Radiationless transitions in trivalent lanthanide ions embedded in solids

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Abstract. Radiationless transitions in lanthanide ions embedded in glassy and crystalline hosts have been briefly reviewed. The correlations of multiphonon relaxation rates with energy gaps, vibrational frequencies, temperatures and electronic symmetries have been discussed. The essence of various theories, such as Nth order methods, non-adiabatic Hamiltonian method, dynamic coupling model has also been presented.

Keywords. Radiationless transitions; lanthanide spectroscopy.

1. Introduction

In spite of great deal of efforts made in understanding radiationless transitions in photophysics, photochemistry and photobiology, our knowledge of these complex phenomena is rather poor. In recent years considerable progress has been made in this area both from experimental and theoretical points of view and the field has been reviewed from-time to time (Reisfeld 1975; Watts 1975; Riseberg and Weber 1976; di Bartalo 1978; MaCarthy and Rhyne 1978; Englman 1979; Lin 1980; Chistian and Taub 1983). The present paper is an attempt to exemplify with a chosen group of molecules the broad generalisations obtained from a vast mass of experimental data, rather than to present an exhaustive survey of the current literature, and to rationalise the key features of the experimental aspects in terms of a theoretical framework. We shall confine ourselves to the nonradiative (NR) relaxation in lanthanide complexes concentrating only on the electronic relaxation in solids which do not involve energy transfer, cross-relaxation (Banerjee et al 1981) or similar processes. The reason behind choosing lanthanide ions in glassy and crystalline matrices for this discussion is given below.

(i) Hardly any generalisation emerges for a complicated process like radiationless transition unless a closely similar group of molecules are chosen. The lanthanide ions in various hosts offer themselves as one of the largest well-knit group of closely similar systems (Dieke 1968).

(ii) The large coupling of electronic and nuclear motion in organic molecules makes the NR rates very fast, except for the lowest singlet π, π^* and triplet n, π^* and π, π^* states. Although in a few cases, the luminescence from the lowest singlet n, π^* states (Lippert et al 1961; Lippert and Boss 1962; Chowdhury and Goodman 1963; Ghosh and Chowdhury 1981, 1982) and upper excited n, π^* (Ghosh and Chowdhury 1982) and

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π, π^* states (Birks 1973; Murata *et al* 1972; Wild *et al* 1976; Levine *et al* 1974; Hui *et al* 1975; Huber and Mahaney 1975; Griesser and Wild 1980; Choi *et al* 1978) have been reported and although picosecond techniques have recently been developed to follow fast NR processes, accurate data essentially exist only for the lowest state and that too is often complicated by the occurrence of side photochemical reactions or energy transfer processes. In the case of lanthanide complexes, on the other hand, one gets luminescence from a large number of upper states which, because of narrow bandwidth, can be resolved to the finest detail, and because of its slowness, can be measured with high precision. The luminescent excited states of lanthanide ions (Dieke 1968) in various hosts offer a variety of energy gaps, electronic symmetries, site symmetries and lattice frequencies for testing the predictions of the theories of nonradiative rates.

(iii) The Born-Oppenheimer (BO) approximation which form the basis of almost any theoretical approach to the photodynamial problem (Avouris *et al* 1977) demands that the coupling of electronic and nuclear motion must be weak. This weak coupling scheme has proven its greatest validity for lanthanide systems (f^N states); the electronic wavefunctions preserve their atomic character predominantly and nuclear motion acts only as a small perturbation. Although asymmetric vibrations do destroy the symmetry slightly, it is still meaningful to talk of electronic symmetry since the crystal field effect is small. The lanthanide ions thus stand between isolated atoms, where no NR transition occurs excepting trivial collisional processes, and stable molecules where a large number of vibrations and rotations not only cause NR transitions but also mess up things considerably.

(iv) The NR transition is an essential step in the population inversion process in lanthanide ions such as Nd^{+3} in glassy and other media, and thus the NR study of these materials are of great practical importance in connection with lasers and phosphors (McCarthy and Rhyne 1978; Brown 1981; Kaminskii 1981).

2. Multi-phonon relaxation and generalisations

Vibrations are responsible for a modulation of the local crystal field experienced by well-shielded $4f$ electrons and thus cause a transition from one electronic state to another. If the energy separation between the two electronic states corresponds to a single phonon frequency of a vibrational mode, the NR process is very fast. If, however, the energy gap is much larger than the upper limit of the phonon spectrum as is frequently the case, it is apparent that a number of phonons must be involved in the non-radiative decay. Although such multi-phonon NR processes have low probability, they are fast enough to compete with the slow ($\sim 10^{-3}$) radiative transition rates of $f^N - f^N$ transitions. We will first present the main observed generalisations regarding the role of energy gaps, vibrational frequencies and electronic symmetries in controlling the NR rates, and discuss later the various theories proposed.

2.1 *Energy gap law*

It has been demonstrated that for a crystal (Weber 1967a, b, 1968, 1973; Riseberg and Moos 1968; Flaherty and di Bartalo 1973; Nakazawa and Shinoyer 1972) or glassy media (Layne *et al* 1977; Reisfeld *et al* 1975) the most critical factor affecting the multiphonon relaxation rate is the energy gap to the next lower level. The multiphonon decay rates measured for several levels of different Ln^{3+} ions exhibit approximate
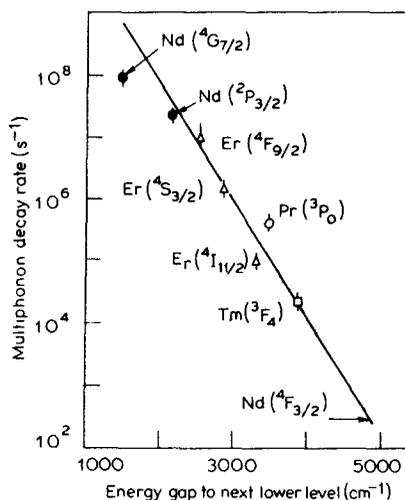
Figure 1. Multiphonon decay rates as a function of energy gap to next lower level for rare earths in silicate glass (from Layne *et al* 1975).

exponential dependence on the energy gap ΔE as $W_{NR} = W_{NR}(0)\exp(-\alpha\Delta E)$, where $W_{NR}(0)$ is the pre-exponential factor and α is a phenomenological constant (whose interpretation we shall find in the next section). Figure 1 illustrates this point (Layne *et al* 1975). The spread of pre-exponential factor with different states, ions and hosts is unexpectedly small. In the case of several glassy hosts different parameters of the exponential energy gap law determined for each glass are valid for a number of transitions and ions. The generality of this exponential gap law is, in fact, so wide that even 'large' isolated organic molecules (Avouris *et al* 1977; Lin 1980) and deep centres in semiconductors conform to the behaviour of ions in crystals, glasses and other condensed media.

2.2 *Effect of vibrational frequencies and temperature*

In organic molecules (Avouris *et al* 1977; Lin 1980) it has been shown through isotopic substitution and dependence of nonradiative rates on temperature that high frequency C–H vibrations play a major role in NR transitions. In the case of lanthanides two types of vibrations offer themselves as candidates *e.g.* metal-ligand vibrations and lattice vibrations. Although the M–L vibrations are strongly coupled with the metal ion electronic states, their frequencies are low, compared to some vibrations within the ligand or lattice, and therefore, they play a relatively minor role. The role of more energetic vibrations of the glassy medium may be illustrated (Reisfeld 1975) with the strong correlation of lifetimes with X–O vibrational frequencies of the lattice (X = B, P, Ge, Te) as shown in table 1. The existence of one dominant high-frequency phonon mode such as lattice cut-off frequency has been assumed by a number of workers (Riseberg and Moos 1967a, b; Fong *et al* 1972). In crystalline hosts the characteristic frequency may at times be substantially less than the maximal one. Thus, for several trivalent rare earth ions in YAG it is nearly $700\,\text{cm}^{-1}$ compared to the top lattice frequency of almost $860\,\text{cm}^{-1}$. Apparently, phonon modes with frequencies lower than the cut-off frequency are also capable of participating in the process (Reed and Moos

Table 1. Phonon energies of various oxide glasses and multiphonon relaxation rate (W) from $^1D_2 \rightarrow {}^1G_4$ of Tm^{3+} at $80°K$*.

Glass	Bond	Phonon energy (cm^{-1})	W $(\times 10^4)$
Borate	B–O	1340–1480	3·6
Phosphate	P–O	1200–1350	1·9
Germanate	Ge–O	975–800	1·5
Tellurite	Te–O	750–600	3·9 (!)

* From Reisfeld (1975).

1973). Due to the differences in local environments, it is impossible to assign single frequency in glasses and the effective transition rates in glasses are the mean values of various sites. The NR rates, in general, are much faster in glasses than in crystalline hosts. The study of multiphonon decay rates in glasses has led to few practical results; for instance, the realisation that the high-frequency vibration of the glass control the NR rate has led to the design of efficient laser amplifiers (Brown 1981; Kaminskii 1981).

From the study of luminescence characteristics of a large number of hydrated crystals (Heber and Hellwege 1967), it has been established that water of crystallisation enhances the nonradiative transitition rate. The replacement of water molecules by D_2O results in the decrease of radiationless decay rate by a factor of 3–7, exemplifying the role of high frequency O–H vibrations. A similar isotope effect has also been demonstrated in transition metal complexes (Sriram et al 1981; Sriram and Hoffman 1982). In this respect the photophysics of RE chelate systems resembles largely that exhibited in hydrocarbon solvents.

The nonradiative decay rates vary with temperature as expected for phonon-induced processes (Weber 1973; Fong and Wassam 1973; Sundberg et al 1974; Lauer and Fong 1976; Riseberg and Moos 1967; Reisfeld et al 1975). It has been shown by a number of workers that the temperature dependence of NR rates can be fitted into an equation $W = W_0 (n + 1)^N$ where n, the occupation number of phonons is given by Bose-Einstein law (*i.e.* $n = (\exp\frac{\hbar\omega}{KT} - 1)^{-1}$) and N is an integer which can be interpreted theoretically as the order of the process (see later). One such fit for Tm^{3+} in silicate glass is shown in figure 2 where the order of the process and frequency of phonon responsible for the decay matches well with expected values. Occasionally several frequencies are required to fit the temperature variation in glasses. The temperature dependence of homogeneous linewidths of some transitions in Eu^{+3} (Selzer et al 1976) and Pr^{+3} (Hegarty et al 1979) in different amorphous solids is shown to be quadratic. These anomalous low temperature behaviour in glassy hosts (Selzer et al 1976; Hegarty and Yen 1979; Morgan et al 1981) is suggestive of a new ion-lattice interaction peculiar to amorphous material.

If there is a metastable fluorescent state just below a state with higher radiative transition rate, frequently the activation energy laws come into the picture at high elevated temperatures (Englman 1979). The temperature dependence of the multiphonon transition has also played an important part in investigating the origin of rare earth fluorescence quenching in connection with the role of $4f^5 5d$ states (Lauer and
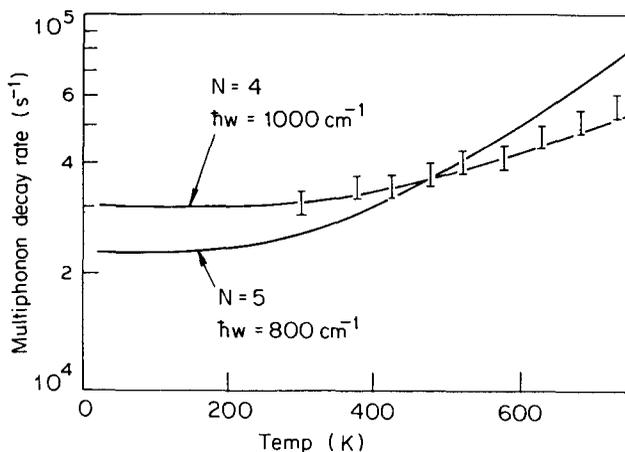
Figure 2. Temperature dependence of $^3F_4$–$^3H_5$ multiphonon emission rate for Tm^{+3} in silicate glass (from Layne *et al* 1975).

Fong 1976; Gaume-Mahn *et al* 1978) and charge-transfer states (Blasse *et al* 1970, 1981; Struck and Fonger 1975, 1976) as intermediary in the nonradiative relaxation processes.

2.3 The selection rules and electronic factor

Exceptions to the exponential energy gap law occur (Weber 1967a, b, 1968, 1973; Fong and Wassam 1973) when the selection rule severely restricts the number of terms in the ion-phonon interaction active in inducing transition. Since the transitions of interest are between the electronic states of a given f^N configuration, they involve no change in parity between the initial and final states. Hence, only the even terms in the interaction potential will be important. For an electronic operator of rank r, the triangle rule governing the transition between the J-states is given by $| J - J' | \leqslant r \leqslant | J + J' |$ with $r \leqslant 6$. J-mixing can act to relax this rule. Thus the transition $^5D_0 \rightarrow {}^5D_1$, $^7F_0 \rightarrow {}^7F_1$ (Eu^{+3}, Tb^{+3}), $^3P_0 \rightarrow {}^3P_1$ (Pr^{+3}, Tm^{+3}) are formally forbidden, but may occur by J-mixing or by other mechanisms. Of these $^5D_1 \rightarrow {}^5D_0$ transition in Eu^{+3} is readily amenable to study and the reduced rates have been observed in a number of cases (Weber 1968; Bhowmick and Nugent 1965). The ion-lattice interaction (and hence the nonradiative rate) is also subject to spin selection rule $\Delta S = 0$. The large spin-orbit interaction in lanthanides (Judd and Pooler 1982), however, reduces the importance of this rule compared to the case of organic molecules.

Selective pulsed excitation of crystal field components of $^5D_1$, $^5D_2$ and $^5D_3$ in Eu^{+3} in Eu^{+3}-oxydiacetate has revealed interesting by-passing of levels. It has been demonstrated by Ray *et al* (1981) that $^5D_2$ can decay nonradiatively to $^5D_0$ by two different channels—one directly and another indirectly *via* $^5D_1$. Evidently the CF components of $^5D_2$ behave differently. The differential behaviour of the different crystal field components of $^5D_2$ (A_1, $2E$ in D_3 point group symmetry) has been explained in terms of a new 'soft' selection rule. A number of workers (Richter *et al* 1982; Andrews *et al* 1980; Gardner and Kasha 1969) have shown that in vibrationally deficient systems (*i.e.* where symmetry species for normal vibrational modes of the molecule fail to span all the irreducible representations of the corresponding point group) the electronic factor may become important and forbid a particular NR transition.

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3. Theoretical aspects

Owing to the quasicontinuum nature of the vibronic levels in condensed phase, Fermi Golden rule may be used with confidence for finding the probability of the transition from an initial state ψ_i to the final state ψ_f:

$$W_{nr} = \frac{2\pi}{\hbar} |\langle \psi_i | H' | \psi_f \rangle|^2 \times \text{density of states.}$$

The various theories make different approximations regarding the wavefunctions ψ_i and ψ_f and the perturbation H'. It is convenient to classify the methods adopted into three broad categories: (a) Nth order methods (Kiel 1964; Hagston and Lowther 1973); (b) nonadiabatic hamiltonian methods (Zewail 1978; Lin 1980) and (c) other methods (Fong *et al* 1972; Perlin 1979; Ray *et al* 1981). The Nth order methods use either the Nth order perturbation theory for the first order crystal field term or the first order perturbation theory for the Nth order crystal field term. The second group of methods utilises the nonadiabatic part of the full hamiltonian as the perturbation inducing first order multiphonon NR transition; though developed for crystals, this method is capable of incorporating the basic features of molecular relaxation processes. The theories of category (c) will be discussed later. To give an overview of the main theoretical results we shall briefly outline these methods.

3.1 *Nth order methods*

3.1a. *Nth order time-dependent perturbation method.* This approach has been investigated by Kiel (1964) and applied to the case of Cr^{+3} and Pr^{+3}, following an approach originated by Orbach for spin-lattice relaxation (Orbach 1964). The hamiltonian for the crystal field is expanded in a Taylor series

$$H_{CF} = H_o + \sum_i \left(\frac{\partial V}{\partial Q_i} \right) Q_i + \tfrac{1}{2} \sum_{i,j} \left(\frac{\partial}{\partial Q_i} \frac{\partial V}{\partial Q_j} \right) Q_i Q_j + \ldots ,$$

where H_0 is the static crystal field potential and Q_i is the ith normal coordinate. The wavefunctions $|\psi_i \rangle$ and $|\psi_f \rangle$ in the transition matrix element are taken as crude BO states and expressed as a product of the electronic wavefunction $|\phi_i \rangle$ and the product of the individual harmonic oscillator wavefunctions $|n_i \rangle$ characterised by phonon occupation number n_i. The phonon wavefunctions are supposed to be the same in both the electronic states. Thus, we have, in general, $|\psi_k \rangle = |\phi_k \rangle \Pi_i |n_i \rangle$. If the energy gap is equal to N phonons *i.e.* $\Delta E = N\hbar\omega$, then the phonon emission rate W_N in the Nth order process is approximately given by the Nth order perturbation theory as

$$W_N = \frac{2\pi}{\hbar} \left| \left(\frac{\hbar}{2M\omega} \right)^{N/2} \sum_{i,j \ldots N = 1,2,\ldots m} (n_i + 1)^{N/2} \times \right.$$

$$\left. \times \frac{\langle \phi_f | \frac{\partial V}{\partial Q_i} | \phi_{i,f} \rangle \langle \phi_{i,f} | \frac{\partial V}{\partial Q_j} | \phi_{i,f} \rangle \ldots \langle \phi_{i,f} | \frac{\partial v}{\partial Q_N} | \phi_i \rangle}{[E_i - E_{i,f} - \hbar\omega][E_i - E_{i,f} - 2\hbar\omega] \ldots [E_i - E_{i,f} - (N-1)\hbar\omega]} \right|^2 ,$$

where M is the reduced mass, $|\phi_{i,f} \rangle$'s stand for intermediate states. If the simplifying assumptions are made that each matrix element in the last expression may be replaced

by an average and that m phonon modes of the same frequency dominate, we obtain

$$W_N = \frac{2\pi}{\hbar}\left(\frac{\hbar}{2M\omega}\right)^N (n+1)^N \, 2^{2(N-1)} \, m^{2N} \frac{|\langle\phi_i|\frac{\partial v}{\partial Q_i}|\phi_f\rangle|^{2N}}{|\hbar\omega|^{2(N-1)}}.$$

Here m denotes the number of phonon modes. The expression for W_N yields the following: (i) The temperature dependence is given by the factor $(n+1)^N$ as observed before. (ii) The most energetic phonons will dominate in the rate process since the order $N = \Delta E/\hbar\omega$ will be lowest for those phonons. (iii) For the same glass network (*i.e.* same $\hbar\omega$ and m), the ratio W_N/W_{N-1} is given by

$$W_N/W_{N-1} = 4\left(\frac{\hbar}{2M\omega}\right)(n+1)m^2\frac{|\langle\phi_i|\frac{\partial v}{\partial Q_i}|\phi_f\rangle|^2}{(\hbar\omega_i)^2},$$

which for a weak perturbation is nearly equal to a constant $Y\,(\ll 1)$ *i.e.*

$$W_N/W_{N-1} = Y.$$

This is the central result of the Nth order perturbation method and its utility in the derivation of the energy gap law will be discussed later.

3.1b. *Nth order crystal field method.* Instead of considering Nth order perturbation method in deriving the ratio $W(N)/W(N-1)$, Hagston and Lowther (1973) considered only the Nth order crystal field term (for the first order perturbation) after showing that it was, in fact, the largest term. Taking for intermediate states those exhibiting stark splitting of the initial free ion level and assuming only one phonon-frequency and considering the ratio of the first order perturbation for the Nth order crystal field term to the Nth order perturbation for the first order crystal field term, they arrive at a relation after a number of simplifying assumptions, as follows

$$W(N) = \frac{2\pi}{\hbar}|\langle\phi_i|\frac{\partial v}{\partial Q_i}|\phi_f\rangle|^2 Y^N,$$

with $Y = W(N)/W(N-1)$.

 Y is then assumed to be almost independent of N as in the previous method. We shall now try to see the implications of the simple result obtained by these two methods.
  (i) Exponential energy gap and vibrational frequency law: In these two methods the key point to obtain a closed form result is to consider the iterative properties of

$$W(N) = W(N-1)Y,$$

which means that we are considering a series in which the succeeding term is smaller by the characteristic constant number Y. Calculating $W(N)$ from $W(0)$ we obtain,

$$W(N) = W(0)Y^N = W(0)e^{N\log Y}.$$

If we now replace N by the ratio of the energy gap ΔE and an effective phonon energy $\hbar\omega$ we get

$$W(N) = W(0)\exp(-\alpha\Delta E)$$

with

$$\alpha = (1/\hbar\omega)\log(1/Y).$$

where α and Y are the characteristics of the matrix and the nature of interaction respectively. This basically is the central feature of the theoretical development by Riseberg and Moos (1968) and others (Layne *et al* 1977; di Bartalo 1978; Soules and Duke 1971) for crystals and glasses.

(ii) *Temperature dependence*: In the two methods temperature dependence occurs through the products of normal mode matrix elements for one-phonon process, as

$$\underbrace{|\langle n_1 + 1 | Q_i | n_i \rangle|^2 \dots |\langle n_j + 1 | Q_j | n_j \rangle|^2}_{N \text{ factors}}$$

where n_i is the average occupation number which is equal to $(\exp \dfrac{\hbar\omega}{kT} - 1)^{-1}$. The last product is proportional to

$$(n_i + 1) \dots (n_j + 1),$$

leading to a temperature-dependent factor $(n + 1)^N$. The application of the result in identifying the phonon responsible for the NR decay and the order of the process has been discussed earlier.

3.2 *The nonadiabatic hamiltonian method*

In the Nth order method, the wavefunctions for the phonons are described by pure harmonic states which are the same for both the initial and the final electronic states of the ion. With such a model the jumps in phonon quantum number can be made one at a time requiring Nth term in the hamiltonian. But if the vibrational states are allowed to differ in both the electronic states either in geometry or in frequency, changes by more than one quantum number can be obtained in the first order (Frenkel 1931; Avouris *et al* 1977). This is the basic idea for generation of N-phonons in the nonadiabatic hamiltonian approach. The approximations used in this method are common to the treatment of molecular relaxation. In the adiabatic approximation, the total wavefunction of the system is given by the product of electronic wavefunction ϕ_j and vibrational wavefunctions θ_{jv}

$$\psi_{jv}(q, Q) = \phi_j(q, Q)\theta_{jv}(Q).$$

The nonadiabatic part of the full hamiltonian for the crystal, acting as the perturbation including nonradiative transitions is derived from the lattice kinetic energy term as follows;

$$H_{NA}\psi_{jv} = -\hbar^2 \sum_s \frac{\partial \phi_s}{\partial Q_s} \frac{\partial \theta_{jv}}{\partial Q_s}.$$

The moment for transition $iv' \to fv''$ is given by

$$\langle fv'' | H_{NA}^s | iv' \rangle = -\hbar^2 \langle \phi_f \Big| \frac{\partial}{\partial Q_s} \Big| \phi_i \rangle \langle \theta_{fv''} \Big| \frac{\partial}{\partial Q_s} \Big| \theta_{iv'} \rangle,$$

where the vibrational wavefunctions are approximated by the product of harmonic oscillator wavefunctions

$$\theta_{fv''} = \prod_s \chi_{fv_s''}(Q_s''), \quad \theta_{iv'} = \prod_s \chi_{iv_s'}(Q_s').$$

The nonradiative transition rate is then given by

$$W_{nr} = \frac{2\pi}{\hbar} \sum_s |\beta_s|^2 |\langle \chi_{fv''_s}| \frac{\partial}{\partial Q_s} |\chi_{iv'_s}\rangle|^2 \times \prod_{j \neq s} |\langle \chi_{fv''_j}|\chi_{iv'_j}\rangle|^2 \delta(E_{fv''} - E_{iv'})$$

with

$$\beta_s = -\hbar^2 \langle \phi_f| \frac{\partial}{\partial Q_s} |\phi_i\rangle..$$

In this method we encounter the promoting modes s and the accepting modes j characterised by the nonvanishing integrals

$$\langle fv''_s| \frac{\partial}{\partial Q_s} |iv'_s\rangle \text{ and } \langle \chi_{fv''_j}|\chi_{iv'_j}\rangle.$$

The explicit expressions for the nonradiative rates can be obtained by using the method of Huang and Rhys (1950) or by the Fourier integral representation method of δ-functions (Gelbert *et al* 1970), or the non-integral quantum number approach (Avouris *et al* 1977), leading to the same energy gap law. The theory gives complicated temperature dependence, which can be reduced after suitable approximations to the result we have already obtained by Nth order methods.

3.3 *Other current approaches*

We have discussed the methods emphasising weak coupling limit. For other treatments, a series of papers by Fong and his co-workers (Fong and Wassam 1973; Sundberg *et al* 1974; Lauer and Fong 1976; Fong *et al* 1972) may be referred to. It is basically a quantum-statistical derivation of the weak-coupling-limit rate constant (Fong *et al* 1972) for multiphonon decay within $4f^N$-configuration. The expression was applied to give a numerical fit to experimental data (Fong *et al* 1972; Fong and Wassam 1973). A generalisation of the theory was made to treat f–d relaxation (Sundberg *et al* 1974) and non-resonant energy transfer (Lauer and Fong 1976).

Observation of anomalous low temperature dependence (Selzer *et al* 1976; Hegarty and Yen 1979; Morgan *et al* 1981) of homogeneous linewidths has prompted Lyo and Orbach (1980) to propose a new model which takes into account interaction between the two two-level systems. Multiphonon emission theory of Perlin (1979) is also worth mentioning.

The above models for multiphonon relaxation in rare earth crystals give satisfactory description of a number of experimental observations such as energy gap law, temperature dependence of nonradiative rate, importance of high frequency vibrations etc. However, the main domain of application of the model is where the ion is embedded in a medium whose function is to provide a 'structureless' heat bath. The validity of the rate expression depends on the extent the individual phonon modes and the participating electronic levels are àveraged out for a high-order process. However, the consideration of the rare earth crystal with polyatomic ligand suggests that the ligand environment around the metal ion certainly possesses some 'structure' which cannot be neglected. We have already pointed out that Eu^{+3} emission is susceptible to the nature of environment (Blasse *et al* 1981, Richter-Lustig *et al* 1982). The detailed feature of the environment, such as, site symmetry, nature of local and internal ligand modes, the electronic properties (*e.g.* dipole moment, polarisability) of the ligand etc are not amenable to theoretical description in terms of a simple crystal field model. In a number

of cases the radiationless transition between $| J = 1 \rangle$ and $| J = 0 \rangle$ states becomes suppressed in certain symmetries (Fong *et al* 1972; Weber 1967a, b, c, 1968, 1973) and sometimes it is difficult to correlate the non-radiative rates with energy gap data (Fong *et al* 1972). An understanding of the role of symmetries of the electronic states (Ray *et al* 1981) and the role of states of opposite parity, such as $4f^{n-1} 5d$ state (Lauer and Fong 1976; Gaumé-Mahn *et al* 1978), also pose problems for the models discussed so far. Keeping in mind the remarkable sensitivity to ligand environment in hypersensitive radiative transitions, it is quite likely that the role of environment should find parallel importance in the nonradiative processes as well. It is in this perspective that a theory of ligand-induced nonradiative transition (Ray and Chowdhury 1981; Strek 1981) has been developed within the framework of 'dynamic coupling' model used earlier in the field of lanthanide spectroscopy to account for hypersensitive transition (Mason *et al* 1975) and optical activity (Sen and Chowdhury 1981; Sen *et al* 1981; Richardson and Faulkner 1982). In this theory the model has been extended from the domain of radiative transition to the realm of nonradiative relaxation and brought into relation with a number of experimental observations. The basic idea is that since in the free lanthanide ion there is no nonradiative decay, the ligand-induced $f^N \rightarrow f^N$ nonradiative process derives transition probability from the polarisability and internal transitions of the ligand. The zero-order wavefunctions are written as the product of wavefunctions of subsystems comprising lanthanide ion with its nearest neighbours and the rest of the ligand. The wavefunctions of the complex are corrected upto first order by taking into account the electrostatic interaction (beyond crystal field) between the two subsystems. The dynamic part of the hamiltonian (nonadiabatic part) brings about the nonradiative transitions from one product state to another. From its consequences the theory may be considered as a synthesis of Nth order methods and nonadiabatic hamiltonian methods, since it incorporates the key features of NR relaxation in solids and in organic molecules. Apart from deriving the usual exponential energy gap and vibration frequency law, the theory clearly brings out the importance of states with opposite parity, electronic symmetries of initial and final states of the rare earth ion, symmetry of the crystal field, internal promoting and accepting modes of the ligand, and finally the dipole moment and the polarisability of the ligand. New nonradiative selection rules including parallalism between radiative and nonradiative rates have been predicted (Ray and Chowdhury 1981; Strek 1981).

4. Concluding remarks

We have outlined the main experimental results in NR processes within the lanthanide Ln^{3+} ions embedded in solids and the various theoretical approaches initiated to explain the results. Although a number of methods of calculation of nonradiative rates between the f^N excited states are in use, the existing data in literature are not extensive enough to provide guidelines to theoreticians working in this field. We hope that with the advent of pulsed mode-locked lasers and time-resolved detection techniques, new experimental data in the short time scale will be available in the near future; the various theoretical predictions and nonradiative selection rules can then be properly examined.

Acknowledgement

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