Theory of energy transfer between molecules near solid state particles

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The theory of energy transfer between a donor molecule and an acceptor molecule near a solid state particle is developed. The particle is modeled as a spheroidal shape and the molecules are allowed to be at arbitrary positions in space. It is found that there exist zones of activity in which the molecules display significantly enhanced energy transfer. We develop a formalism which allows us to describe nonradiative and radiative decay and energy transfer in a unified manner.

I. INTRODUCTION

Interest in energy transfer between molecules stems from the fact that it plays a fundamental role in such phenomena as quenching of luminescence, sensitizing of luminescence, photosynthesis, and fluorescence phenomena in general. Early theoretical attempts at describing energy transfer were put forth by Perrin[1] and Perrin[2] in which the long-range electromagnetic interaction was identified as the mechanism responsible for energy transfer. Later Vavilov[3] incorporated these ideas into a phenomenological theory. The first successful theory was proposed by Förster[4] and later elaborated on by Dexter[5] and others.[6] The basic idea was that it is the dipole–dipole interaction between the donor molecule and the acceptor molecule that causes a simultaneous quantum transition in which the donor molecule is deexcited and the acceptor molecule is excited. A simple quantum mechanical theory based on the Fermi Golden Rule was developed which allowed the energy transfer rate to be expressed in terms of the emissivity of the donor molecule and the absorptivity of the acceptor molecule. The theories that have been developed have focused primarily on homogeneous media, usually solutions. In this paper we shall extend the theory to a particular class of inhomogeneous media, namely systems in which granular particles may be present. Our goal shall be to develop a theory of energy transfer between donor and acceptor molecules in the presence of such particles.

In recent years attention has focused on a variety of optical processes that take place on molecules in the vicinity of solid state particles. It was found that the solid state particle can strongly modify the optical process. For example, in Raman scattering the cross section can be enhanced by as much as six orders of magnitude[7] over what it would be in the absence of the solid. It is currently believed that a large component of the enhancement mechanism is of purely electrodynamic origin,[8] although there is also evidence for purely chemical factors as well. In the electromagnetic process the local field in the vicinity of the molecule is modified by the ability of the particle to concentrate electric field lines, as in a lighting rod, as well as by the particle's ability to store electromagnetic energy, particularly if it is resonantly excited. The electromagnetic theory has also been applied to explaining enhanced fluorescence,[9] photochemistry,[10] and second harmonic generation.

In previous work[11] we have shown how the Forster–Dexter theory of energy transfer may be generalized to include the presence of a solid state particle and made some simple estimates of the size of the effect. However we restricted our attention to the somewhat idealized case of a collinear geometry, in which the molecules and the symmetry axis of the particle were all aligned and the dipoles of the molecules were also parallel to the axis. This left open the qualitative question as to how general the results were and the quantitative question as to how to take off-axis effects into account. One of the results of our present work, as we shall see, will be to define zones of activity in which the molecules behave as if they were on the axis. The present work will also generalize our previous work[12] on radiative and nonradiative lifetimes of molecules near particles to the case where the molecules may be at arbitrary positions in space with arbitrary directions for their dipoles.

The basic mechanism for energy transfer to be developed here differs from energy transfer mechanisms in homogeneous media in that it is a coherent process. Transfer mechanisms involving incoherent processes like exciton migration[13] view transfer as coming about by a kind of random walk process in which the energy jumps from site to site. In the mechanism discussed here the transfer is from the donor to the acceptor by the agent of coherently exciting the particle. Because of the coherent virtual excitation of the particle the energy transfer is able to occur very rapidly. We shall find that the energy transfer rate can be enhanced by many orders of magnitude over what the rate would be in the absence of the particle.

The paper is arranged as follows. In Sec. II we develop the theory of energy transfer. In Sec. III we develop the theory of nonradiative decay and establish its connection to the energy transfer process. In Sec. IV we focus our attention on radiative decay. Finally, in Sec. V we present the results of our computations and discuss them.

II. THEORY OF ENERGY TRANSFER

We shall study the transfer of energy between a donor molecule (d) and an acceptor molecule (a) in the vicinity of a solid state particle. The particle will be taken to have a spheroidal shape with semimajor axis a and semiminor axis b. It will be assumed to possess a frequency-dependent dielectric

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function $\epsilon(\omega)$. The donor and acceptor molecules will be represented by point electric dipoles μ_d and μ_a at locations $\mathbf{r}_d$ and $\mathbf{r}_a$, respectively. It will be assumed that all distances of relevance (a,b,r_d, and r_a) are small compared with the wavelength of light whose frequency corresponds to molecular electronic transitions of interest, so that retardation effects may be neglected. On the other hand, it will be assumed that the distance scales are sufficiently large that nonlocal dielectric effects are not of significant importance.

Let us take the z axis parallel to the symmetry axis (the major axis) and introduce prolate spheroidal coordinates ξ, η, and ϕ. The surface of the particle will be denoted by $\xi = \xi_0$, where $\xi_0 = a/f$ and $f = (a^2 - b^2)^{1/2}$. While this description more naturally applies to prolate shaped particles, the generalization to oblate structures may readily be obtained by analytic continuation. The coordinates of the donor and acceptor molecules will be denoted by (ξ_d, η_d, ϕ_d) and (ξ_a, η_a, ϕ_a). The Cartesian coordinates are related to the spheroidal coordinates by

$$x = f[(\xi^2 - 1)(1 - \eta^2)]^{1/2}\cos\phi, \tag{2.1a}$$

$$y = f[(\xi^2 - 1)(1 - \eta^2)]^{1/2}\sin\phi, \tag{2.1b}$$

$$z = f\xi\eta. \tag{2.1c}$$

Before developing the theory for the general case, consider first the situation in the absence of the particle. Förster and Dexter have described the energy transfer rate from the donor to the acceptor molecule in terms of Fermi's Golden Rule, taking the dipole–dipole interaction as the perturbation responsible for driving the transition. The donor molecule is initially in an excited state $|f_d)$ with energy ϵ_{f_d} and falls to a lower state $|i_d)$ with energy ϵ_{i_d}. At the same time the acceptor molecule is promoted from an initial state $|i_a)$ to some excited state $|f_a)$, with corresponding energies ϵ_{i_a} and ϵ_{f_a}, respectively. Because of the presence of a high density of vibrational levels associated with the electronic states we expect some distribution of initial donor and acceptor levels. These will be described by the distribution functions $F_d(f_d)$ and $F_a(i_a)$. The average transition rate is given by

$$K_0 = \frac{2\pi}{\hbar}\sum_{i_a}\sum_{f_d} F_d(f_d)F_a(i_a)|(i_d\, f_a|U_0|f_d i_a)|^2 \times\delta(\epsilon_{f_d} + \epsilon_{i_a} - \epsilon_{i_d} - \epsilon_{f_a}), \tag{2.2}$$

where U_0 is the dipole–dipole interaction

$$U_0 = \frac{\boldsymbol{\mu}_d\cdot\boldsymbol{\mu}_a - 3\boldsymbol{\mu}_d\cdot\hat{\mathbf{r}}\boldsymbol{\mu}_a\cdot\hat{\mathbf{r}}}{r^3}, \tag{2.3}$$

and $\mathbf{r} = \mathbf{r}_d - \mathbf{r}_a$ is the intermolecular displacement vector. Let

$$(i_d|\boldsymbol{\mu}_d|f_d) = \chi_d(i_d,f_d)\mathbf{m}_d \tag{2.4a}$$

and

$$(f_a|\boldsymbol{\mu}_a|i_a) = \chi_a(f_a,i_a)\mathbf{m}_a, \tag{2.4b}$$

where $\mathbf{m}_d$ and $\mathbf{m}_a$ are transition moments and $\chi_d(i_d,f_d)$ and $\chi_a(f_a,i_a)$ are Franck–Condon factors. Then U_0 may be written as

$$(i_d f_a|U_0|f_d i_a) = m_a m_d\,\chi_d(i_d,f_d)\chi_a(f_a,i_a)A_0, \tag{2.5}$$

where A_0 is an angular-dependent factor

$$A_0 = \frac{\hat{m}_d\cdot\hat{m}_a - 3\hat{m}_d\cdot\hat{r}\hat{m}_a\cdot\hat{r}}{r^3}. \tag{2.6}$$

Then, introducing an auxiliary integration, we obtain

$$K_0 = 2\pi A_0^2\int_{-\infty}^{\infty} d\omega\sum_{i_a} F_a(i_a)|\chi_a(f_a,i_a)|^2|m_a|^2 \times\delta(\epsilon_{i_a} - \epsilon_{f_a} + \hbar\omega)\sum_{f_d} F_d(f_d)|\chi_d(i_d,f_d)|^2|m_d|^2 \times\delta(\epsilon_{f_d} - \epsilon_{i_d} - \hbar\omega), \tag{2.7}$$

which may be rewritten as

$$K_0 = \frac{9A_0^2c^4}{8\pi}\int_{-\infty}^{\infty} d\omega\,\frac{\sigma_a(\omega)\Gamma_d(\omega)}{\omega^4}, \tag{2.8}$$

where $\sigma_a(\omega)$ is the electromagnetic absorption cross section for the acceptor molecule

$$\sigma_a(\omega) = \frac{4\pi^2\omega}{3c}\sum_{i_a} F_a(i_a)|\chi_a(f_a,i_a)|^2|m_a|^2\delta(\epsilon_{i_a} - \epsilon_{f_a} + \hbar\omega) \tag{2.9}$$

and $\Gamma_d(\omega)$ is the emission rate per unit frequency of the donor

$$\Gamma_d = \frac{4\omega^3}{3c^3}\sum_{f_d} F_d(f_d)|\chi_d(i_d,f_d)|^2|m_d|^2\delta(\epsilon_{f_d} - \epsilon_{i_d} - \hbar\omega). \tag{2.10}$$

Let us now introduce the particle. Since Eq. (2.8) involves an integration over angular frequencies ω associated with both the donor and acceptor transitions it is reasonable to assume that the dielectric properties of the solid at frequency ω will now enter the formalism. What we need is a generalization of the expression for the dipole–dipole interaction U_0. To obtain this we must first solve the general electrostatic problem presented by having two point dipoles in proximity to a spheroidal particle. The electrostatic potential inside the particle ($\xi < \xi_0$) may be expanded as

$$\Phi(\xi,\eta,\phi) = \sum_{n=0}^{\infty}\sum_{m=0}^{n}[A_{nm}\cos m\phi + B_{nm}\sin m\phi] \times P_n^m(\xi)P_n^m(\eta) \tag{2.11a}$$

and the potential outside the particle ($\xi > \xi_0$) as

$$\Phi(\xi,\eta,\phi) = \sum_{n=0}^{\infty}\sum_{m=0}^{n}[A'_{nm}\cos m\phi + B'_{nm}\sin m\phi] \times Q_n^m(\xi)P_n^m(\eta) + \Phi_d + \Phi_a. \tag{2.11b}$$

Here $P_n^m(\xi)$ and $Q_n^m(\xi)$ denote associated Legendre functions of the first and second kind, respectively. The dipolar potentials associated with isolated donor and acceptor molecules are denoted by Φ_d and Φ_a. Expansions for these potentials may be obtained starting with the Coulomb Green function

$$\frac{1}{|\mathbf{r} - \mathbf{r}'|} = \sum_{n=0}^{\infty}\sum_{m=0}^{n} F_{nm}\,P_n^m(\xi_<)Q_n^m(\xi_>) \times P_n^m(\eta)P_n^m(\eta')\cos m(\phi - \phi'), \tag{2.12}$$

where

$$F_{nm} = \frac{1}{f}(-)^m(2 - \delta_{m,0})(2n + 1)\left[\frac{(n-m)!}{(n+m)!}\right]^2, \tag{2.13}$$

and $\xi_< = \min(\xi,\xi')$ and $\xi_> = \max(\xi,\xi')$. The potential due to a dipole $\boldsymbol{\mu}_d$ located at $\mathbf{r}_d$ is

$$\Phi_d = \frac{\boldsymbol{\mu}\cdot(\mathbf{r}-\mathbf{r}_d)}{|\mathbf{r}-\mathbf{r}_d|^3} = \boldsymbol{\mu}\cdot\nabla_d \frac{1}{|\mathbf{r}-\mathbf{r}_d|}. \tag{2.14}$$

The components of the gradient operator may be written as

$$\nabla_d = \frac{\hat{\xi}_d}{h_{\xi_d}}\frac{\partial}{\partial\xi_d} + \frac{\hat{\eta}_d}{h_{\eta_d}}\frac{\partial}{\partial\eta_d} + \frac{\hat{\phi}_d}{h_{\phi_d}}\frac{\partial}{\partial\phi_d}, \tag{2.15}$$

where $\hat{\xi}_d$, $\hat{\eta}_d$, and $\hat{\phi}_d$ are unit vectors and h_{ξ_d}, h_{η_d}, and h_{ϕ_d} are metric coefficients defined by

$$h_{\xi_d} = f[(\xi_d^2-\eta_d^2)/(\xi_d^2-1)]^{1/2}, \tag{2.16a}$$

$$h_{\eta_d} = f[(\xi_d^2-\eta_d^2)/(1-\eta_d^2)]^{1/2}, \tag{2.16b}$$

$$h_{\phi_d} = f[(\xi_d^2-1)(1-\eta_d^2)]^{1/2}, \tag{2.16c}$$

so

$$\begin{aligned}\Phi_d = \sum_{n=0}^{\infty}\sum_{m=0}^{n} F_{nm}\Bigg\{&\frac{\mu_{\xi_d}}{h_{\xi_d}}\frac{\partial}{\partial\xi_d}[P_n^m(\xi_<)Q_n^m(\xi_>)]P_n^m(\eta)\\ &\times P_n^m(\eta_d)\cos m(\phi-\phi_d)\\ &+\frac{\mu_{\eta_d}}{h_{\eta_d}}P_n^m(\xi_<)Q_n^m(\xi_>)P_n^m(\eta)\\ &\times[P_n^m(\eta_d)]'\cos m(\phi-\phi_d)+\frac{m\mu_{\phi_d}}{h_{\phi_d}}P_n^m(\xi_<)Q_n^m(\xi_>)\\ &\times P_n^m(\eta)P_n^m(\eta_d)\sin m(\phi-\phi_d)\Bigg\}.\end{aligned} \tag{2.17}$$

A similar formula holds for Φ_a with d replaced by a.

We now demand that Φ be continuous at the surface of the dielectric and also that the normal component of the electric displacement vector be continuous there. This allows us to solve for the unknown constants A'_{nm} and B'_{nm} appearing in Eq. (2.11b):

$$\begin{aligned}\begin{pmatrix}A'_{nm}\\ B'_{nm}\end{pmatrix} &= \frac{1-\epsilon(\omega)}{\Delta_{nm}(\omega)}F_{nm}P_n^m(\xi_0)[P_n^m(\xi_0)]'\\ &\times\sum_{i=a,d}\Bigg(\Bigg\{\frac{\mu_{\xi_i}}{h_{\xi_i}}[Q_n^m(\xi_i)]'P_n^m(\eta_i)+\frac{\mu_{\eta_i}}{h_{\eta_i}}Q_n^m(\xi_i)[P_n^m(\eta_i)]'\Bigg\}\\ &\times\begin{pmatrix}\cos m\phi_i\\ \sin m\phi_i\end{pmatrix}+m\frac{\mu_{\phi_i}}{h_{\phi_i}}Q_n^m(\xi_i)P_n^m(\eta_i)\begin{pmatrix}-\sin m\phi_i\\ \cos m\phi_i\end{pmatrix}\Bigg),\end{aligned} \tag{2.18}$$

where

$$\Delta_{nm}(\omega) = \epsilon(\omega)Q_n^m(\xi_0)[P_n^m(\xi_0)]' - P_n^m(\xi_0)[Q_n^m(\xi_0)]'. \tag{2.19}$$

The interaction energy is obtained from the expression

$$U = -\tfrac{1}{2}[\boldsymbol{\mu}_a\cdot\mathbf{E}_a + \boldsymbol{\mu}_d\cdot\mathbf{E}_d]. \tag{2.20}$$

Here $\mathbf{E}_a$ is the electric field at the position of the acceptor molecule and $\mathbf{E}_d$ is the corresponding field at the donor molecule. These fields are obtained from Eq. (2.11b) using

$$\mathbf{E} = -\nabla\Phi, \tag{2.21}$$

and omitting the terms Φ_a of Eq. (2.11b) when computing $\mathbf{E}_a$ and Φ_d when computing $\mathbf{E}_d$. Thus we may write

$$U = U_0 + \Delta U(\omega), \tag{2.22}$$

where U_0 is given by Eq. (2.3) and

$$\Delta U(\omega) = \tfrac{1}{2}[\boldsymbol{\mu}_a\cdot\nabla\tilde{\Phi}|_{\mathbf{r}=\mathbf{r}_a} + \boldsymbol{\mu}_d\cdot\nabla\tilde{\Phi}|_{\mathbf{r}=\mathbf{r}_d}], \tag{2.23}$$

where

$$\tilde{\Phi} = \sum_{n=0}^{\infty}\sum_{m=0}^{n}[A'_{nm}\cos m\phi + B'_{nm}\sin m\phi]Q_n^m(\xi)P_n^m(\eta). \tag{2.24}$$

Here $\tilde{\Phi}$ is the potential just due to the induced charges of the dielectric and $\Delta U(\omega)$ is the additional interaction energy between the donor and acceptor caused by the presence of the nearby particle. Thus,

$$\begin{aligned}\Delta U(\omega) = \frac{1}{2}\sum_{j=d,a}\sum_{n=0}^{\infty}\sum_{m=0}^{n}\Bigg(&\frac{m\mu_{j_\phi}}{h_{\phi_j}}Q_n^m(\xi_j)P_n^m(\eta_j)\\ &\times[-A'_{nm}\sin m\phi_j + B'_{nm}\cos m\phi_j]\\ &+\Bigg\{\frac{\mu_{j_\xi}}{h_{\xi_j}}[Q_n^m(\xi_j)]'P_n^m(\eta_j)+\frac{\mu_{j_\eta}}{h_{\eta_j}}Q_n^m(\xi_j)[P_n^m(\eta_j)]'\Bigg\}\\ &\times[A'_{nm}\cos m\phi_j + B'_{nm}\sin m\phi_j]\Bigg).\end{aligned} \tag{2.25}$$

Equation (2.25) contains three types of terms: terms bilinear in $\boldsymbol{\mu}_d$ and $\boldsymbol{\mu}_a$, terms quadratic in $\boldsymbol{\mu}_d$, and terms quadratic in $\boldsymbol{\mu}_a$. Only the terms bilinear in $\boldsymbol{\mu}_d$ and $\boldsymbol{\mu}_a$ cause energy transfer. The other terms, however, are responsible for modifying the decay rates of the donor and acceptor molecules and will be studied later. We will denote the bilinear terms collectively as $\Delta U_{da}(\omega)$.

When the spheroidal particle is in proximity to the donor–acceptor pair the transition rate is

$$\begin{aligned}K = \frac{2\pi}{\hbar}\sum_{i_a}\sum_{f_d}F_d(f_d)F_a(i_a)|(i_d f_a|U_0+\Delta U_{da}|f_d i_a)|^2\\ \times\delta(\epsilon_{f_d}+\epsilon_{i_a}-\epsilon_{i_d}-\epsilon_{f_a}).\end{aligned} \tag{2.26}$$

In place of Eq. (2.8) we now obtain

$$K = \frac{9c^4}{8\pi}\int_{-\infty}^{\infty}d\omega\,\frac{|A(\omega)|^2\sigma_a(\omega)\Gamma_d(\omega)}{\omega^4}. \tag{2.27}$$

The frequency dependent factor $A(\omega)$ replaces the factor A_0 of Eq. (2.6) and is defined as

$$A = A_0 + \Delta A, \tag{2.28}$$

where

$$\Delta A = \hat{\mu}_d\cdot\Delta\overleftrightarrow{M}^{da}\cdot\hat{\mu}_a, \tag{2.29}$$

and $\Delta\overleftrightarrow{M}^{da}$ is a tensor which may be written as

$$\Delta\overleftrightarrow{M}^{da} = \sum_{n=0}^{\infty}\sum_{m=0}^{n}T_{nm}\overleftrightarrow{\Omega}^{da}(n,m). \tag{2.30}$$

Here

$$T_{nm} = \frac{1-\epsilon(\omega)}{\Delta_{nm}(\omega)}F_{nm}P_n^m(\xi_0)[P_n^m(\xi_0)]', \tag{2.31}$$

and the spheroidal components of the $\overleftrightarrow{\Omega}^{da}$ tensor are

$$\begin{aligned}\Omega_{\xi\xi}^{da} = [h_{\xi_d}h_{\xi_a}]^{-1}&[Q_n^m(\xi_d)]'[Q_n^m(\xi_a)]'P_n^m(\eta_d)P_n^m(\eta_a)\\ &\times\cos m(\phi_d-\phi_a),\end{aligned} \tag{2.32a}$$

$$\begin{aligned}\Omega_{\eta\eta}^{da} = [h_{\eta_d}h_{\eta_a}]^{-1}&Q_n^m(\xi_d)Q_n^m(\xi_a)[P_n^m(\eta_d)]'[P_n^m(\eta_a)]'\\ &\times\cos m(\phi_d-\phi_a),\end{aligned} \tag{2.32b}$$

$$\Omega^{da}_{\phi\phi} = [h_{\phi_d} h_{\phi_a}]^{-1} m^2 Q^m_n(\xi_d) Q^m_n(\xi_a) P^m_n(\eta_d) P^m_n(\eta_a) \times \cos m(\phi_d - \phi_a), \quad (2.32c)$$

$$\Omega^{da}_{\xi\eta} = [h_{\xi_d} h_{\eta_a}]^{-1} [Q^m_n(\xi_d)]' Q^m_n(\xi_a) P^m_n(\eta_d) [P^m_n(\eta_a)]' \times \cos m(\phi_d - \phi_a), \quad (2.32d)$$

$$\Omega^{da}_{\xi\phi} = [h_{\xi_d} h_{\phi_a}]^{-1} m [Q^m_n(\xi_d)]' Q^m_n(\xi_a) P^m_n(\eta_d) P^m_n(\eta_a) \times \sin m(\phi_d - \phi_a), \quad (2.32e)$$

$$\Omega^{da}_{\eta\phi} = [h_{\eta_d} h_{\phi_a}]^{-1} m Q^m_n(\xi_d) Q^m_n(\xi_a) [P^m_n(\eta_d)]' P^m_n(\eta_a) \times \sin m(\phi_d - \phi_a). \quad (2.32f)$$

Expressions for $\Omega^{da}_{\eta\xi}$, $\Omega^{da}_{\phi\xi}$, and $\Omega^{da}_{\phi\eta}$ are obtained from the last three equations by interchanging d and a. Similarly, we may express A_0 in spheroidal coordinates by writing

$$A_0 = \hat{\mu}_d \cdot \overleftrightarrow{M}_0 \cdot \hat{\mu}_a, \quad (2.33)$$

where

$$\overleftrightarrow{M}_0 = \sum_{n=0}^{\infty} \sum_{m=0}^{n} F_{nm} \overleftrightarrow{\Lambda}(n,m), \quad (2.34)$$

and $\overleftrightarrow{\Lambda}$ is a tensor whose spheroidal components are

$$\Lambda_{\xi\xi} = [h_{\xi_d} h_{\xi_a}]^{-1} [P^m_n(\xi_<)]' [Q^m_n(\xi_>)]' P^m_n(\eta_d) P^m_n(\eta_a) \times \cos m(\phi_d - \phi_a), \quad (2.35a)$$

$$\Lambda_{\eta\eta} = [h_{\eta_d} h_{\eta_a}]^{-1} P^m_n(\xi_<) Q^m_n(\xi_>) [P^m_n(\eta_d)]' [P^m_n(\eta_a)]' \times \cos m(\phi_d - \phi_a), \quad (2.35b)$$

$$\Lambda_{\phi\phi} = [h_{\phi_d} h_{\phi_a}]^{-1} m^2 P^m_n(\xi_<) Q^m_n(\xi_>) P^m_n(\eta_d) P^m_n(\eta_a) \times \cos m(\phi_d - \phi_a), \quad (2.35c)$$

$$\Lambda_{\xi\eta} = [h_{\xi_d} h_{\eta_a}]^{-1} \frac{\partial}{\partial \xi_d} [P^m_n(\xi_<) Q^m_n(\xi_>)] P^m_n(\eta_d) [P^m_n(\eta_a)] \times \cos m(\phi_d - \phi_a), \quad (2.35d)$$

$$\Lambda_{\xi\phi} = [h_{\xi_d} h_{\phi_a}]^{-1} m \frac{\partial}{\partial \xi_d} [P^m_n(\xi_<) Q^m_n(\xi_>)] P^m_n(\eta_d) P^m_n(\eta_a) \times \sin m(\phi_d - \phi_a), \quad (2.35e)$$

$$\Lambda_{\eta\phi} = [h_{\eta_d} h_{\phi_a}]^{-1} m P^m_n(\xi_<) Q^m_n(\xi_>) P^m_n(\eta_d) [P^m_n(\eta_a)]' \times \sin m(\phi_d - \phi_a). \quad (2.35f)$$

Expressions for $\Lambda_{\eta\xi}$, $\Lambda_{\phi\xi}$, and $\Lambda_{\phi\eta}$ are obtained from the last three equations by interchanging d and a. In the above, $\xi_< = \min(\xi_d, \xi_a)$ and $\xi_> = \max(\xi_d, \xi_a)$. The spheroidal components of the dipole unit vectors are related to the Cartesian components by

$$\hat{\mu}_\xi = \frac{\xi f}{h_\eta} [\hat{\mu}_x \cos\phi + \hat{\mu}_y \sin\phi] + \frac{\eta f}{h_\xi} \hat{\mu}_z, \quad (2.36a)$$

$$\hat{\mu}_\eta = \frac{\eta f}{h_\xi} [\hat{\mu}_x \cos\phi + \hat{\mu}_y \sin\phi] - \frac{\xi f}{h_\eta} \hat{\mu}_z, \quad (2.36b)$$

$$\hat{\mu}_\phi = -\hat{\mu}_x \sin\phi + \hat{\mu}_y \cos\phi. \quad (2.36c)$$

A comparison of Eq. (2.27) to Eq. (2.8) shows that the integrands differ by a factor

$$R(\omega) = \left| \frac{A(\omega)}{A_0} \right|^2. \quad (2.37)$$

We shall refer to this quantity as the enhancement factor. In addition to its frequency dependence it also depends on the locations of the molecules, their orientation, and the size, shape, and composition of the particle.

The present theory may be adapted somewhat so that it may also apply to intramolecular energy transfer. Consider, for example, a molecule which is in some vibrational state associated with a given electronic state. Assume this molecule also possesses another electronic state associated with a given electronic state. This level is embedded in the vibrational manifold associated with lower electronic states and if the latter are dense enough intramolecular radiationless transitions usually occur. Consider now the effect of the presence of the dielectric particle on such transitions. Since we now will be concerned with one molecule rather than two, we must talk in terms of donor modes and acceptor modes of that given molecule. The physical location of these modes are given by $r_d = r_a$ but there still can be independent transition dipole moments associated with the different electronic states.

Unlike the case of intermolecular energy transfer, the direct dipole–dipole interaction between the modes is no longer an appropriate concept. Since the modes are attached to the same molecule, the idea of representing them by point dipoles which will then interact is not very meaningful. Rather their direct interaction is incorporated into the Hamiltonian which will describe the internal dynamics of the isolated molecule. However, it is meaningful to talk about the donor and acceptor modes being represented by point dipoles when describing their interaction with the solid particle and indirectly with each other through the presence of the solid. The interaction to be used in place of the dipole–dipole interaction is then simply $\Delta U(\omega)$ given by Eq. (2.25). One simply sets $(\xi_d, \eta_d, \phi_d) = (\xi_a, \eta_a, \phi_a)$. The rate of energy transfer induced by the coupling is

$$K' = \frac{9c^4}{8\pi} \int_{-\infty}^{\infty} \frac{d\omega}{\omega^4} |\Delta A(\omega)|^2 \sum \sigma_a(\omega) \Gamma_d(\omega), \quad (2.38)$$

where ΔA is given by Eq. (2.29) and $\sigma_a(\omega)$ is the absorption cross section for the acceptor band and $\Gamma_d(\omega)$ is the corresponding emission function for the donor band. This rate K' is in addition to the normal intramolecular energy rate that may be present for the isolated molecule. In Eq. (2.38) we have included now a summation over all intermediate electronic states, where $\sigma_a(\omega)$ and $\Gamma_d(\omega)$ are the line shapes related to virtual transitions involving these states. The reason for this summation becomes apparent if we compare the Förster–Dexter matrix element of Eq. (2.2) with the corresponding matrix element for the intramolecular case. In the former case the interaction is bilinear in the donor and acceptor dipole operators, so it only deexcited the donor molecule and excited the acceptor molecule. In the case of intramolecular energy transfer, where the donor and acceptor are the same molecule, the interaction is quadratic in the dipole operator. Thus, by inserting a complete set of states, we see that we may first virtually excite the molecule and then virtually deexcite the molecule to some final electronic state.

III. NONRADIATIVE DECAY

Let us now focus our attention on the other terms appearing in Eq. (2.25) which were previously neglected. These terms are quadratic in μ_d or μ_a. We shall show that they are simply related to the nonradiative decay rates of the molecules. Let us consider one molecule at a time. Let

$$U_{dd} = -\tfrac{1}{2}\mu_d^* \cdot \mathbf{E}_d. \tag{3.1}$$

Note that μ_d is assumed real, but we have written μ_d^* in place of μ_d, for reasons which will soon become clear. Consider the quantity

$$\Gamma_d = \frac{1}{\hbar}\,\mathrm{Im}\,U_{dd}, \tag{3.2}$$

which has the dimensions of a frequency. For a point dipole we may write the corresponding charge density as

$$\rho_d = -\mu_d \cdot \nabla\delta(\mathbf{r}-\mathbf{r}_d), \tag{3.3}$$

as may readily be seen by computing the first moment of the charge density:

$$\int \rho_d x_i d\mathbf{r} = -\int \nabla\cdot[\mu_d x_i \delta(\mathbf{r}-\mathbf{r}_d)]d\mathbf{r} + \int \delta(\mathbf{r}-\mathbf{r}_d)(\mu_d)_i d\mathbf{r}. \tag{3.4}$$

The first integral vanishes so we obtain

$$\int \rho_d \mathbf{r}\, d\mathbf{r} = \mu_d, \tag{3.5}$$

as conjectured. Consider next the integral

$$\int_{\text{out}} \rho_d^*\Phi\, d\mathbf{r} = -\int_{\text{out}} d\mathbf{r}\nabla\cdot(\mu_d^*\Phi\delta(\mathbf{r}-\mathbf{r}_d)) + \int \delta(\mathbf{r}-\mathbf{r}_d)\mu_d^*\cdot\nabla\Phi d\mathbf{r}, \tag{3.6}$$

where the region of integration is outside the particle. Again the first integral vanishes and we obtain

$$\int_{\text{out}} \rho_d^*\Phi\, d\mathbf{r} = -\mu_d\cdot\mathbf{E}_d. \tag{3.7}$$

Thus we have

$$\Gamma_d = \frac{1}{\hbar}\,\mathrm{Im}[-\tfrac{1}{2}\mu_d^*\cdot\mathbf{E}_d] = \frac{1}{2\hbar}\int_{\text{out}} \rho_d^*\Phi\, d\mathbf{r}. \tag{3.8}$$

Using the Poisson equation, this becomes

$$\Gamma_d = \frac{1}{2\hbar}\,\mathrm{Im}\int_{\text{out}} \Phi\frac{\nabla\cdot\mathbf{E}^*}{4\pi}d\mathbf{r} = \mathrm{Im}\frac{1}{8\pi\hbar}\int_{\text{out}}\nabla\cdot(\Phi\mathbf{E}^*)d\mathbf{r} - \mathrm{Im}\frac{1}{8\pi\hbar}\int_{\text{out}}\mathbf{E}^*\cdot\nabla\Phi\, d\mathbf{r}. \tag{3.9}$$

The last term vanishes while the first term can be converted to an integral over the particle's surface

$$\Gamma_d = \frac{1}{8\pi\hbar}\,\mathrm{Im}\int \hat{n}_{\text{in}}\cdot\mathbf{E}^*\Phi\, dS, \tag{3.10}$$

where $\hat{n}_{\text{in}}$ denotes an inward pointing normal. Using the continuity of the normal component of $\mathbf{D}$, this may also be rewritten as

$$\Gamma_d = -\frac{1}{8\pi\hbar}\,\mathrm{Im}\int \hat{n}_{\text{out}}\cdot\mathbf{D}^*\Phi\, dS, \tag{3.11}$$

where $\hat{n}_{\text{out}}$ is an outward pointing normal and the integral is now over a surface slightly inside the particle. Then converting the integral to one over the particle's volume we obtain

$$\Gamma_d = -\frac{1}{8\pi\hbar}\,\mathrm{Im}\int_{\text{in}}\nabla\cdot(\Phi\mathbf{D}^*)d\mathbf{r} = \frac{1}{8\pi\hbar}\,\mathrm{Im}\int_{\text{in}}\epsilon|\mathbf{E}|^2 d\mathbf{r}. \tag{3.12}$$

Finally we use the relation

$$\mathrm{Im}\,\epsilon = \frac{4\pi\sigma}{\omega}, \tag{3.13}$$

where σ is the conductivity to obtain

$$\Gamma_d = \frac{1}{2\hbar\omega}\int_{\text{in}}\sigma|\mathbf{E}|^2 d\mathbf{r}. \tag{3.14}$$

The interpretation of the right-hand side is that it is the power delivered to Ohmic heating divided by the photon energy. This is the nonradiative decay rate if the magnitude of the dipole is chosen to correspond to the molecule being excited with one quantum of energy.

The expression for the nonradiative decay rate becomes

$$\Gamma_d = \alpha\omega\,\mathrm{Im}\sum_{n=0}^{\infty}\sum_{m=0}^{n} T_{nm}\,\hat{\mu}_d\cdot\overleftrightarrow{\Omega}^{dd}\cdot\hat{\mu}_d. \tag{3.15}$$

Here $\overleftrightarrow{\Omega}^{dd}$ is given by Eqs. (2.32a)–(2.32f) but with a replaced by d. A similar expression may be found for the nonradiative decay rate of the acceptor by replacing d by a in the above equation. We have expressed Γ_d in terms of the static polarizability α rather than in terms of the transition dipole so that the classical nature of the formula is manifest. Thus we have replaced $|\mu_d|^2$ by $2\alpha\hbar\omega$.

We note in passing that the real parts of U_{dd} and U_{aa} are associated with the level shifts of the molecules due to the interaction with the solid state particle.

IV. RADIATIVE DECAY

Just as the nonradiative decay of a molecule near a particle may be enhanced, the same is true of the radiative decay. The donor molecule induces a dipole in the particle in response to its own dipole. The coherent sum of these dipoles is responsible for the net emission at the donor molecule frequency. (In addition a similar effect can occur at the acceptor molecule frequency.) In previous work we have derived formulas for the enhanced dipole moment of the system for a collinear geometry. The generalizations of this formula is readily obtained from the previous formulas.

If we examine the system far away from the molecule or particle we can describe the system as consisting of a dipole

located at the origin: $(\xi_1,\eta_1,\phi_1)=(1,0,0)$. The field due to such a dipole may be obtained from Eq. (2.17) and is

$$\Phi=\frac{F_{10}}{f}Q_1(\xi)P_1(\eta)\mu_\eta+\frac{F_{11}}{f}Q_1^1(\xi)P_1^1(\eta)\times[\mu_\xi\cos\phi+\mu_\phi\sin\phi]. \tag{4.1}$$

On the other hand, an expression for Φ has been given in Eq. (2.11b). Substituting the values for A'_{nm} and B'_{nm} of Eq. (2.18) leads to an alternate expression for Φ in terms of the molecular dipole components. Equating the coefficients of terms with similar angular behavior leads to the following:

$$\begin{bmatrix}\mu_\xi\\ \mu_\eta\\ \mu_\phi\end{bmatrix}=\begin{bmatrix}F_{\xi\xi} & F_{\xi\eta} & F_{\xi\phi}\\ F_{\eta\xi} & F_{\eta\eta} & F_{\eta\phi}\\ F_{\phi\xi} & F_{\phi\eta} & F_{\phi\phi}\end{bmatrix}\begin{bmatrix}\mu_{\xi_d}\\ \mu_{\eta_d}\\ \mu_{\phi_d}\end{bmatrix}, \tag{4.2}$$

where μ_{ξ_d},μ_{η_d}, and μ_{ϕ_d} are the donor molecular coordinates and

$$F_{\xi\xi}=\frac{f\cos\phi_d}{h_{\xi_d}}P_1^1(\eta_d)\times\left\{[P_1^1(\xi_d)]'+\frac{1-\epsilon}{\Delta_{11}}P_1^1(\xi_0)P_1^1(\xi_0)[Q_1^1(\xi_d)]'\right\}, \tag{4.3a}$$

$$F_{\xi\eta}=\frac{f\cos\phi_d}{h_{\eta_d}}[P_1^1(\eta_d)]'\times\left\{P_1^1(\xi_d)+\frac{1-\epsilon}{\Delta_{11}}P_1^1(\xi_0)[P_1^1(\xi_0)]'Q_1^1(\xi_d)\right\}, \tag{4.3b}$$

$$F_{\xi\phi}=-\frac{f\sin\phi_d}{h_{\phi_d}}P_1^1(\eta_d)\times\left\{P_1^1(\xi_d)+\frac{1-\epsilon}{\Delta_{11}}P_1^1(\xi_0)[P_1^1(\xi_0)]'Q_1^1(\xi_d)\right\}, \tag{4.3c}$$

$$F_{\eta\xi}=\frac{f}{h_{\xi_d}}P_1(\eta_d)\times\left\{[P_1(\xi_d)]'+\frac{1-\epsilon}{\Delta_{10}}P_1(\xi_0)[P_1(\xi_0)]'[Q_1(\xi_d)]'\right\}, \tag{4.3d}$$

$$F_{\eta\eta}=\frac{f}{h_{\eta_d}}[P_1(\eta_d)]'\times\left\{P_1(\xi_d)+\frac{1-\epsilon}{\Delta_{10}}P_1(\xi_0)[P_1(\xi_0)]'Q_1(\xi_d)\right\}, \tag{4.3e}$$

$$F_{\eta\phi}=0, \tag{4.3f}$$

$$F_{\phi\xi}=\frac{f\sin\phi_d}{h_{\xi_d}}P_1^1(\eta_d)\times\left\{[P_1^1(\xi_d)]'+\frac{1-\epsilon}{\Delta_{11}}P_1^1(\xi_0)[P_1^1(\xi_0)]'[Q_1^1(\xi_d)]'\right\}, \tag{4.3g}$$

$$F_{\phi\eta}=\frac{f\sin\phi_d}{h_{\eta_d}}[P_1^1(\eta_d)]'\times\left\{P_1^1(\xi_d)+\frac{1-\epsilon}{\Delta_{11}}P_1^1(\xi_0)[P_1^1(\xi_0)]'Q_1^1(\xi_d)\right\}, \tag{4.3h}$$

$$F_{\phi\phi}=\frac{f\cos\phi_d}{h_{\phi_d}}P_1^1(\eta_d)\times\left\{P_1^1(\xi_d)+\frac{1-\epsilon}{\Delta_{11}}P_1^1(\xi_0)[P_1^1(\xi_0)]'Q_1^1(\xi_d)\right\}. \tag{4.3i}$$

The decay rate due to radiation may be written as

$$\Gamma_{r,d}=\Gamma^0_{r,d}\left|\frac{\vec{\vec{F}}\cdot\mu_d}{\mu_d}\right|^2. \tag{4.4}$$

Here $\Gamma^0_{r,d}$ is the radiative decay rate of the free molecule and $\Gamma_{r,d}$ is the rate in the presence of the particle.

V. RESULTS AND DISCUSSION

In the previous sections we have developed a theory for the energy transfer between a donor and acceptor molecule in the presence of a small solid state particle in the shape of a spheroid. The energy transfer may be enhanced by having the particle actively assist in the transfer process. Secondly, the presence of the particle opens up decay channels which would tend to compete with the energy transfer. A complete theory of energy transfer must take these two aspects into account.

In order to understand how energy transfer may be enhanced consider first the case of energy transfer in the absence of the particle. It is brought about by the dipole–dipole interaction. The dipole operator of the donor molecule deexcites the donor while the dipole operator of the acceptor molecule excites the acceptor. The strength of the interaction falls off rapidly with distance, as r^{-3} and the energy transfer rate, which is proportional to the square of the matrix element of this interaction, falls off as r^{-6}. If a solid state particle is in the presence of the molecules, however, the donor dipole will induce multipole moments on the particle. In particular, the dipole that is induced on the particle may be much larger than the donor dipole itself. This phenomenon is partly responsible for the enhanced electrodynamic processes on rough surfaces or near small particles, including surface-enhanced Raman scattering, enhanced fluorescence, enhanced photochemistry and enhanced second-harmonic generation. The degree of enhancement of the dipole depends on the shape of the particle, the location of the molecular dipole and whether or not a resonance of the solid is excited. Once the dipole (and other multipoles) have been excited in the particle, the fields set up by the moment(s) can couple to the acceptor dipole and affect the energy transfer. Whereas in the absence of the particle the rate of energy transfer depends primarily on the molecule–molecule separation, now the energy transfer depends primarily on the molecule-solid distance. For a large particle size the molecules may be rather far apart and still have rapid energy transfer occur. However, if the molecules are far away from the solid, then the solid has little influence on the transfer process again. One of the main goals of this work is to define precisely how the location of the molecules influence transfer dynamics. We shall see the concept of "activity zones" emerge.

We have developed side-by-side a theory for energy transfer and for nonradiative decay as well as for radiative decay. Just as the energy transfer depends sensitively on the

location of the molecules relative to the particle, so do the decay losses. At those locations where there will be large internal fields in the solid, one would also expect large Ohmic losses to occur, as we shall see.

In Fig. 1 we show the geometrical arrangement of the molecules and the particle. Figure 2 shows the dependence of the enhancement factor R of Eq. (2.37) on acceptor molecule location $(r_d,\theta_d,\phi_d) = (125\ \text{Å},0°,0°)$, $(\theta_a,\phi_a) = (180°,0°)$, $(\theta_{\mu_d},\phi_{\mu_d}) = (0°,0°)$, and $(\theta_{\mu_a},\phi_{\mu_a}) = (0°,0°)$. The semimajor axis of the spheroid was $a = 100$ Å and the semiminor axis of the spheroid was $b = 50$ Å. The particle is made of silver and curves for several energies $\hbar\omega$ are shown. We note that when the acceptor molecule is close to the particle the enhancement rate grows fairly large, i.e., by as much as five or more orders of magnitude. As the acceptor is moved away from the particle the falloff is at first rapid, but tapers off to a slower falloff at larger distances. Significant enhancements persist out to $r_a = 500$ Å, corresponding to a donor–acceptor separation of 725 Å. There is also evidence in Fig. 2 for a strong resonance at $\hbar\omega = 3.12$ eV. This is close to the energy of the dipolar plasmon for a 2:1 prolate spheroidal silver particle.

In Fig. 3 we study the effect of rotating the acceptor dipole orientation, still keeping everything else in a collinear geometry. Here $(r_d,\theta_d,\phi_d) = (125\ \text{Å},0°,0°)$, $(r_a,\theta_a,\phi_a) = (125\ \text{Å},180°,0°)$, $(\theta_{\mu_d},\phi_{\mu_d}) = (0°,0°)$, $\phi_{\mu_a} = 0°$, and $(a,b) = (100\ \text{Å},50\ \text{Å})$. The energy is held fixed at $\hbar\omega = 3.0$ eV. Two curves are drawn, the solid curve is $|A(\omega)|^2$, where $A(\omega)$ is the interaction energy associated with unit dipoles near a particle and is given by Eqs. (2.28) and (2.29). The dashed curve is $|A_0|^2$, where A_0 is the interaction energy of two free unit dipoles. We note that in both cases the interaction energy is a maximum for a parallel alignment and falls to zero as the acceptor molecule is rotated to a perpendicular configuration. The interaction strengths are seen to differ by more than two orders magnitude. The enhancement ratio $R = |A(\omega)/A_0|^2$ is found not to depend on the acceptor angle orientation, as is shown in Fig. 4. The parameters are the same as in Fig. 3, but curves are given for several energies, $\hbar\omega$.

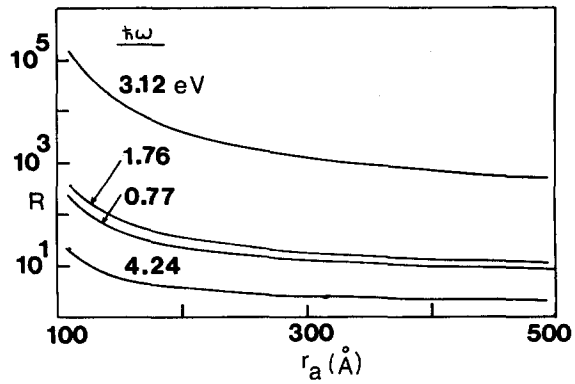

FIG. 2. Enhancement factor R as a function of acceptor location r_a for a collinear geometry. The particle is a prolate silver spheroid with a 2:1 aspect ratio. Curves are drawn for several energies $\hbar\omega$. The donor molecule is held fixed 25 Å from the tip of the particle.

In Fig. 5, we plot the enhancement ratio as a function of the shape of the particle, keeping a collinear geometry. Here a was held fixed at 100 Å but b was allowed to vary between 10 Å (a needle-like structure) to 80 Å (a nearly spherical structure). The donor and acceptor molecules had the same parameters as in Fig. 3. Curves are drawn for several ener-

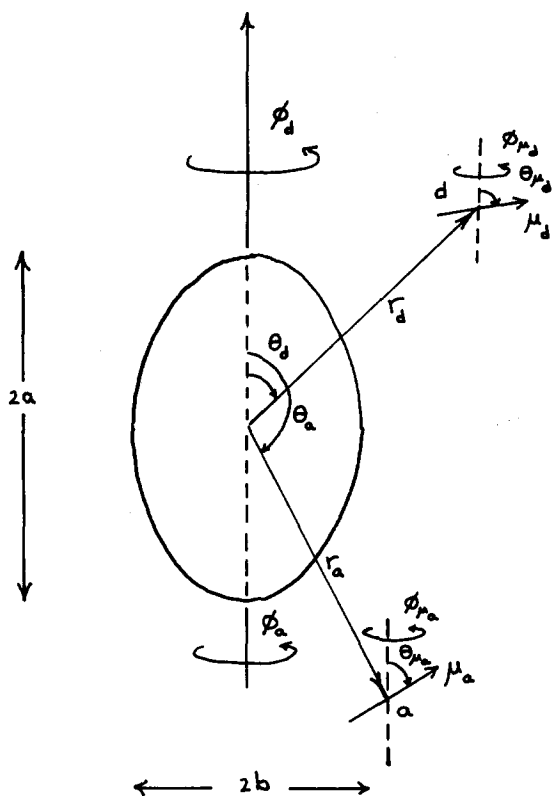

FIG. 1. Geometrical arrangement of donor (d) and acceptor (a) molecules. The locations of d and a are specified by spheroidal coordinates (r_d,θ_d,ϕ_d) and (r_a,θ_a,ϕ_a), respectively. The donor and acceptor dipoles have orientations given by the polar angles $(\theta_{\mu_d},\phi_{\mu_d})$ and $(\theta_{\mu_a},\phi_{\mu_a})$, respectively.

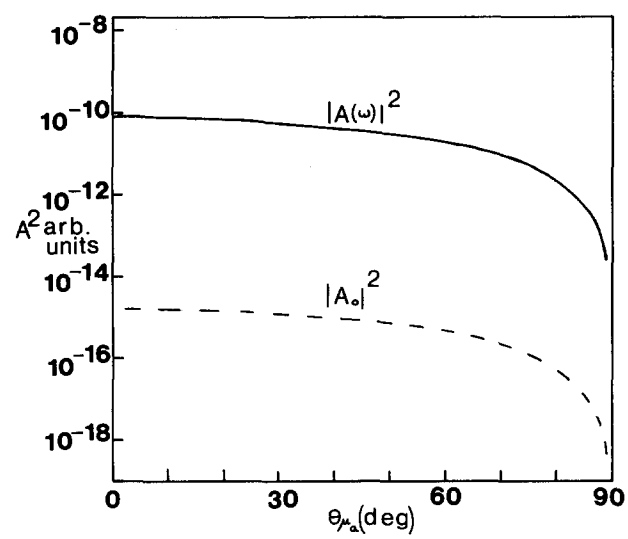

FIG. 3. Absolute square of the interaction energy as a function of acceptor dipole orientation for an otherwise collinear geometry. The solid curve is with the particle present and the dashed curve is with it absent. The donor and acceptor molecules are held 25 Å away from the opposite tips of a prolate 2:1 silver spheroid.

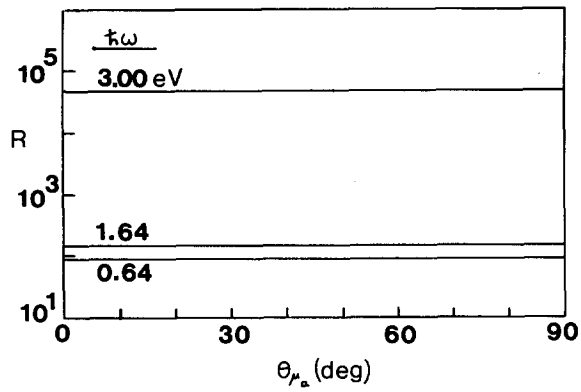

FIG. 4. The enhancement ratio as a function of dipole orientation for the case of Fig. 3. Curves for several energies are shown.

gies. We note the presence of resonance structure appearing in the optical region of the spectrum. As the particle's shape is varied the multipolar resonances of the particle sweep through the spectrum. Evidence for dipolar and quadrupolar resonances appear in this figure. Whenever the resonance peak overlaps with the donor emission band and the acceptor absorption band, we would expect strong energy transfer to occur, as should be clear from an examination of the integrand of Eq. (2.27). This should be kept in mind when attempting to design a particle to optimize the energy transfer.

In Fig. 6 we vary both the angular location of the donor and acceptor molecules, keeping their orientations antiparallel to each other. The angular location is specified by giving the spheroidal coordinate η. The two are related by the formula

$$\tan\theta = \frac{1}{\xi\eta}\,[(\xi^2-1)(1-\eta^2)]^{1/2}. \tag{5.1}$$

A plot is made of $R(\omega)$ vs η_a with $\eta_d = -\eta_a$. Here the molecules are allowed to move over the spheroidal surfaces which pass through the points $z = \pm 125$ Å along the symmetry axes. The molecules are oriented parallel to the normals to these spheroidal surfaces. Curves are drawn for several values of b, keeping a fixed at 100 Å. We note that as the molecules are moved away from the vicinity of the sharp tips of the spheroid, the enhancement factor starts to fall off dramatically. In some cases, there may even be deenhancement occuring. The largest degree of falloff at small η_a values occurs for the sharpest spheroid.

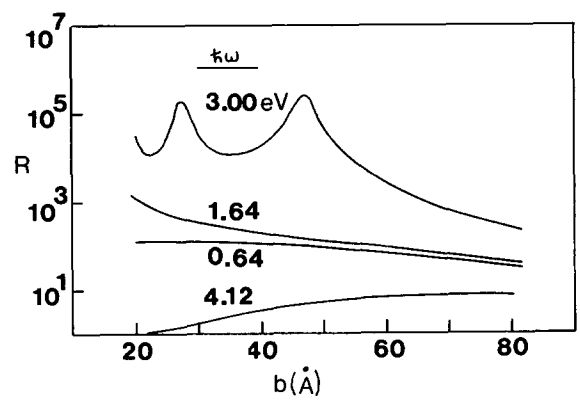

FIG. 5. The enhancement ratio as a function of semiminor axis size b for the collinear geometrical arrangement of Fig. 3. Curves are presented for several energies.

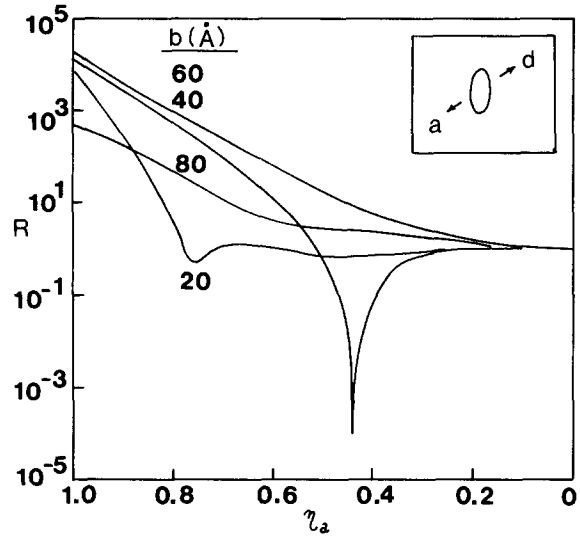

FIG. 6. The enhancement ratio plotted against the spheroidal coordinate associated with angular location of the donor and acceptor. The geometry is depicted in the inset. Curves are presented for several values of b, for fixed a.

The general trends exhibited by Figs. 2 and 6 are consistent with the existence of activity zones near the tips of the spheroid. If the donor and acceptor molecules lie within these activity zones they are able to couple to the solid effectively and efficient energy transfer ensues. If either or both of the molecules lie outside these zones the coupling is diminished and the energy transfer enhancement is quenched. This is in agreement with a lightning rod picture in which electric field lines tend to be concentrated near the sharpest features of a structure. The size of the activity zone may crudely be taken as the characteristic size of the sharpest feature on the solid. For the spheroid this is the radius of curvature of the tip: $r_c = b^2/a$. Thus, if the molecules both lie within a distance r_c of either tip strong energy transfer will occur. If the molecule is allowed to move out of the activity zone in the radial direction, as in Fig. 2, or in an angular direction, as in Fig. 6, the coupling drops off dramatically. Nevertheless, there is still some remnant long range nature of the transfer due the presence of the particle, even when the activity zone is left. This is because it is the distances to the solid that are now more significant than the interparticle distances. It is not until the distance from the particle is large compared with the size of the particle that these will become unimportant.

In Fig. 7 we keep the donor fixed along the symmetry axis and move the position of the acceptor over a spheroidal surface. The donor dipole is fixed parallel to the symmetry axis and the acceptor dipole is perpendicular to the spheroidal surface, so it varies as the acceptor molecule is moved. The geometry is shown in the inset. Here $(r_d,\theta_d,\phi_d) = (125$ Å$,180°,0°)$ $\phi_a = 0°$, $(\theta_{\mu_d},\phi_{\mu_d}) = (0°,0°)$, and $r_a = 125$ Å for $\eta_a = +1$, corresponding to $\theta_a = 0°$. Curves are shown for several values of the energy. As before, $a = 100$ Å and $b = 50$ Å. The results here are consistent with those of Fig. 6, but the falloff with η_a is less dramatic. Since only one molecule is

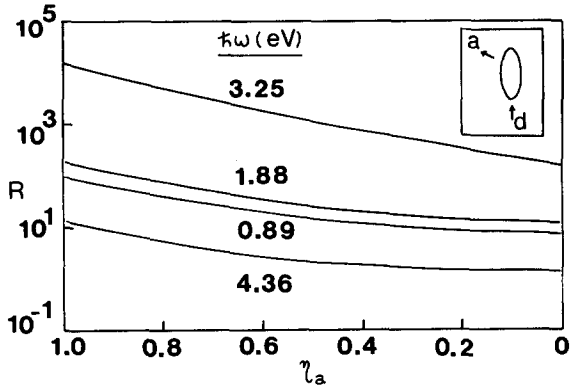

FIG. 7. Enhancement ratio as a function of acceptor location on a spheroidal surface. The acceptor dipole is perpendicular to the spheroid. The geometry is depicted in the inset. Curves are drawn for several energies.

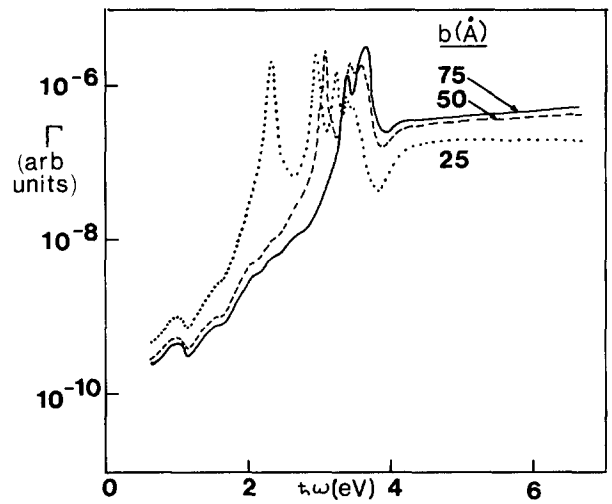

FIG. 9. Damping rate as a function of energy of the molecular resonance for several shapes of the solid. Here $a = 100$ Å and $r_a = 125$ Å, in a collinear arrangement.

being taken out of the activity zone while the other molecule remains inside, this is to be expected.

In Fig. 8 a graph is made of the enhancement ratio as a function of energy for spheroids of several different shapes. Here the molecules were held as in Fig. 3. In addition to the resonance structure seen below the plasmon energy we also see a region of deenhancement. The curves are presented here for silver. Curves for other materials may be generated by using the corresponding optical properties of those materials. Having studied the energy transfer rate in some detail, let us now look at the behavior of the decay rate. This too we expect to depend strongly on such factors as the molecular location and orientation. In Fig. 9 we present the nonradiative decay rate as a function of frequency for the same geometrical arrangements as were used in Fig. 8. The dipole is taken to be of unit strength. We see that when there is a resonance in energy transfer there is also a peak in the decay rate. Since nonradiative decay is a competition mechanism, having a resonance situation is not a guarantor of efficient energy transfer. However, in affecting energy transfer we want the resonance to be located in the spectral region where there is the most overlap between donor and acceptor bands. This need not necessarily coincide, e.g., with the donor emission band itself. Thus, to some extent, it is possible to "tune" the structure to optimize energy transfer while not at the same time maximizing the nonradiative decay.

In Fig. 10 the decay rate is presented as a function of molecular location on a spheroidal surface as in Fig. 7. Curves are presented for several values of the molecular resonance energy. Some structure is seen as the angular position is varied, which is probably due to the coupling of the molecule to the various multipolar modes of the solid. Associated with each mode is a particular angular pattern and, depending on the energy one of these patterns may tend to dominate the electrodynamics.

In Fig. 11 the damping rate is plotted as a function of dipole orientation θ_μ for several locations on a spheroidal surface. Some sensitivity of the orientation of the dipole relative to the spheroid and its model structure are again noted. As in Fig. 10, the spheroidal surface is taken as one which

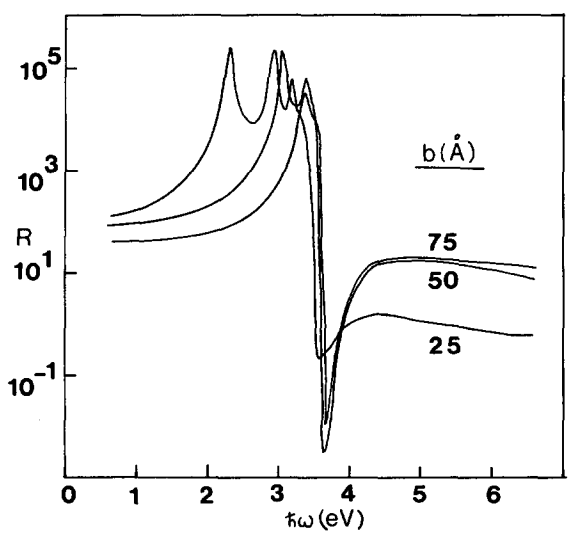

FIG. 8. Enhancement ratio as a function of energy for fixed donor and acceptor positions arranged in a collinear geometry. Curves are presented for several values of the semiminor axis b for semimajor axis $a = 100$ Å.

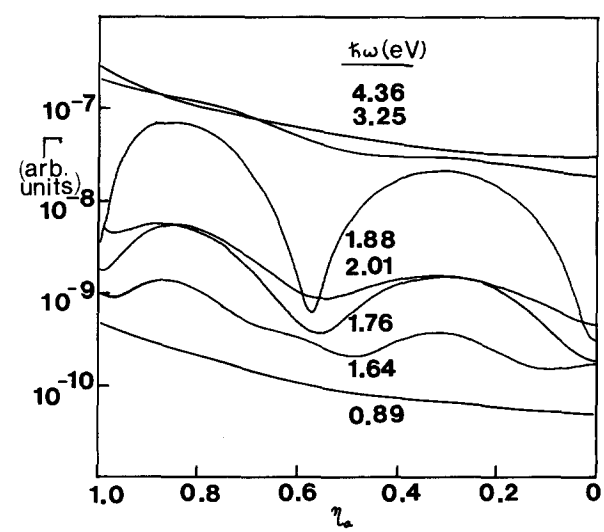

FIG. 10. Damping rate as a function of the molecular location on a spheroidal surface. Curves are shown for several energies.

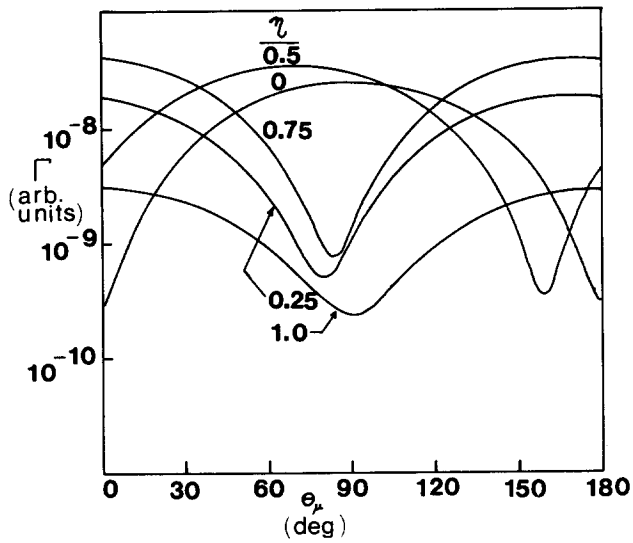

FIG. 11. Damping rate as a function of molecular dipole orientation angle θ_μ for several locations on a spheroidal surface.

passes within 25 Å of the particle along the symmetry axis.

In addition to nonradiative decay there is also enhanced radiative decay. This comes about because the dipole that is induced in the particle adds coherently to the donor dipole and leads to a system dipole which may be much larger than the molecular dipole. Since the decay rate goes as the square of this dipole, radiative decay can be significant. These effects have been considered by us[11] in a previous work for the case of a collinear geometry.

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