ENERGY TRANSFER

In the past there have been many investigations, which established that electronic excitation energy could, in certain circumstances, be transferred between ions or molecules in the solid phase. The three basic mechanisms for energy transfer are photoconductive, radiative, and nonradiative.\cite{1} The photoconductive mechanism occurs when an absorbed photon creates free electron-hole pairs capable of migration. Many studies have been conducted on the photoconductivity of semiconductors, and these have generally involved measurement of the electrical current that results after optical excitation. The second basic energy transfer mechanism is radiative reabsorption in which a photon is emitted and then reabsorbed by the same system.\cite{1} This process does not shorten the fluorescence lifetimes, and can usually be minimized by adjusting sample size and experimental configuration. The mechanism most extensively studied, and most relevant to this thesis, is nonradiative energy transfer between ions without charge migration. In this case Coulomb interactions of the Van der Waals type allow energy to be transferred directly between the ions.\cite{2}
The theory of nonradiative energy transfer was first developed by Forster\textsuperscript{[3]}, who used quantum mechanics to describe energy transfer in terms of a resonant dipole-dipole interaction. It was assumed that interactions would be strongest if the two dipole-dipole transitions were symmetry allowed.\textsuperscript{[2]} The interaction energy is then proportional to the inverse third power of the interionic distance and transfer probability is given by:

\[ P_{SA} = \frac{2\pi}{h} \left| \langle S^e A^o | H_{SA} | S^e A^o \rangle \right|^2 \rho E \]  

\( H_{SA} \) interaction Hamiltonian

\( \rho E \) density of states provided by the vibrational motion contributing to the line broadening of the transition

which is proportional to the inverse sixth power of that distance. The wavefunctions to be considered for the matrix element are describing an initial state of the system with the donor in its excited state and the acceptor in its ground state, the final state having the sensitizer in its ground state and the acceptor in its excited state.

Therefore, the transfer probability can be written as
\[ P_{\text{SA}} = \frac{1}{\tau_S} \left( \frac{R_0}{R} \right)^6 \]  

(2)

\( \tau_S \) actual lifetime of the donor excited state  
\( R_0 \) critical transfer distance for which excitation transfer and spontaneous deactivation of the donor have equal probability.

\( R_0 \) can be written as

\[
R_0^6 = \frac{3.10^3 \eta S^0}{64\pi^6 n^4 N^4} \int_0^\infty f_\lambda(\nu) \varepsilon_A(\nu) d\nu
\]  

(3)

where \( \nu \) is the wavenumber, \( \varepsilon_A(\nu) \) the molar extinction coefficient, \( \eta S^0 \) the quantum efficiency of the donor in the absence of the acceptor, \( n \) the refractive index, \( N \) Avogadro’s number, \( \bar{\nu} \) the average frequency of the transition, and the integral represents the energy overlap between the absorption in the donor and the acceptor emission.\(^{[2]}\)

Forster’s theories on energy transfer in terms of dipole-dipole interactions were expanded by Dexter to also include multipole and exchange interactions.\(^{[4]}\)

In fact, for an isolated atom, one can consider the transition probability as decreasing as \((a_0/\lambda)^{2n}\) where \(a_0\) is the Bohr radius, \(\lambda\) the wavelength, and \(n\) an integer. However, in an energy transfer process with a dependence on near-zone interactions, the transition probabilities drops off as \((a_0/\rho)^{2n}\) where \(\rho\) is the separation of the interacting ions. \(\rho\) can be as much as three orders of magnitude
smaller than \( \lambda \), so that the energy transfer effect tends to be more pronounced in systems with forbidden transitions. This holds true for the rare-earth ions, which we shall discuss later.

The energy transfer probability for electric multipolar interactions can be more generally written as

\[
P_{sa} (R) = \frac{1}{\tau_s} \left( \frac{R_0}{R} \right)^s
\]

where \( s \) is a positive integer taking the following values:

- \( s = 6 \) for dipole-dipole interactions
- \( s = 8 \) for dipole-quadrupole interactions
- \( s = 10 \) for quadrupole-quadrupole interactions.\(^{[2]}\)

Inokuti and Hirayama\(^{[5]}\) advanced Dexter’s theoretical treatment of exchange interactions by determining relationships to experimentally observable phenomena. They developed a quantitative relationship between yield and decay time of donor luminescence as a function of acceptor concentration.\(^{[5]}\)

When the two ions involved in energy transfer have excited states of different energies, the overlap integral \( \int_0^\infty f_s(\nu) e_A(\nu) d\nu \) goes to zero and according to equation (3) the probability for energy transfer should also be zero.\(^{[2]}\) Experimentally, however, it is found that energy transfer can still take place between nonresonant ions as long as the energy difference is compensated by
the production or annihilation of a lattice phonon. The incorporation of lattice
vibrational states called phonons allows energy transfer while maintaining the
overall energy conservation of the system. For a one phonon-assisted
nonradiative energy transfer the energy of the phonon created or destroyed
should approach $k\theta_d$ or $kT$, where $\theta_d$ is the Debye temperature of the host
crystal.\textsuperscript{[2]} If the energy transfer between ions involves an energy mismatch larger
than the Debye cutoff frequency of the host, the transfer is described in terms of
a multiphonon process.

**MACROSCOPIC MODELS**

Much effort has been made in finding experimental evidence for the
specific terms of the microscopic interaction equations. Of course examining the
energy transfer from individual excited ions is experimentally impossible and
microscopic interactions must be deduced from luminescence measurements
made on a macroscopic scale. Commonly the nature of the transfer
mechanism is inferred by examining how the luminescence decay of an
ensemble of “equivalent” ions within a host lattice depends on their concentration
and temperature.\textsuperscript{[6]} Figure 21 shows a schematic of the possible luminescence
processes which can occur when ion within a larger ensemble is excited.
Figure 20. Schematic representation of the possible luminescence processes of a crystal system with donor D and acceptor A ions. Following excitation D may: (1) emit radiatively, (2) decay nonradiatively, (3) transfer energy to another D ion, or (4) transfer energy to an A ion. In the last case, energy transfer to A is followed by either radiative or nonradiative decay.

In the host lattice the ion which absorbs the radiation is referred to as the donor, and the ion which excitation energy is transferred is the acceptor. From the schematic presented in Figure 21, four different processes following excitation of D can be distinguished: (1) D may luminesce, (2) D may decay nonradiatively producing heat, (3) D may transfer energy to another D type ion, or (4) D may transfer energy to an A type ion. If energy transfer to A is followed by nonradiative decay, A is referred to as a killer site, because it acts to quench luminescence.\[^7\]
A great deal of progress in this field of research has been made since the introduction of tunable dye lasers.\textsuperscript{[7]} This instrument has led to the development of site selective spectroscopy, in which only specific types of ions are initially excited. The short and intense excitation pulses produced by the lasers also make it possible to perform time-resolved spectroscopy, where the sample luminescence following excitation is measured as a function of time.\textsuperscript{[7]}

For systems where the D ions are isolated, no energy transfer to A ions can take place, and luminescence decay following pulsed excitation is exponential. The intensity of emission is described by the following expression

\[ I = I_0 \exp(-A_s t) \]  \hspace{1cm} (5)

where \( I_0 \) is the emission intensity immediately after excitation, and \( A_s \) is the spontaneous transition probability. The exponential term can also be written as \( \exp(-t/\tau_R) \), where \( \tau_R \) is the radiative lifetime of the excited state, with \( \tau_R^{-1} = A_s \).\textsuperscript{[8]}

For systems where D ions are not isolated, and energy transfer from D to A is possible, time-resolved spectroscopy provides a method to follow energy migration through the host lattice. Provided the lifetime of the D excited state is known, information about D to D and D to A transfer can be obtained by fitting the decay curve to appropriate theoretical expressions.\textsuperscript{[9]} However, these expressions involve a statistical averaging of the microscopic interactions taking place and are only exact for two limiting cases. The first case assumes no D to
D transfer, no A to A transfer, and a random distribution of D and A ions.\textsuperscript{[10]} The following expression developed by Inokuti and Hirayam\textsuperscript{[5]} describes this decay

\[
I(t) = I_0 \exp \left( - \frac{t}{\tau_R} - \sqrt{1 - \frac{3s}{C_{a0}}} \left( \frac{t}{\tau_R} \right)^{3/2} \right)
\]

\text{(6)}

where $\Gamma$ is the gamma function, $C_a$ is the concentration of acceptor ions, $C_{a0}$ is the critical acceptor concentration, and $s$ is the multipolar interaction parameter. Due to the random distribution of acceptors some donors will find acceptors in very close proximity. These donors will decay rapidly by energy transfer causing an initially fast decay. As time passes only the more distantly separated D-A pairs remain excited, the decay rate decreases, and will eventually approach an exponential decay with a slope of $\tau_R^{-1}$.\textsuperscript{[7, 8]}

The second case that can be calculated exactly occurs for concentrated systems in which D to D transfer is much faster than D to A transfer. The fast transfer between D ions allows the D system to reach equilibrium before transfer to an A ion can occur. This is referred to as the fast diffusion limit. The following expression describes the decay

\[
I(t) = I_0 \exp \left( - \frac{t}{\tau_R} - C_a \cdot P_{sa} \cdot t \right)
\]

\text{(7)}

The resulting curve is a single exponential with a decay constant related to the concentration of A ions ($C_a$), and the D to A transfer probability ($P_{sa}$).\textsuperscript{[7]}
ENERGY TRANSFER IN Eu$_2$O$_3$

The decay curve of Eu$_2$O$_3$ shows an initial nonexponential decay which becomes exponential at long times, this points to three-dimensional diffusion-limited energy migration (refer to figure 20). The exponential part of the decay can be expressed by

$$\tau^{-1} = \tau_0^{-1} + \tau_D^{-1}$$

(8)

where $\tau_0$ is the intrinsic decay time of an isolated Eu$^{3+}$ ion and $\tau_D$ is the decay time due to migration. Assuming that energy transfer occurs by a dipolar donor-acceptor interaction the following expression for $\tau_D^{-1}$ can be derived:

$$\tau_D^{-1} = 11.404 N_a C^{1/4} D^{3/4}$$

(9)

where $N_a$ is the amount of acceptor ions (in this case impurity ions) per unit volume, $C$ is the interaction parameter for donor-acceptor interaction and $D$ is the diffusion constant. The following expression approximates luminescence decay in Eu$_2$O$_3$:

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_0}\right) \exp\left\{ -\frac{4}{3} \pi^{3/2} N_a (Ct)^{1/2} \left( \frac{1 + 10.87 x + 15.50 x^2}{1 + 8.743 x} \right)^{3/4} \right\}$$

(10)

where $x = DC^{-1/3} t^{2/3}$. When $t \to \cdot$ the expression within the brackets transforms to the right hand side of eq. (9). Fitting eq. (10) to the experimental decay curves of Eu$_2$O$_3$ works well at low temperatures. However at higher temperatures a deviation occurs at the beginning of the curves, this likely due to the fact that
donor-acceptor interactions are not only of a dipolar nature.\textsuperscript{[11]} Due to the close proximity of Eu\textsuperscript{3+} ions in Eu\textsubscript{2}O\textsubscript{3} an exchange interaction is also expected. Nonlinear luminescence quenching may also be a factor at very early times in the decay, this further complicates any attempts at mathematical modeling.
Appendix References


