non-adiabatic character of the reaction between triplets and Eu^{3+}, and the higher polarizability of singlets compared with triplets were suggested by Sabbatini et al. to explain the observed differences in the rate constants for triplet and singlet quenching [69]. For more examples of quenching of excited states of organic molecules by lanthanide ions in solution, readers are recommended to look at the review tables in refs. 9 and 56 as well as in ref. 55(b).

The quenching of excited states of organic molecules by lanthanide chelates has been the subject of only a few studies. The energy transfer between excited states of aromatic molecules and lanthanide(III) chelates depends on the energy levels of the lanthanide complex. For complexes with ff^* levels of the central metal ion lying higher than the T_1 state of the ligand (Fig. 2, case (c)), and for La^{3+} and Lu^{3+} chelates (Fig. 2, case (b)) the sensitized ligand-localized phosphorescence can be observed. Using a donor with a triplet state higher than the corresponding T_1 state of the ligand, T–T energy transfer can occur, as shown by the observation of the ligand phosphorescence. This type of process is observed when the benzophenone triplet state is used as the donor and $Gd(hfac)_3$ as the acceptor in EPA glass at 77 K [70]. The decrease in benzophenone phosphorescence together with the appearance of the sensitized emission from the ligand of $Gd(hfac)_3$ can be taken as evidence for the intermolecular energy transfer. Moreover, the presence of heavy gadolinium ions does not enhance the T–T energy transfer [70].

For complexes with low-lying ff^* levels (Fig. 2, case (a)), however, after intermolecular energy transfer to the ligand-localized triplet followed by an efficient intramolecular energy transfer, the emission from ff^* levels can be observed. This type of sensitized luminescence has been detected for benzophenone and triphenylene as donors and $Eu(hfac)_3$ as the acceptor [40,70]. From studies of temperature, viscosity and concentration effects, the transfer was shown to be diffusion controlled. The participation of the ligand-localized T_1 state in the sensitization process is additionally supported by the following observations: (i) when the same experimental conditions as for the benzophenone–$Eu(hfac)_3$ system are used for a mixture of benzophenone–$EuCl_3$, no red emission from Eu^{3+} is detected, and (ii) for $Tb(acac)_3$, having the ligand T_1 state close to that of benzophenone but

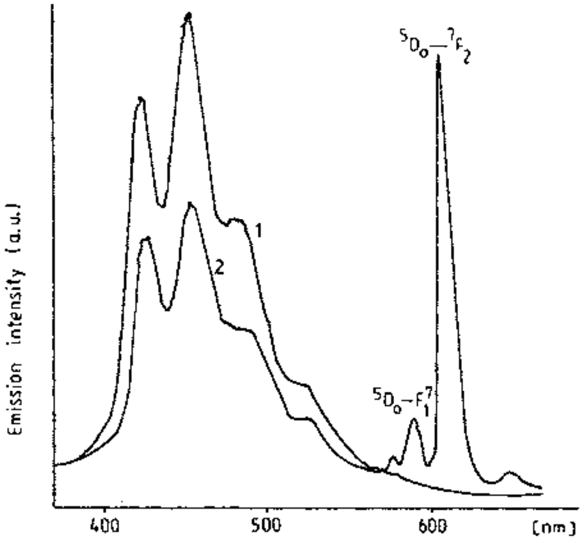

Fig. 10. Emission spectra of benzophenone in the absence (1) and in the presence (2) of Eu(acac)$_3$ in benzene solution at room temperature [72].

higher than the *ff** level, emission from Tb(acac)$_3$ is not observed, whereas Tb(hfac)$_3$, having a triplet level lower than that of benzophenone, is sensitized by the latter. The triplet–triplet energy transfer was also suggested by Ermolaev et al. [71] as a mechanism for the quenching of the triplet state of naphthalene and derivatives by europium(III) thenoyltrifluoroacetonate.

The first observation can be easily explained by the slow quenching of excited triplets by lanthanide ions ($k_q \approx 10^6$ M^{-1} s^{-1}). The second observation has been discussed recently in terms of new qualitative data [72]. The phosphorescence of benzophenone in benzene (and acetonitrile) is quenched by a series of Ln(acac)$_3$, where Ln = Sm, Eu, Gd, Tb and Dy, with similar rate constants of the order of $k_q \approx 6 \times 10^8$ M^{-1} s^{-1} for all complexes used. In the case of europium(III) and terbium(III) where sensitized metal ion emission is observed (see Fig. 10), the results of Stern–Volmer analysis for quenching and sensitization indicate that energy transfer is the main quenching process. The diffusion-controlled character of the energy transfer is indicated by comparing the rate constants for the quenching of benzophenone phosphorescence by Tb(acac)$_3$ and Tb(hfac)$_3$ with the donor–acceptor energy differences (Fig. 11). These data, together with similar values of Stern–Volmer quenching constants obtained for all Ln(acac)$_3$ used (including Gd(acac)$_3$), are comparable with rate constants obtained from sensitized emission measurements which indicate that energy transfer takes place from the triplet state of benzophenone to the ligand-localized triplet state of the lanthanide 1,3-diketonate chelates. It is important to note that a

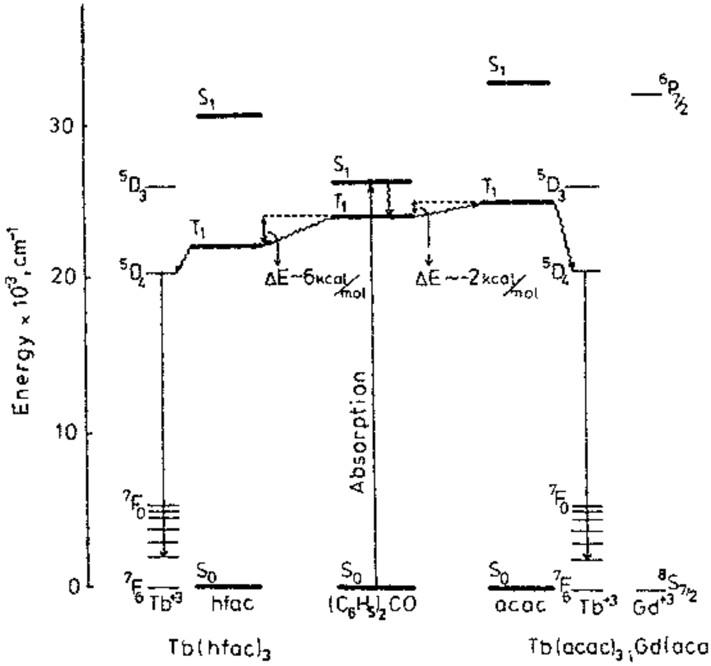

Fig. 11. Energy level diagram for the lowest excited states of benzophenone, $Tb(acac)_3$, $Gd(acac)_3$ and $Tb(hfac)_3$ [72].

ground state complex between benzophenone and $Ln(acac)_3$ is not formed and that a static quenching mechanism can therefore be neglected in this case.

This situation is quite different when compared with the quenching of benzophenone triplets by transition metal acetylacetonates where rate constants are several times higher, and for certain metal ions, suggest that both energy and electron transfer mechanisms may be involved [73,74].

Whereas triplet state energy transfer has been studied extensively, much less attention has been given to the quenching of singlet states of aromatic molecules by lanthanide(III) complexes. Bhaumik and El-Sayed suggested that S–S energy transfer could be neglected in the quenching of triphenylene by $Eu(hfac)_3$ [70]. Recently it was reported that benzene fluorescence can be quenched by $Eu(acac)_3$ with a rate constant of 4×10^{10} M^{-1} s^{-1} [74]. The quantitative agreement between the Stern–Volmer constants for quenching and sensitization (europium emission) provides direct proof of the involvement of singlet energy transfer. The k_q value is very close to that obtained for the quenching of benzene fluorescence by transition metal acetylacetonates [75].

Further systematic studies on the interaction between excited states of organic molecules and lanthanide β-diketonates are necessary. The possibility of using a variety of sensitizers (with different excited state energies and lifetime) and complexes (with different energetic levels), as well as the application of dynamic spectroscopic techniques can give more insight into the mechanism of quenching.

In contrast with the quenching of excited state organic compounds by lanthanide(III) ions or complexes, luminescence of Eu^{3+}, Tb^{3+} and Dy^{3+} nitrate salts can be quenched by organic compounds with triplet levels lying below, or close to, the emission levels of lanthanide(III) ions [76]. Generally, quenching occurs by a radiationless energy transfer via an exchange mechanism:

$$^{m}[\mathrm{Ln(III)}]^{*} + {}^{1}\mathrm{Q} \rightarrow {}^{n}[\mathrm{Ln(III)}] + {}^{3}\mathrm{Q} \qquad (12)$$

The quenching rate constants, however, are much lower than diffusion rate constants ($k_q \approx 10^3$–10^7 M^{-1} s^{-1}) and strongly dependent on the possible coordinate bond formation between lanthanide ions and quencher molecules, in particular with acetyl or =N– containing groups [76] (a static quenching effect). They are also strongly affected by temperature, solvent properties and possible penetration of quencher molecules into the first and second coordination spheres of lanthanide(III) ions. A comparative study of these effects on k_q values for energy transfer from terbium(III) ion to 9-anthrylmethyl ketone and anthracene was presented by Ermolaev and Tachin [77].

The dipole–dipole energy transfer may also be the mechanism of quenching as demonstrated by the investigation of the non-radiative energy transfer from excited lanthanide ions, europium(III) and terbium(III), to dyes in solid and liquid solutions [78] and to organic radical ions [79]:

$$[\mathrm{Ln(III)}]^{*} + {}^{1}\mathrm{Q} \rightarrow \mathrm{Ln(III)} + {}^{1}\mathrm{Q}^{*} \qquad (13)$$

The rate constants depend on solvent properties and the specific interaction between dyes and lanthanide ions. In the case of anionic and cationic dyes, k_q is strongly influenced by the electrostatic interaction forces between donor and acceptor. Therefore the addition of acetate ions, forming neutral complexes with terbium(III) ions, also affects the k_q values [80].

However, luminescence of $Eu(NO_3)_3$ is quenched by several aromatic amines possessing T_1 states higher than the lanthanide emission levels, e.g. the europium $^5D_0$ state. Triplet energies and reduction potentials for the aromatic amines, and rate constants for quenching of Eu^{3+} emission by these compounds are given in Table 2. Since the quenching rate constants ($k_q \approx (1 \times 10^4)$–$(6 \times 10^5)$ M^{-1} s^{-1}) decrease proportionally with the increase in the ionization potentials of the amines, an electron transfer mechanism has been suggested for the quenching [76]:

$$^{m}[\mathrm{Ln(III)}]^{*} + {}^{1}\mathrm{Q} \rightarrow {}^{n}[\mathrm{Ln(II)}] + {}^{2}\mathrm{Q}^{+} \qquad (14)$$

TABLE 2

Triplet energies (E_T), ionization potentials (IP) and rate constants for quenching (k_q) of $Eu(NO_3)_3$ luminescence by some aromatic amines (in acetone at room temperature) [a]

Amine [b]	E_T (cm^{-1}) [c]	IP (eV)	k_q (M^{-1} s^{-1})
PA	26800	7.69	5.0×10^4
NA	20100	7.30	4.4×10^5
DPA	25200	7.25	4.2×10^5
DMPA	26600	7.14	5.3×10^5
MCA	–	7.90	1.1×10^4

[a] From ref. 76. [b] PA = phenylamine; NA = α-naphthylamine; DPA = diphenylamine; DMPA = *N*,*N*-dimethylphenylamine; MCA = *m*-chloroaniline. [c] The energy of the europium(III) ion $^5D_0$ level is 17200 cm^{-1} and the lifetime τ_0 is 350 μs.

The quenching of excited states of lanthanide chelates by organic molecules has also been reported in the literature [43,76,78,81–85]. It was found that both ligand-localized triplets and *ff** levels of metal ions can be quenched by a typical "triplet quencher" such as naphthalene, anthracene, 1,3-pentadiene etc. The results were discussed in terms of non-radiative energy transfer via a Förster-type dipole–dipole mechanism or exchange mechanism. Further elaborations of the non-radiative mechanism of energy transfer with the application of direct excitation to the metal-localized state are needed to obtain a more quantitative picture of the observed processes. The europium(III) chelate luminescence can also be quenched by an electron transfer mechanism, as has been shown for SCN^- ions [86,87]. The luminescence of several lanthanide(III) complexes is only slightly dependent on the removal of oxygen (up to a factor of about 4) [88,89].

The intermolecular energy transfer between lanthanide ions and their complexes has been studied by several research groups [45,90–102]. Because of the luminescence properties of the Tb^{3+} ions and the position of the radiative *ff** level $^5D_4$ (Figs. 1 and 2), these ions are often used as donors. The rate constants for energy transfer between Tb^{3+} and lanthanide ions such as Eu^{3+}, Ho^{3+} and Nd^{3+} were determined (in DMSO at room temperature) to be 2.2×10^3 M^{-1} s^{-1}, 2.7×10^3 M^{-1} s^{-1} and 1×10^4 M^{-1} s^{-1} respectively [90,91]. Generally, the rate constants for luminescence quenching between lanthanide ions are very small (dynamic quenching) and dependent on the nature of the solvent and its ability to form a complex with the lanthanide(III) ion (vide infra).

Energy transfer from an excited level of Tb^{3+} to several lanthanide(III) ions in *n*-butanol solutions of $Tb(acac)_3 \cdot 3H_2O$ and $Ln(acac)_3 \cdot 3H_2O$ has been shown to occur with rate constants ranging from 0.5 to 4.9×10^5 M^{-1} s^{-1} [96]. It was found that the lifetime of the $^5D_4$ emission level of terbium(III) decreased as the Ln(acac)$_3$ concentration increased. Since the $^5D_4$ level lies below the ligand T_1 state (Fig. 2), energy transfer may occur from this level to the excited levels of Ln^{3+} ions, probably via an exchange mechanism. Intermolecular energy transfer between lanthanide(III) β-diketonates is strongly solvent dependent [98]. In non-polar solvents such as benzene, the lanthanide complexes exist almost entirely in the dimeric form and no decrease in the terbium $^5D_4$ emission lifetime (τ) can be observed due to the slow rate of exchange between dimers. The decrease in the terbium(III) emission yield and the appearance of the sensitized europium(III) luminescence can be explained by a $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer occurring in the mixed dimer Tb–Eu(acac)$_6 \cdot 6H_2O$. In polar but not very strongly coordinating solvents such as acetone, a monomer–dimer equilibrium exists and the decrease in τ may be related to the monomer–dimer reaction rate. In strongly coordinating solvents such as pyridine, only monomeric species exist and no significant energy transfer may occur.

The experimental results for intermolecular energy transfer among lanthanide ions and their complexes seem to indicate that in fluid solutions, quenching may occur by two mechanisms: (i) dynamic quenching, requiring a collision between donor and acceptor (both donor lifetime and emission quantum yield decrease as the acceptor concentration increases), and (ii) static quenching, where donor and acceptor are physically or even chemically bonded (only emission quantum yields of donor decrease). When the quenching takes place by the dynamic mechanism, the species must be monomeric and the quenching rate constants are quite low. However, if quenching occurs via the static mechanism the presence of dimeric and polymeric species is indicated and the rate constants are much higher [99–103].

Thus the intermolecular energy transfer process between lanthanide ions and complexes is very sensitive to the donor and acceptor environments and, as shown by Brittain and coworkers [100–103], can be used as a probe to investigate the bonding in mixed-metal complexes such as the terbium(III) donor and europium(III) acceptor complexes of aminopolycarboxylic acids [102].

The energy transfer between trivalent rare earths has also been investigated in the solid state (vitreous materials, molecular and non-molecular solids, crystals etc.) by several research groups [7,9,104–106]. A dipole–dipole interaction was shown to be the main mechanism operating especially in diluted systems. However, dipole–quadrupole interactions and electron transfer mechanisms are also involved in the quenching of lanthanide ion luminescence.

E. CHEMICAL QUENCHING AND PHOTOCHEMISTRY

Quenching of excited states can also occur by chemical processes in which lanthanide ions or complexes quench donor excited states by chemical reactions, or excited states of lanthanide ions or complexes can undergo chemical reactions (direct photochemistry). The number of systems for which a chemical quenching mechanism has definitely been established for coordination compounds is small and chemical reactions are mainly of the oxidation–reduction type (electron transfer reactions). A similar situation can be found in the case of quenching of organic donors by lanthanide complexes and ions. The participation of an electron transfer mechanism in the quenching of singlet and triplet states of aromatic hydrocarbons by europium(III) ions has been discussed in Section D. The quenching of excited singlet states of aromatic hydrocarbons (D) (eqn. (6)) leads to the photo-oxidation of the donor by europium(III) ions. The rate of the reversible reaction (eqn. (15))

$$D^{\cdot +} + Eu^{2+} \rightarrow D^{\cdot} + Eu^{3+} \tag{15}$$

is related to its reduction potentials, and storage of chemical energy for a limited time might be achieved by choosing an appropriate combination of hydrocarbons and transition metal salts [67].

The direct photolysis of *f*-block elements is poor. However, there have been a few studies concerning the photochemistry of lanthanide ions and complexes in solution. Most of this work has been concentrated on the study of photoredox processes in charge transfer and *f–d* bands in cerium(III,IV) [107–110] and europium(III,II) [107,111–118] in aqueous and methanol solutions.

The photochemistry of cerium(IV) and cerium(III) systems in aqueous solution and its application in organic synthesis have been reviewed in detail by Ford et al. [107]. In this section we will discuss as examples only the photochemistry of europium(II) and europium(III) ions in solution.

The irradiation of the charge transfer band (254 nm) of europium(III) ions in aqueous solution leads to the redox reaction

$$Eu^{3+}(H_2O)_n \xrightarrow{h\nu} Eu^{2+}(H_2O)_{n-1} + H^+ + {}^{\cdot}OH \tag{16}$$

This reaction is readily reversed through reoxidation of Eu^{2+} by the $^{\cdot}OH$ radical and the reversal can be prevented by adding $^{\cdot}OH$ scavengers (such as 2-propanol or formate):

$${}^{\cdot}OH + RH_2 \rightarrow H_2O + {}^{\cdot}RH \tag{17}$$

Since Eu^{2+} ions have an absorption coefficient several orders of magnitude higher than Eu^{3+} at 254 nm, Eu^{2+} becomes the light absorber and photo-oxidation of Eu^{2+} occurs:

$$Eu^{2+}(H_2O) \xrightarrow{h\nu} Eu^{3+} + OH^- + {}^{\cdot}H \tag{18}$$

RH_2 also scavenges $^{\cdot}H$ atoms:

$$^{\cdot}H + RH_2 \rightarrow H_2 + {}^{\cdot}RH \tag{19}$$

However, $^{\cdot}RH$ radicals from reactions (17) and (19) reduce Eu^{3+}:

$$Eu^{3+} + {}^{\cdot}RH \rightarrow Eu^{2+} + {}^{\cdot}R + H^+ \tag{20}$$

Thus the net reaction is as follows:

$$RH_2 \xrightarrow[Eu^{2+}]{h\nu} {}^{\cdot}R + H_2 \tag{21}$$

where Eu^{2+} is acting as a sensitizer.

The photo-oxidation of Eu^{2+} ions is also observed in aqueous acid solutions (in the presence of $^{\cdot}H$ atom scavenger):

$$Eu^{2+} + H_3O^+ \xrightarrow{h\nu} Eu^{3+} + {}^{\cdot}H + H_2O \tag{22}$$

$$^{\cdot}H + RH_2 \rightarrow {}^{\cdot}RH + H_2 \tag{23}$$

It is important to note that because of the absorption bands of Eu^{2+} ions up to 400 nm and the formation of "colourless" Eu^{3+} ions, this reaction is a convenient model system for studying the mechanism of photo-oxidation and solar energy conversion schemes.

In contrast, Eu^{3+} ions in methanol solutions show an absorption band around 280 nm which is assigned to a solvent-to-metal charge transfer band [118]. The irradiation of a methanol solution of $EuCl_3$ with light of $\lambda > 300$ nm results in the formation of hydrogen, ethylene glycol and formaldehyde. The reaction scheme is shown below:

$$Eu^{3+} + CH_3OH \xrightarrow[\lambda > 300\ nm]{h\nu} Eu^{2+} + CH_3O^{\cdot} + H^+ \tag{24}$$

$$Eu^{2+} + H^+ \xrightarrow{h\nu} Eu^{3+} + {}^{\cdot}H \tag{25}$$

$$CH_3O^{\cdot} + CH_3OH \rightarrow CH_3OH + {}^{\cdot}CH_2OH \tag{26}$$

$$^{\cdot}H + CH_3OH \rightarrow H_2 + {}^{\cdot}CH_2OH \tag{27}$$

$$2\,{}^{\cdot}CH_2OH \rightarrow HOCH_2CH_2OH \tag{28}$$

$$Eu^{3+} + {}^{\cdot}CH_2OH \rightarrow Eu^{2+} + HCHO + H^+ \tag{29}$$

The above europium(III)/europium(II) photoredox system has been applied to reactions with some organic substrates. For example, Ishido et al. [117,118] reported the photochemical hydroxymethylation of alicyclic and aliphatic alkenes induced by a europium(III)/europium(II) photoredox system in methanol:

$$R^1R^2C{=}CR^1R^2 \xrightarrow[\text{EuCl}_3,\ \text{CH}_3\text{OH}]{h\nu(\lambda > 300\ \text{nm})} R^1R^2CHCR^1R^2CH_2OH + (R^1R^2CHCR^1R^2{-})_2 \qquad (30)$$

The formation of the products was explained as resulting from the efficient trapping of hydrogen atoms and hydroxymethyl radicals (formed in reactions (25) and (27)) by the added alkene.

Donohue [119] reported the first example of lanthanide photochemistry initiated by *f–f* transitions. The irradiation with an argon ion laser of praseodymium(III), europium(III) and holmium(III) complexes of 2,2,6,6-tetramethyl-3,5-heptanedionate (thd) in coordinating solvents such as pyridine, ethanol and acetone in the presence of oxygen leads to the formation of 3,4,5-triketone. A chemical mechanism for the photoreactions was shown to be the photosubstitution of the thd ligand by the solvent.

The photochemistry of $Tb(thd)_3$ in a variety of alcohol solvents, upon irradiation in the near-UV region, i.e. mainly in the intraligand transitions, has been examined by Brittain [120]. The primary photochemical step was found to be the photodissociation of a 1,3-diketone ligand. The photodissociation quantum yields were in the range of 10^{-3} for all solvents used and they correlated with the formation constants of the complex–alcohol adducts.

More recently Wallo and Brittain [121] showed that the irradiation of neodymium(III) and holmium(III) EDTA complexes in the near-UV region (i.e. in ligand field and charge transfer bands) leads to the photodecomposition of these complexes. It was found that a photodecarboxylation of an EDTA ligand occurred with the formation of CO_2 gas. A redox process with the involvement of solvent was suggested as a chemical mechanism.

It follows from the data presented in this section that the mechanism of photodecomposition of lanthanide complexes is still unclear and that further systematic investigations are required in this area of lanthanide chemistry.

F. FINAL REMARKS

The growing interest in the study of energy transfer mechanisms in lanthanide ions and chelates can be understood for the most part in terms of the possible applications of these processes. The use of intermolecular energy transfer among lanthanide ions for the characterization of polymeric species has been recently reviewed by Brittain [103]. If energy transfer occurs by a Förster-type dipole–dipole mechanism, the distance between donor and acceptor can be calculated.

The application of intermolecular and intramolecular energy transfer processes in the spectrofluorometric determination of traces of lanthanides is a well-known method [9,11]. The chelating 1,3-diketonate ligand used in this case leads to the following effects: (i) an increase in the fluorescence quantum yield of the lanthanide(III) ion; (ii) an increase in the efficiency of energy transfer by formation of a complex with the lanthanide(III) ion (static quenching); (iii) the use of excitation to ligand-localized singlet states, which are characterized by strong and broad absorption bands in the UV region ($\epsilon \approx 10^4$–10^5 M^{-1} cm^{-1}) (*f*–*f* transitions in lanthanide(III) ions $\epsilon \approx 10$ M^{-1} cm^{-1}).

The use of appropriate experimental conditions (proper ligands, excitation wavelength, geometry of excitation etc.) can lower the limit of determination of several lanthanide(III) ions in solution by spectrofluorometric methods. For example, a detailed spectroscopic investigation of the terbium(III)–acetylacetone system in ethanol has shown the formation of a 1 : 1 Tb(III)–acacH complex in the ground state with a stability constant of $K = 1.0 \times 10^4$ M^{-1} [122]. The formation of this complex plays a fundamental role in the mechanistic interpretation of the terbium(III) emission sensitized by acacH and in the spectrofluorometric determination of this ion [123].

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