

ACCELERATED ENERGY TRANSFER BETWEEN MOLECULES NEAR A SOLID PARTICLE *

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The Forster–Dexter theory of energy transfer between molecules is generalized to include the effects of a nearby solid state particle. It is found that the energy transfer rate between a donor and acceptor molecule may be enhanced by many orders of magnitude when the molecular transition frequencies lie in the vicinity of the resonance frequency of the particle and when the particle possesses sharp features. Due to increased damping near the particle, however, this may or may not lead to increased acceptor molecule radiation.

In recent years considerable attention has been focused on elementary molecular processes occurring in the proximity of small solid state particles or rough surfaces. It was found that the cross sections or rates for these processes could be dramatically altered from what they would be in the absence of these particles. Included in such studies are: surface-enhanced Raman scattering [1] from molecules on rough surfaces, in colloidal suspensions, or on island films; the modification of fluorescence lifetimes and yields near island films [2]; photochemical reaction rates [3]; and non-linear optical effects [4]. In all of these phenomena particularly strong modifications occur if the molecular resonance frequency coincides with the resonance frequency of the solid state particle. Stated simply, the reason for this is that under such conditions the molecule and solid couple very strongly and are able to share their electrodynamic properties readily. Thus, for example, the electric field in the vicinity of a particle which is resonating with light at a particular frequency can become very large and this field can affect processes going on in a nearby molecule. Likewise, the physical shape of the particle can act in such a way as to increase the field near an adjacent molecule.

In this paper we investigate the process of energy transfer between molecules and ask how its rate is modified by the presence of a nearby particle. Energy transfer between free molecules is described quite well by the standard Forster–Dexter theory [5]. In that theory it is the dipole–dipole interaction which is responsible for the energy transfer process. Our objective will be to see how this picture is affected by the presence of the particle. We shall see that it is possible to define an enhancement factor for the energy transfer rate and that this factor may be very large in practise, even for substantial intermolecular separations.

Our goal will be to study the influence of a small solid state particle on the energy transfer between two nearby molecules. A simplified model will be introduced to enable us to study the general order of magnitude of the energy transfer rate and to draw general conclusions concerning trends. In this model the particle will be taken to be a prolate spheroid with semi-major axis equal to a and semi-minor axis equal to b . The molecules will be taken to be

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polarizable point particles lying along a line passing through the major axis on opposite sides of the spheroid. We will also restrict our attention here to the case where the dipole moments are oriented parallel to the major axis. Relaxation of the above constraints will be relegated to future work.

The prolate spheroidal coordinates of an arbitrary point in space are (ξ, η, ϕ) , the coordinates of the center of molecule 1 (the donor) are $(\xi_d, 1, 0)$, and those of molecule 2 (the acceptor) are $(\xi_a, -1, 0)$. The particle occupies the space $\xi \leq \xi_0 = a/f$ where $f = (a^2 - b^2)^{1/2}$. The complex dielectric constant of the particle is $\epsilon(\omega)$. Non-local electrodynamic effects will be neglected in our description.

In the absence of the particle, the energy transfer rate, k_0 , is determined primarily by the dipole-dipole interaction in accordance with the Forster-Dexter theory. Thus

$$k_0 = (2\pi/r^6) \sum_{f_a} |\langle i_d f_a | [\boldsymbol{\mu}_d \cdot \boldsymbol{\mu}_a - 3\boldsymbol{\mu}_d \cdot \hat{r} \boldsymbol{\mu}_a \cdot \hat{r}] | f_d i_a \rangle|^2 \delta(\epsilon_{f_d} + \epsilon_{i_a} - \epsilon_{f_a} - \epsilon_{i_d}), \quad (1)$$

where r is the intermolecular displacement vector, $|f_d\rangle$ and $|i_d\rangle$ are the excited and de-excited donor states, respectively, and $|f_a\rangle$ and $|i_a\rangle$ are the corresponding acceptor states. The energies of these states are denoted by ϵ_{f_d} , ϵ_{i_d} , ϵ_{f_a} , and ϵ_{i_a} . Atomic units ($\hbar = e = m = 1$) will be used throughout this work. Since collinearity is assumed, we replace the dipole-dipole interaction, $U_0 = (\boldsymbol{\mu}_d \cdot \boldsymbol{\mu}_a - 3\boldsymbol{\mu}_d \cdot \hat{r} \boldsymbol{\mu}_a \cdot \hat{r})/r^3$ by $-2\mu_d\mu_a/r^3$. In spheroidal coordinates, $r = f(\xi_d + \xi_a)$; and the distance of the molecules from the origin are $r_d = f\xi_d$ and $r_a = f\xi_a$.

Next let us calculate the energy transfer rate in the presence of the spheroid, k . It will be assumed that both the spheroid's size and the intermolecular separation are sufficiently smaller than the wave length of light (for the transition $|f_d\rangle \rightarrow |i_d\rangle$) so that retardation effects may be neglected and an electrostatic approximation to electrodynamics will suffice. The problem then reduces to the solution of Laplace's equation for the electrostatic potential produced by two dipoles in the presence of a spheroid. We must find the modified dipole-dipole interaction operator and evaluate the appropriate matrix element for use in eq. (1).

The potential at an arbitrary point in space is

$$\begin{aligned} \Phi &= \sum_n A_n P_n(\xi) P_n(\eta), & \xi < \xi_0, \\ &= \sum_n B_n Q_n(\xi) P_n(\eta) + \Phi_d + \Phi_a, & \xi > \xi_0, \end{aligned} \quad (2)$$

where A_n and B_n are a set of coefficients to be determined by matching boundary conditions, and Φ_d and Φ_a are the potentials produced by the point dipoles:

$$\Phi_d = (\mu_d/h_{\xi_d}) \sum_n [(2n+1)/f] [\partial P_n(\xi_d^d) Q_n(\xi_d^d)/\partial \xi_d] P_n(\eta), \quad (3a)$$

$$\Phi_a = -(\mu_a/h_{\xi_a}) \sum_n [(2n+1)/f] (-)^n [\partial P_n(\xi_a^a) Q_n(\xi_a^a)/\partial \xi_a] P_n(\eta). \quad (3b)$$

Here ξ_d^i denotes the lesser of ξ and $\xi_d = r_d/f$ and ξ_d^l denotes the larger of the two. The metric coefficients (we follow the notation of ref. [6]) have been denoted by h_{ξ_i} . Employing the boundary conditions that potential and normal component of electric displacement vector at the particle surface be continuous allows us to solve for A_n and B_n :

$$A_n = [(2n+1)/f(\xi_0^2 - 1) Q_n(\xi_0) P_n'(\xi_0) (\epsilon + \bar{\epsilon}_n)] [\mu_d Q_n'(\xi_d)/h_{\xi_d} - (-)^n \mu_a Q_n'(\xi_a)/h_{\xi_a}], \quad (4a)$$

$$B_n = [(2n+1) P_n(\xi_0)/f(\xi_0^2 - 1) Q_n(\xi_0)] [\mu_d Q_n'(\xi_d)/h_{\xi_d} - (-)^n \mu_a Q_n'(\xi_a)/h_{\xi_a}], \quad (4b)$$

where

$$\bar{\epsilon}_n = -P_n(\xi_0)Q_n'(\xi_0)/Q_n(\xi_0)P_n'(\xi_0). \quad (5)$$

The interaction energy between the dipoles, as modified by the presence of the spheroid, is

$$U = -\boldsymbol{\mu}_d \cdot \mathbf{E}^d = -\boldsymbol{\mu}_a \cdot \mathbf{E}^a. \quad (6)$$

Here $\mathbf{E}^{(i)}$ denotes that part of the electric field at the position of dipole i arising from the presence of the other dipole. It is obtained from eqs. (2)–(4) by omitting the terms proportional to μ_i and evaluating the negative of the gradient. After some lengthy algebra we find

$$U = (\mu_d \mu_a / h_{\xi_d} h_{\xi_a}) \sum_n [(2n+1)/f] (-)^n P_n'(\xi_{<}^{da}) Q_n'(\xi_{>}^{da}) \\ + \sum_n (-)^n [(2n+1)/f] [(1-\epsilon)/(\epsilon + \bar{\epsilon}_n)] [P_n(\xi_0)/Q_n(\xi_0)] (\mu_d \mu_a / h_{\xi_d} h_{\xi_a}) Q_n'(\xi_d) Q_n'(\xi_a). \quad (7)$$

Here $\xi_{<}^{da}$ denotes the lesser of ξ_d and ξ_a and $\xi_{>}^{da}$ denotes the greater of these. The first term in eq. (7) may be evaluated using the sum rule:

$$(\xi_d + \xi_a)^3 \sum_n (n + \frac{1}{2}) (-)^n P_n'(\xi_{<}^{da}) Q_n'(\xi_{>}^{da}) = 1. \quad (8)$$

We form the ratio of U to the free dipole–dipole interaction, U_0 , to get

$$U = A(\omega) U_0, \quad (9)$$

where A may be called the interaction energy amplification factor and is given by

$$A(\omega) = 1 + \sum_{n=1}^{\infty} (n + \frac{1}{2}) (-)^n [(1-\epsilon)/(\epsilon + \bar{\epsilon}_n)] [P_n(\xi_0)/Q_n(\xi_0)] Q_n'(\xi_d) Q_n'(\xi_a) (\xi_d + \xi_a)^3. \quad (10)$$

Having obtained the expression for A for the case of a spheroid, let us now specialize to the case of a sphere. As the spheroid approaches a sphere, $b \rightarrow a$ so $f \rightarrow 0$ and $\xi_0 \rightarrow \infty$. Likewise $\xi_d \rightarrow \infty$ and $\xi_a \rightarrow \infty$. After some algebra we find the following expression for A :

$$A(\omega) = 1 + \frac{1}{2} [(r_d + r_a)/a]^3 \sum_{n=1}^{\infty} (-)^n (n+1)^2 (a^2/r_d r_a)^{n+2} (\epsilon - 1)/(\epsilon + \tilde{\epsilon}_n), \quad (11)$$

where $\tilde{\epsilon}_n$ represents the limit of $\bar{\epsilon}_n$ as $\xi_0 \rightarrow \infty$:

$$\tilde{\epsilon}_n = (n+1)/n. \quad (12)$$

Note that molecular properties enter into these results only through the ω dependence of $\epsilon(\omega)$, which should be calculated at the donor frequency.

The sums appearing in eqs. (10) and (11) are infinite sums of the form $\sum_{n=1}^{\infty} T_n$. In evaluating these sums we replace the sums by a finite number of terms and check to see that convergence is achieved as the number of terms is increased. In order to accelerate the convergence it was found that the sum $T_1 + \dots + T_{N-3} + (7T_{N-2} + 4T_{N-1} + T_N)/8$ converges rapidly even in cases where $T_1 + \dots + T_N$ converges only very slowly, so this method of acceleration of the convergence was adopted throughout the numerical work.

The basic theoretical results are embodied in eqs. (10) and (11) in which expressions for the energy transfer rate enhancement factor are given. The reasons for the enhancement are simple to state. A fluctuating dipole in the donor molecule induces a fluctuating dipole in the dielectric spheroid. This dipole may be much larger than the molecular dipole of the donor. This will be especially true if a resonance frequency of the spheroid coincides with the molecular transition frequency. The sharpness of the spheroid, determined by the aspect ratio a/b , also

plays a role in enhancing the dipole moment. Finally the proximity of the molecule to the spheroid is important in determining the degree of enhancement. Once this sympathetic dipole moment is established in the spheroid, it produces an electric field which couples to the acceptor molecule and drives an upward transition. The strength of this electric field can be much larger than that field which would have existed had the spheroid not been present.

In the free molecular case, where no particle is present, it is customary to express the energy transfer rate, k_0 , of eq. (1) as an integral over frequencies of the product of the acceptor absorption cross section, $\sigma(\omega)$, and the donor emission rate per unit angular frequency, $G(\omega)$:

$$k_0 = (3c^4/2\pi r^6) \int_{-\infty}^{\infty} d\omega G(\omega)\sigma(\omega)/\omega^4. \quad (13)$$

When the particle is present, the energy transfer rate, k , is given by

$$k = (3c^4/2\pi r^6) \int_{-\infty}^{\infty} d\omega [G(\omega)\sigma(\omega)/\omega^4] |A(\omega)|^2, \quad (14)$$

with $A(\omega)$ given by eq. (10). The transfer rate enhancement factor may be defined as

$$\rho = k/k_0. \quad (15)$$

In order to obtain estimates for the above rates it is convenient to adopt lorentzian models for $\sigma(\omega)$ and $G(\omega)$. Thus

$$\sigma(\omega) = \frac{4\pi^2\omega|\mu_a|^2}{\hbar c} \frac{\gamma_a/2\pi}{(\omega_a - \omega)^2 + (\gamma_a/2)^2}, \quad (16)$$

and

$$G(\omega) = \frac{4\omega^3|\mu_d|^2}{3\hbar c^3} \frac{\gamma_d/2\pi}{(\omega_d - \omega)^2 + (\gamma_d/2)^2}, \quad (17)$$

where $|\mu_a|^2$ and $|\mu_d|^2$ denote the square of the transition dipoles for the acceptor and donor, ω_a and ω_d denote the resonance frequencies, and γ_a and γ_d denote the lorentzian widths, and are typical of the inhomogeneous broadening that is present. Insertion of eqs. (16) and (17) into (13) and (14) gives

$$k_0 = \frac{72\pi c^6}{\hbar^2 r^6 (\omega_a \omega_d)^3} \Gamma_{r,d}^0 \Gamma_{r,a}^0 \frac{(\gamma_a + \gamma_d)/2\pi}{(\omega_d - \omega_a)^2 + (\gamma_a + \gamma_d)^2/4}, \quad (18)$$

and

$$\rho = \frac{1}{2\pi} \frac{\gamma_a \gamma_d}{\gamma_a + \gamma_d} [(\omega_d - \omega_a)^2 + (\gamma_a + \gamma_d)^2/4] \int_{-\infty}^{\infty} d\omega \frac{|A(\omega)|^2}{[(\omega_d - \omega)^2 + (\gamma_d/2)^2] [(\omega_a - \omega)^2 + (\gamma_a/2)^2]}, \quad (19)$$

where $\Gamma_{r,d}^0$ and $\Gamma_{r,a}^0$ denote the free radiative decay rates of the donor and acceptor molecules.

Consider a process in which the donor molecule is excited and its energy is transferred to the acceptor molecule via the particle. If one wishes to monitor the modified transfer rate experimentally, one could examine S , the ratio of the emission from the acceptor with the particle present to the emission from the acceptor without the particle. The presence of the particle modifies not only the energy transfer rate, but also the radiative and non-radiative decay rates of the particles [2]. Thus, in our model, the radiative rate of the acceptor is

$$\Gamma_{r,a} = \Gamma_{r,a}^0 |1 + \{[1 - \epsilon(\omega_a)]/[\epsilon(\omega_a) + \bar{\epsilon}_1]\} \xi_0 Q'_1(\xi_a)/Q_1(\xi_0)|^2, \quad (20)$$

and the non-radiative decay rate of the acceptor is

$$\Gamma_{nr,a} = \Gamma_{nr,a}^0 - (3c^3/2f^3)(\Gamma_{r,a}^0/\omega_a^3) \text{Im} \sum_n (2n+1) \{(1 + \bar{\epsilon}_n)/[\epsilon(\omega_a) + \bar{\epsilon}_n]\} [P_n(\xi_0)/Q_n(\xi_0)] [Q_n'(\xi_a)]^2, \quad (21)$$

where $\Gamma_{nr,a}^0$ denotes the non-radiative decay of the acceptor in the absence of the particle. The acceptor radiation may be written as the product of the transfer yield from the donor and the acceptor emission yield

$$I_{r,a} = [k/(\Gamma_{r,d} + \Gamma_{nr,d} + k)] \Gamma_{r,a}/(\Gamma_{r,a} + \Gamma_{nr,a}) \quad (22)$$

(where we are neglecting back-transfer from the acceptor to the donor). The ratio S is then

$$S = I_{r,a}/I_{r,a}^0, \quad (23)$$

where the superscript "0" denotes the absence of the particle.

Another quantity of possible experimental interest is T , the ratio of the initial growth of acceptor emission in the presence of the particle to that in the absence of the particle. This quantity is obtainable from a time-resolved spectroscopy experiment. One may readily show from rate equation considerations that

$$T = (\Gamma_{r,a}/\Gamma_{r,a}^0)\rho. \quad (24)$$

Since the radiative rates are themselves enhanced, according to eq. (20), one would expect an even greater enhancement for T than for ρ .

Fig. 1 illustrates the variation of the energy transfer rate enhancement factor, $|A(\omega)|^2$, with positions r_d and r_a of the donor and acceptor molecules situated along a line passing through the major axis. In fig. 1 we idealize matters somewhat and take the acceptor and donor molecules to be identical. Note that $|A(\omega)|^2$ is a symmetric function of r_d and r_a . Curves A and B correspond to a slightly prolate silver spheroid with $a = 100 \text{ \AA}$ and $b = 63.92 \text{ \AA}$ possessing a dielectric constant ϵ appropriate to bulk silver at a photon energy of 3.25 eV. It is assumed that the molecules are in resonance with the dipolar mode of the sphere. $|A(\omega)|^2$ varies roughly between 10^2 and 10^5 depending on the particular locations of the molecules. Generally, the enhancement factor falls off as either the donor or acceptor molecule is taken away from the sphere. It is interesting to note that significant enhancement

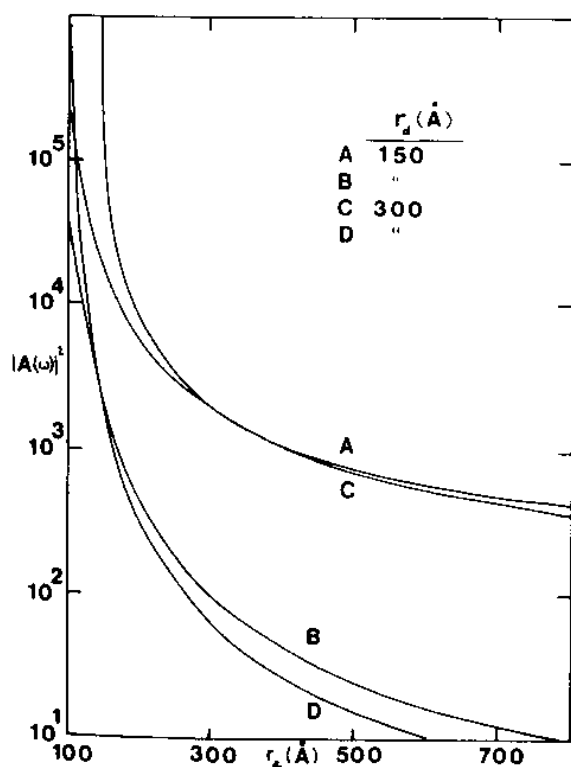


Fig. 1. Energy transfer rate enhancement factor, $|A(\omega)|^2$, as a function of acceptor position, r_a , for various donor positions r_d . Curves A and B are for a mildly prolate silver spheroid and C and D are for a more prolate silver spheroid. The curves correspond to cases where the molecular resonance frequency coincides with the dipole resonance of the particle.

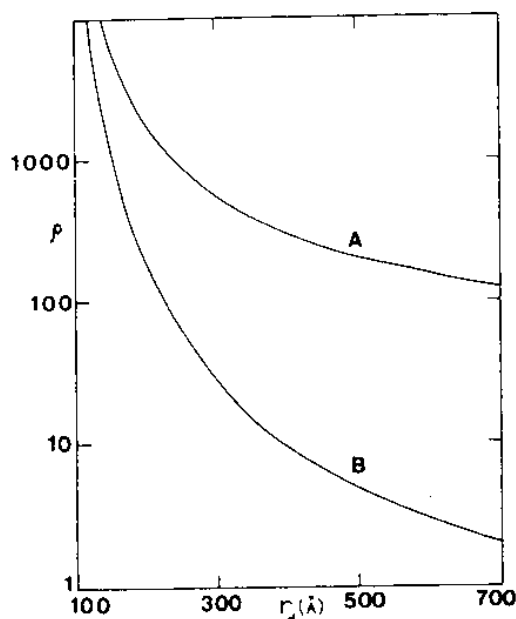


Fig. 2. Energy transfer enhancement ratio ρ , as a function of donor distance, r_d for fixed acceptor distance, r_a . Curve A corresponds to a resonance case and B to a non-resonance case.

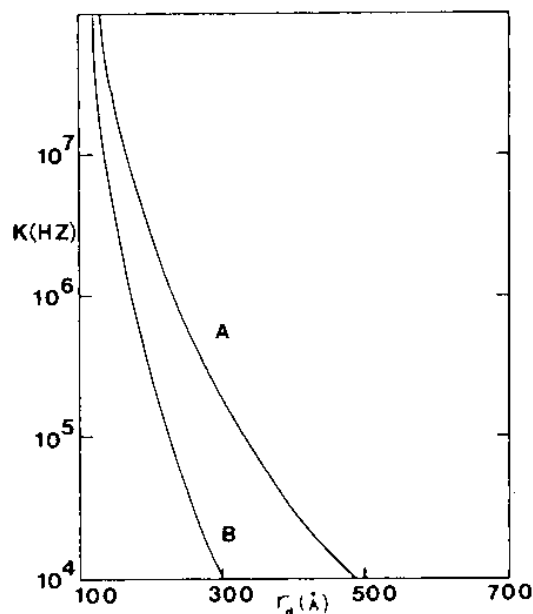


Fig. 3. Absolute energy transfer rate, k , as a function of donor distance, r_d . A and B correspond to resonance and non-resonance cases, respectively.

factors persist out to several sphere radii, illustrating the long ranged nature of the effect.

In curves C and D we present similar curves for R as a function of r_a for various values of r_d , but for a more prolate spheroid. The size of the spheroid is given by $a = 100 \text{ \AA}$ and $b = 29.82 \text{ \AA}$. We again assume resonance with the longitudinal dipole mode. We note that now the enhancement factor may exceed 10^6 as r_d approaches the spheroid. The increase in enhancement over the case of the sphere is due to the "lightning rod effect" – the concentration of field lines near the tips of a sharp object.

In fig. 2 a plot is made of the energy transfer enhancement ratio, ρ , of eq. (19) as a function of r_d , the donor distance from the center of a silver spheroid. The molecular parameters were taken to be $\omega_d = 26000 \text{ cm}^{-1}$, $\omega_a = 25000 \text{ cm}^{-1}$, $\gamma_d = 100 \text{ cm}^{-1}$ and $\gamma_a = 100 \text{ cm}^{-1}$. The acceptor distance was held constant at $r_a = 150 \text{ \AA}$. Two curves are shown. In curve A the spheroid semi-axes were taken as $a = 100 \text{ \AA}$ and $b = 57.14 \text{ \AA}$. The dipolar resonance of this spheroid occurs at $\omega = 25500 \text{ cm}^{-1}$ and thus overlaps somewhat with both the donor and acceptor molecules. In curve B the semi-axes are $a = 100 \text{ \AA}$ and $b = 40 \text{ \AA}$, corresponding to a case of non-resonance between the spheroid and the molecules. As expected, resonance leads to an increased transfer enhancement.

In fig. 3 the absolute energy transfer rates, k , are plotted as a function of r_d for fixed r_a . Again the trend noted for fig. 2 applies.

A study was made of the acceptor emission ratio, S , given by eq. (23). In general, S was found to be quite insensitive to the value of r_d for fixed r_a . For a high quantum efficiency donor-acceptor pair ($\Gamma_{nr,d}^0 = \Gamma_{nr,a}^0 = 0$, $\Gamma_{r,d}^0 = \Gamma_{r,a}^0 = 0.001 \text{ cm}^{-1}$) near the resonating spheroid of fig. 2, S was found to be equal to 0.049. As the quantum efficiency was lowered, S was found to increase. Thus for $\Gamma_{nr,d}^0 = \Gamma_{nr,a}^0 = 0.01 \text{ cm}^{-1}$ (and the same radiative rates as above), corresponding to a 10% quantum efficiency, $S = 0.53$. For $\Gamma_{nr,d}^0 = \Gamma_{nr,a}^0 = 0.1 \text{ cm}^{-1}$, corresponding to a 1% quantum efficiency, $S = 4.4$. This trend of increasing S with decreasing quantum efficiency may be traced to the role played by non-radiative damping to the spheroid. For low quantum efficiencies, where the intrinsic non-radiative damping dominates over the spheroid contribution, it is the accelerated energy transfer that is important and S is larger than 1. For high quantum efficiency cases, however, the reverse is true and the non-radiative damping to the spheroid quenches the acceptor emission. A similar phenomenon has been noted in the case of fluorescence on an island film.

Finally we note that in computing the growth rate ratio, T , of eq. (24) one must know $\Gamma_{r,a}/\Gamma_{r,a}^0$. This ratio is

44 for the case of our resonant spheroid of figs. 2 and 3. Thus fig. 2 may also be interpreted as a graph of T versus r_d provided that this factor is included.

In summary, we see that the dynamics of energy transfer in the neighborhood of a particle is strongly modified by the presence of a particle and is sensitive to detailed molecular parameters.

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