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# NON-RADIATIVE DE-EXCITATION OF DEEP CENTRES

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**Abstract**—We develop a quantitative theory of the ratio $R$ of radiative to non-radiative de-excitation based on the Dexter–Klick–Russell criterion for the occurrence of luminescence. The model invokes three essential elements: a promoting mode, an accepting mode, and a set of lattice modes which ultimately absorb the vibrational energy. The ratio $R$ is determined by the relative population of the relaxed excited and ground states. We show that $R \sim n_x^{(a)}/n_g^{(a)}$, where $n_x^{(a)}$ and $n_g^{(a)}$ are the numbers of vibrational quanta in the accepting mode associated with the excited state and the ground state, respectively, at the crossing of their adiabatic potential energy curves. The result is consistent with experiment.

## 1. INTRODUCTION

In the model of Dexter *et al.*[1], the probability for non-radiative de-excitation of a deep centre depends critically on whether the intersection of adiabatic potential energy curves lies above or below the excited-state energy reached in a Frank-Condon optical transition from the ground state. This model is illustrated in Fig. 1; it is asserted that if $X$ lies below $B$, the system cannot reach the relaxed excited state $C$, but rather decays non-radiatively to $A$ instead. The model appears to work well for $F$ centres in ionic crystals [2]. Actually, one would expect the quenching of fluorescence by this mechanism to be less than absolute, and the object of the present investigation is to provide a quantitative determination of the ratio $R$ of radiative to non-radiative de-excitations for cases where $X$ lies below $B$.

For clarity of presentation, we will assume that both ground and excited electronic states are non-degenerate, but are of opposite parity in order to ensure a clear distinction between promoting and accepting modes. Wave functions and symmetry-adapted displacements are illustrated schematically in Fig. 2 for a hypothetical center with tetragonal symmetry. Thus the analysis presented here does not apply to the $F$ center in alkali halides, for which the excited state has symmetry-induced degeneracy, and there is a degenerate set of promoting modes. However, the extension of the theory to that case presents no difficulty in principle.

Three types of modes form essential elements in the present analysis of non-radiative de-excitation: the accepting mode of Figs. 1 and 2(c), which can take up any excess electronic energy in the transition; the promoting mode of Fig. 2(d), which provides the symmetry-mixing perturbation required to couple the electronic states; and sets of lattice modes of the same symmetries as the accepting and promoting modes, which ultimately absorb their vibrational excitation energy. The latter element distinguishes the present problem from that of the non-radiative de-excitation of a system in thermal equilibrium [3]. We are concerned with the sequence of events following the absorption of a photon, as the combined electronic and accepting-mode system "cool off" by emitting lattice photons until its vibronic energy passes through the energy of the cross-over (point $X$ of Fig. 1).

The nature of the coupling of accepting and promoting modes to lattice modes is discussed in Section 2 in connection with the optical absorption process. The cooling process for the accepting mode is considered in Section 3, and the effect of the promoting interaction in Section 4.

## 2. OPTICAL ABSORPTION PROCESS

The electronic states of our model defect are strongly coupled to the accepting and promoting modes, which in turn are weakly coupled to lattice modes. In favourable circumstances, there may be true local or gap modes associated with the defect which serve as accepting and promoting modes, and which are coupled to lattice modes by anharmonic interactions [4]. In the more usual circumstance, the electronic system is weakly coupled to very many normal modes, which are perturbed by the defect in such a way that the coupling is appreciable only in a relatively narrow frequency range [4]. This resonance can be represented by an "effective local mode" together with a set of "effective lattice modes", which are coupled to one another simply as a consequence of not being true normal modes [5]. However, the utility of such a description depends critically on how the initial state is prepared, as we shall demonstrate.

The Hamiltonian for our model defect in the approximation of linear coupling can be written in terms of the true normal modes in the form

$$\mathcal{H} = \mathcal{H}^{(a)} + \mathcal{H}^{(p)}, \tag{1a}$$

where

$$\mathcal{H}^{(a)} = (E_0 + E_M)[(1-\rho^{(a)})/2] + \sum_{i=1}^{N_a} \hbar\omega_i^{(a)}\left(a_i^{(a)+}a_i^{(a)} + \frac{1}{2}\right) + \sum_{i=1}^{N_a} \hbar\omega_i^{(a)}k_i^{(a)}(a_i^{(a)} + a_i^{(a)+})[(1-\rho^{(a)})/2], \tag{1b}$$

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$$\mathcal{H}^{(p)} = \sum_{i=1}^{N_p} \hbar\omega_i^{(p)} \left( a_i^{(p)+} a_i^{(p)} + \frac{1}{2} \right) + \sum_{i=1}^{N_p} \hbar\omega_i^{(p)} k_i^{(p)} (a_i^{(p)} + a_i^{(p)+}) \rho^{(p)}, \quad (1c)$$

where energies $E_0$ and $E_M$ are defined in Fig. 1, and where $\rho^{(a)}$ and $\rho^{(p)}$ are electronic operators defined by

$$\rho^{(a)} \equiv |g\rangle\langle g| - |x\rangle\langle x|, \quad (1d)$$

and

$$\rho^{(p)} \equiv |g\rangle\langle x| + |x\rangle\langle g|. \quad (1e)$$

Eigenkets $|g\rangle$ and $|x\rangle$ correspond respectively to electronic wave functions $\psi_g$ and $\psi_x$ of Fig. 2. Superscripts $(a)$ and $(p)$ distinguish accepting and promoting modes, respectively, and $N_a$ and $N_p$ are the numbers of modes of each type. The coupling constants $k_i^{(a)}$ simply reflect the relative displacement of accepting-mode potential-energy minima corresponding to the two electronic states. The coupling constants $k_i^{(p)}$ are derived from the non-adiabaticity operator [3], and are given by

$$k_i^{(p)} = \langle x|\partial\mathcal{H}/\partial Q_i^{(p)}|g\rangle/(2\hbar\omega_i^3), \quad (2)$$

where the $Q_i^{(p)}$ are normal coordinates for promoting modes.

In this section and the following section we will be concerned just with that part of the Hamiltonian, $\mathcal{H}^{(a)}$, which involves coupling to accepting modes. It is convenient to define an operator $\zeta_i$ by the relation

$$\zeta_i = a_i^{(a)} + k_i^{(a)}(1 - \rho^{(a)})/2. \quad (3)$$

Then $\mathcal{H}^{(a)}$ can be rewritten as

$$\mathcal{H}^{(a)} = E_0(1 - \rho^{(a)})/2 + \sum_{i=1}^{N_a} \hbar\omega_i^{(a)} \left( \zeta_i^{+} \zeta_i + \frac{1}{2} \right), \quad (4)$$

where we have used the relation

$$E_M = \sum_{i=1}^{N_a} k_i^{(a)2} \hbar\omega_i^{(a)} \quad (5)$$

The eigenkets of $\mathcal{H}^{(a)}$ are $|g\{n_g\}\rangle$ and $|x\{n_x\}\rangle$, where

$$\{n_g\} \equiv \{n_{g1}, n_{g2}, \ldots, n_{gNa}\}, \quad (6a)$$

$$\{n_x\} \equiv \{n_{x1}, n_{x2}, \ldots, n_{xNa}\}, \quad (6b)$$

(The superscript $(a)$ is suppressed in the remainder of this section and in the following section, since only accepting mode quantities are involved.) Note that, in general, scalar products $\langle n_{gi}|n_{xj}\rangle$ represent overlap integrals of displaced harmonic oscillator wave functions, so that orthonormality does not apply.

Consider a transition from the ground state $|g\{0_g\}\rangle$ to an excited state $|x\{n_x\}\rangle$ induced by absorption of a photon polarized parallel to the tetragonal axis of the defect. It follows from first-order time-dependent perturbation theory that illumination of sufficient intensity can be considered to induce a transition to a non-stationary

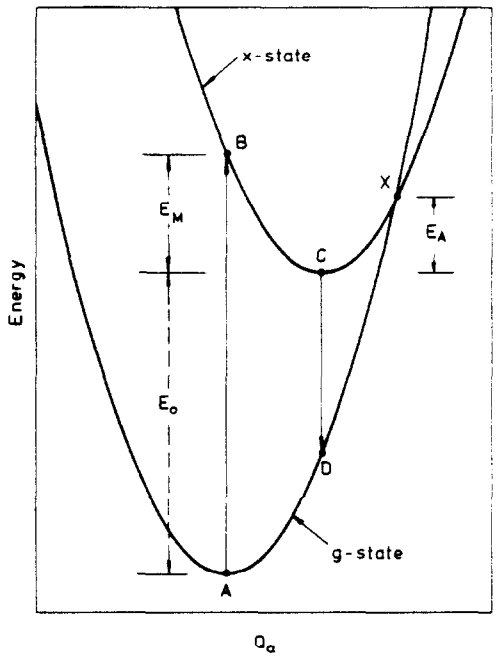


Fig. 1. Configuration co-ordinate diagram for the accepting mode, illustrating the Dexter–Klick–Russell model.

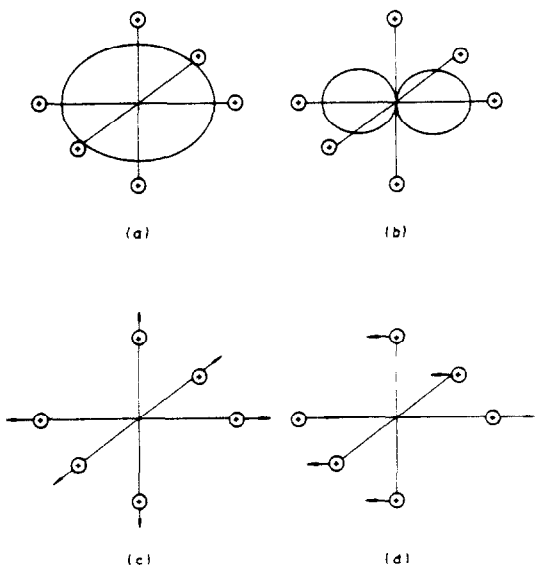


Fig. 2. A hypothetical center with tetragonal symmetry. (a) Ground state electronic wave function, $\psi_g$. (b) Excited state electron wave function, $\psi_x$. (c) Symmetry-adapted displacement of accepting mode, $Q_a$. (d) Symmetry-adapted displacement of promoting mode, $Q_p$.

state of the form

$$|\Psi(t)\rangle = \sum_{\{n_x\}} |x\{n_x\}\rangle\langle\{n_x\}|\{0_g\}\rangle e^{-i\mathcal{E}(\{n_x\})t/\hbar} \times \left\{ \sum_{0\neq\{n'_x\}\neq 0} |\langle\{n'_x\}|\{0_g\}\rangle|^2 \right\}^{-1/2} \quad (7)$$

This state provides a starting point for the processes to be discussed in subsequent sections, and serves as a basis for the introduction of an effective local mode.

Since, in a solid, the number of true normal modes is very large and the coupling to any one mode is very weak, the chance of exciting two or more vibrational quanta in any one mode is negligably small, and we may approximate $|\Psi(0)\rangle$ as follows:

$$|\Psi(0)\rangle \approx \left\{1+\sum_{n=1}^{\infty}\frac{1}{n!}\sum_{i_1}^{N_a}\cdots \times\sum_{i_n}^{N_a}\langle 1_{xi_1}|0_{gi\,1}\rangle\ldots\langle 1_{xi_n}|0_{gi_n}\rangle\zeta_{i_1}^{+}\ldots\zeta_{i_1}^{+}\right\}|x\{0_x\}\rangle \times\left\{\sum|\langle\{n_x'\}|\{0_g\}\rangle|^2\right\}^{-1/2} \tag{8}$$

where $\langle 1_{xi}|0_{gi}\rangle$ is a vibrational overlap integral for the $i$th accepting mode, with $n_{xi}=1$ and $n_{gi}=0$. An effective local mode may be introduced by the transformation

$$\eta \equiv \sum A_{1i}\zeta_i, \tag{9a}$$

where

$$A_{1i}=\langle 1_{xi}|0_{gi}\rangle\Big/\left\{\sum_j|\langle 1_{xj}|0_{gj}\rangle|^2\right\}^{1/2} \approx k_1\Big/\left\{\sum_j k_j^2\right\}^{1/2} \tag{9b}$$

We can write

$$\eta=\sum_i A_{1i}+k_{\text{eff}}(1-\rho)/2, \tag{10a}$$

where

$$k_{\text{eff}}^2\equiv\sum_i k_i^2 \tag{10b}$$

The transformation so defined is identical with that advocated by O'Brien [5] for Jahn–Teller systems. With this transformation, $|\Psi(0)\rangle$ may now be written in the form

$$|\Psi(0)\rangle=\sum_{n_x}|xn_x\rangle\exp(-k_{\text{eff}}^2)(k_{\text{eff}}^2)^{n_x}/n_x!, \tag{11}$$

where $n_x$ is the vibrational quantum number of the local effective mode.

We see that under the postulated conditions of illumination, all of the vibrational excitation in the excited state is associated with an effective local accepting mode. The ensuing redistribution of this excitation energy is considered in subsequent sections.

### 3. "COOLING" PROCESS

The results of the preceding section may be interpreted as follows: Suppose that the effective local mode is predominantly associated with displacements of the nearest-neighbour ions, as illustrated in Fig. 2(c). Then according to eqn (11), the transition takes place in such a fashion that the nearest-neighbour ions acquire initial velocities but are not initially displaced (Frank–Condon principle). Their subsequent oscillation at the local-mode frequency is described by the motion of a wave packet formed by coherent superposition of the local-mode eigenfunctions. However, the system is in a non-stationary state which develops in time in accordance with eqn (7). The wave packet spreads within a single period of oscillation, but the individual local-mode excitations may persist much longer if the resonance is sufficiently narrow. Ultimately, however, the initial phase relations of the true normal modes are lost. The vibrational excitation is no longer localized at the nearest-neighbour ions, which become relatively quiescent at their new equilibrium positions, but is shared among all the ions of the crystal. The purpose of the present section is to explore the way in which the local-mode vibrational excitation is transferred to the lattice.

We can complete the specification of effective modes by assigning values of coefficients $A_{ij}$, $i\neq 1$, which, together with the $A_{1j}$ of eqn (9), comprise an orthogonal matrix. The Hamiltonian $\mathcal{H}^{(a)}$ can then be written in the form [5]

$$\mathcal{H}^{(a)}=\mathcal{H}_0+\mathcal{H}_I, \tag{12a}$$

$$\mathcal{H}_0=E_0(1-\rho^{(a)})/2+\hbar\omega_{\text{eff}}\left(\eta^{+}\eta+\frac{1}{2}\right)+\sum_{i\neq 1}^{N_a}\hbar\psi_i'\left(\alpha_i^{+}\alpha_i+\frac{1}{2}\right), \tag{12b}$$

$$\mathcal{H}_I=\sum_{i\neq 1}c_i(\eta\alpha_i^{+}+\eta^{+}\alpha_i), \tag{12c}$$

where

$$\alpha_i=\sum_j A_{ij}a_j,\quad i\neq 1, \tag{12d}$$

and

$$\omega_{\text{eff}}=\sum_i K_i^2\omega_i/k_{\text{eff}}^2. \tag{12e}$$

The coupling $\mathcal{H}_I$ of the effective local mode to the effective lattice modes is a consequence of the fact that neither are true normal modes. The coupling coefficients $c_i$ are defined by

$$c_i=\sum_j\hbar\omega_j k_j A_{ij}/k_{\text{eff}}. \tag{13}$$

From the orthogonality of the matrix $A$, they can be shown to satisfy a sum rule [5],

$$\sum_{i\neq 1}c_i^{(c)2}=\hbar^2(\overline{\omega^2}-\bar{\omega}^2)\equiv\hbar^2(\Delta\omega)^2, \tag{14a}$$

where

$$\overline{\omega^2}\equiv\sum_i k_i^2\omega_i^2/k_{\text{eff}}^2, \tag{14b}$$

and $\bar{\omega}(\equiv\psi_{\text{eff}})$ is defined by eqn (12e). If the coupling is sufficiently weak, it can be treated by first-order time-dependent perturbation theory; in that case we obtain the remarkable result that the excitation of the effective lattice phonons, *one at a time*. A crude estimate of the transition rate can be derived from eqn (14a). We assume that the $c_i$ have a constant value $c$ in the frequency range $\omega_{\text{eff}}-\Delta\omega\leq\omega_{\text{eff}}+\Delta\omega$, and vanish otherwise. The transition rate at $T=0$ is then

$$W=\frac{2\pi}{\hbar}n_x c^2\rho(\hbar\omega_{\text{eff}})=\pi n_x\Delta\omega, \tag{15}$$

where $\rho(E)$ is the density of modes per unit energy range. However, the use of first order perturbation theory is justified only if the inequality $n_x\Delta\omega \ll \omega_{\text{eff}}$ is satisfied; otherwise, multiphonon transitions dominate.

In the case of a true local mode or gap mode, the coupling constants $c_i$ vanish and the cooling process is effected by anharmonic interactions. In that case, the interaction term $\mathcal{H}_I$ of eqn (13c) is replaced by

$$\mathcal{H}_I' = \sum_{i\neq 1}\sum_{j\neq 1} c_{ij}'\eta\alpha_i^+\alpha_j^+, \tag{16}$$

where the $c_{ij}'$ are determined by the degree of anharmonicity. This case was discussed briefly in an earlier account [10].

## 4. PROMOTING INTERACTION

Non-radiative de-excitation may be visualized qualitatively in terms of the theory of Landau and Zener[6]. They postulate a *static* perturbation which produces an avoided crossing at the point $X$ in Fig. 1. The probability that the system passes through the intersection *adiabatically*, resulting in a *non-radiative* transition, is

$$P = 1 - \exp(-2\pi\epsilon_{xg}^2/\hbar v|S_x - S_g|), \tag{17}$$

where $\epsilon_{xg}$ is the matrix element of the static perturbation, $S_x$ and $S_g$ are the slopes of the potential energy curves at the cross-over, and $v$ is the speed with which the system passes through the cross-over. We add to their picture the additional feature that the vibronic energy is progressively diminished by "cooling", as described in the preceding section, until it equals the potential energy at the cross-over. The cross-over then coincides with the classical turning point, with the result that $v = 0$ and $P = 1$ in eqn (17), and the system jumps back and forth rapidly between the two electronic states until it cools further.

An alternative description can be based on the work of Lewis and Hougen[7], who also consider a static perturbation, but who derive stationary vibronic states for fixed energies near the cross-over. The present treatment resembles theirs, except that the static perturbation is replaced by a dynamic interaction with promoting modes.

We now consider the mechanism by which promoting modes effect non-radiative transitions. The relevant part of the Hamiltonian, $\mathcal{H}^{(p)}$ of eqn (1c), involves weak coupling to very many promoting modes. Again, it is possible to transform to an effective local mode plus a set of effective lattice modes.

It is convenient to rewrite the Hamiltonian in a representation spanned by eigenkets $|gn_g^{(a)}\rangle$ and $|xn_x^{(a)}\rangle$ of $\mathcal{H}^{(a)}$. With omission of the lattice modes, a $2\times 2$ block for fixed $n_g^{(a)}$, $n_x^{(a)}$ has the form

$$\mathcal{H}(n_g^{(a)}, n_x^{(a)}) = \left(n_g^{(a)} + \frac{1}{2}\right)\hbar\omega_{\text{eff}}^{(a)} + [E_0 + (n_x^{(a)} - n_g^{(a)}) \times \hbar\omega_{\text{eff}}^{(a)}](1 - \rho^{(a)\gamma})/2 + \hbar\omega_{\text{eff}}^{(p)}\left[\left(\alpha_1^{(p)+}\alpha_1^{(p)} + \frac{1}{2}\right) + k_{\text{eff}}^{(p)}\langle n_x^{(a)}|n_g^{(a)}\rangle(\alpha_1^{(p)} + \alpha_1^{(p)+})\rho^{(p)\gamma}\right], \tag{18}$$

where we have introduced new vibronic operators $\rho^{(a)\gamma}$ and $\rho^{(p)\gamma}$ defined by

$$\rho^{(a)\gamma} \equiv |gn_g^{(a)}\rangle\langle gn_g^{(a)}| - |xn_x^{(a)}\rangle\langle xn_x^{(a)}|, \tag{19a}$$

and

$$\rho^{(p)\gamma} \equiv |gn_g^{(a)}\rangle\langle xn_x^{(a)}| + |xn_x^{(a)}\rangle\langle gn_g^{(a)}|. \tag{19b}$$

Only the term containing $\rho^{(p)\gamma}$ can mix the two electronic states, and its effect is appreciable only when $E_0 + (n_x^{(a)} - n_g^{(a)})\hbar\omega_{\text{eff}}^{(a)} \approx 0$; i.e. when the two vibronic states $|gn_g^{(a)}\rangle$ and $|xn_x^{(a)}\rangle$ are nearly degenerate. Furthermore, the mixing term contains as a reduction factor the vibrational overlap integral $\langle n_x^{(a)}|n_g^{(a)}\rangle$, which is appreciably different from zero only when the classical turning points coincide. Thus, the importance of the cross-over of the adiabatic potential energy curves (point $X$ of Fig. 1) becomes apparent. If $k_{\text{eff}}^{(p)}$ is large enough, the mixing may be appreciable for several pairs of vibronic states, but to a first approximation the states are only mixed in pairs.

For simplicity, we will neglect $E_0 + (n_x^{(a)} - n_g^{(a)})\hbar\omega_{\text{eff}}^{(a)}$; then we are left with a simple Jahn–Teller problem. The Hamiltonian can be written in the form

$$H(n_g^{(a)}, n_x^{(a)}) = \left(n_g^{(a)} + \frac{1}{2}\right)\hbar\omega_{\text{eff}}^{(a)} + \hbar\omega_{\text{eff}}^{(p)}\left(\eta^{(p)\gamma+}\eta^{(p)\gamma} + \frac{1}{2}\right) - E_p \tag{20}$$

where

$$\eta^{(p)\gamma} \equiv \alpha_1^{(p)} + k_{\text{eff}}^{(p)}\langle n_x^{(a)}|n_g^{(a)}\rangle\rho^{(p)\gamma}, \tag{20b}$$

$$E_p \equiv k_{\text{eff}}^{(p)2}|\langle n_x^{(a)}|n_g^{(a)}\rangle|^2\hbar\omega_{\text{eff}}^{(p)}, \tag{20c}$$

and has eigenkets

$$|\pm\rangle|n_\pm^{(p)}\rangle \equiv (2)^{-1/2}(|xn_x^{(a)}\rangle \pm |gn_g^{(a)}\rangle)|n_\pm^{(p)}\rangle. \tag{21}$$

The corresponding adiabatic potential energy curves as functions of the promoting mode configuration coordinate $Q_p$ are shown in Fig. 3, together with the vibronic energy levels.

A "cooling" transition from the state $|xn_x^{(a)} + 1\rangle|0_0^{(p)}\rangle$ terminates in a combination of degenerate eigenkets $|+\rangle|n_+^{(p)}\rangle + |-\rangle|n_-^{(p)}\rangle$, where

$$n_+^{(p)} = n_-^{(p)} \approx E_p/\hbar\omega_{\text{eff}}^{(p)}, \tag{22}$$

The probability for a subsequent cooling transition to the state $|xn_x^{(a)} - 1\rangle|0_0^{(p)}\rangle$ is

$$W_x \approx \pi n_x^{(a)}\Delta\omega\,\frac{1}{2}|\langle 0_0^{(p)}\rangle + \langle 0_0^{(p)}\rangle|^2, \tag{23}$$

and that for a cooling transition to the state $|gn_g^{(a)} - 1\rangle|1_0^{(p)}\rangle$ is

$$W_x \approx \pi n_x^{(a)}\Delta\omega\,\frac{1}{2}|\langle 0_0^{(p)}|n_+^{(p)}\rangle + \langle 0_0^{(p)}|n_-^{(p)}\rangle|^2, \tag{24}$$

provided that

$$n_g^{(a)}\Delta\omega \ll \omega_{\text{eff}}^{(a)}.$$

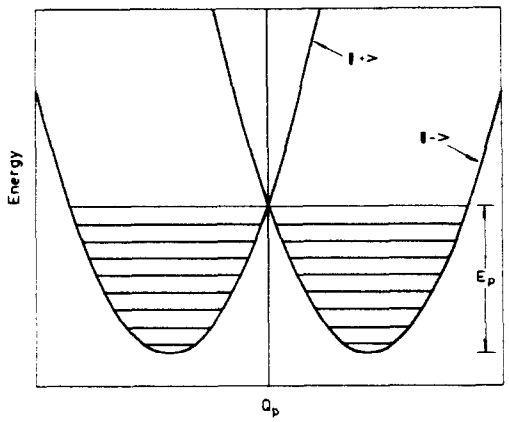


Fig. 3. Configuration coordinate diagram for the promoting mode, for fixed degenerate accepting mode vibronic states $|xn_x^{(a)}\rangle$ and $|gn_g^{(a)}\rangle$

Here, the kets $|0_0^{(p)}\rangle$ and $|1_0^{(p)}\rangle$ refer to the local promoting mode in the absence of a promoting interaction. The factors involving vibrational overlap integrals in eqn (23) and (24) are expected to be comparable; accordingly the ratio of transition probabilities is given approximately by

$$R \equiv W_x/W_g \approx n_x^{(a)}/n_g^{(a)}, \tag{25}$$

where $n_x^{(a)}$ and $n_g^{(a)}$ are the quantum numbers appropriate to the cross-over. This is also the ratio of radiative to non-radiative de-excitations. It is convenient to introduce a parameter $\Lambda$ defined by [2]

$$\Lambda \equiv E_M/(E_0 + E_M), \tag{26}$$

where the energies $E_0$ and $E_M$ are defined in Fig. 1. In terms of $\Lambda$, the ratio of probabilities is simply

$$R = (1 - 2\Lambda)^2 \tag{27}$$

In order to preserve symmetry, the terminal ground electronic state must have associated with it at least one vibrational quantum of the local promoting mode, which is ultimately transferred to lattice modes of the same symmetry. As a consequence of this requirement, $k_{\text{eff}}^{(p)}\langle n_x^{(a)}|n_g^{(a)}\rangle$ must be large enough ($\geq 1$) to mix pairs of states above and below the cross-over; in particular, energy conservation demands that

$$E_0 + (n_x^{(a)} - n_g^{(a)})\hbar\omega_{\text{eff}}^{(a)} \approx \hbar\omega_{\text{eff}}^{(p)}, \tag{28}$$

for the lowest state of the sequence.

## 5. DISCUSSION

It is evident from eqn (25) that the ratio $R$ of radiative to non-radiative de-excitations satisfies the inequality $R \ll 1$, since $n_g^{(a)} \gg n_x^{(a)}$; this result lends strong support to the model of Dexter *et al.*[1], but shows clearly that luminescence is not absolutely prohibited when $X$ lies below $B$ in Fig. 1.

Several assumptions have been incorporated in the present derivation. Our description of the cooling process relies on the inequalities $n_x^{(a)}\Delta\omega \ll \omega_{\text{eff}}^{(a)}$ and $n_g^{(a)}\Delta\omega \ll \omega_{\text{ep}}^{(a)}$; accordingly, we have assumed a relatively narrow resonance. If only the former inequality is satisfied, the ratio $R$ is substantially diminished since the mixed state can decay very rapidly to the ground state by multiphonon transitions. On the other hand, if neither inequality is satisfied, the excited state relaxes by multiphonon transitions in a fraction of a vibrational period. This is the process envisioned by Seitz[8]; physically, it means that the motion of the near-neighbour ions is over-damped and they proceed directly to their new equilibrium positions (point $C$ of Fig. 1) without ever reaching the intersection of adiabatic potential-energy curves. Non-radiative de-excitation is then improbable, and $R$ is very large.

If follows from the discussion of section 2 that the intersection of adiabatic potential energy curves may also be avoided, with consequent enhancement of $R$, by the use of low-intensity monochromatic illumination. The optical transition is then directly to a vibronic state in which the vibrational excitation is shared among many ions rather than localized at the near neighbours.

We have also assumed that the effective promoting interaction satifies the inequality $k_{\text{eff}}^{(p)}\langle n_x^{(a)}|n_g^{(a)}\rangle \geq 1$, in order that several pairs of states above and below the cross-over be mixed. Weaker coupling than this would increase the value of $R$. If the promoting interaction were weaker than the coupling of effective local modes to effective lattice modes, it would be more appropriately treated by time-dependent perturbation theory, as was done by Brailsford and Chang[9].

We have assumed throughout that the lattice is at the absolute zero of temperature. Thermal phonons would modify the initial state and affect the cooling process, but would not radically alter our conclusions. However, thermally activated non-radiative de-excitation from the relaxed excited state, which was not included in the present analysis, could have a significant effect on the quantum efficiency of fluorescence, which in our theory is given simply by $R/(1+R)$. Our prediction is in accord with the observed success of the Dexter–Klick–Russell model [2, 10]. A quantitative comparison with experiment will be given elsewhere.

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