

Resonance energy transfer from a fluorescent dye to a metal nanoparticle

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A quantum mechanical theory of the rate of excitation energy transfer from a fluorescent dye molecule to the surface plasmonic modes of a spherical metal nanoparticle is presented. The theory predicts the distance dependence of the transfer rate to vary as $1/d^\sigma$, with $\sigma=3-4$ at intermediate distances, in partial agreement with the recent experimental results. Förster's $1/d^6$ dependence is recovered at large separations. The predicted rate exhibits nontrivial nanoparticle size dependence, ultimately going over to an asymptotic, a^3 size dependence. Unlike in conventional fluorescence resonance energy transfer, the orientational factor is found to vary between 1 and 4. © 2006 American Institute of Physics. [DOI: [10.1063/1.2400037](https://doi.org/10.1063/1.2400037)]

The distance dependence of the rate of resonance energy transfer (RET) from a dye to a metallic (gold, silver) nanoparticle is currently a subject of great interest because of its potential use in many material science and biomedical applications.¹ Fluorescence resonance energy transfer (FRET) is often designated as a “spectroscopic ruler”² because the strong distance dependence of the energy transfer rate provides us with a microscopic scale to measure separations *in vivo*. Naturally, FRET has played a key role in understanding the conformational dynamics of single (bio)molecules in microscopic detail.³⁻⁷ In conventional FRET both the donor and the acceptor are dye molecules suitably placed along the biopolymer. The rate of FRET in such systems, separated by a distance d , is usually analyzed in terms of the following expression,

$$k_{\text{Förster}} = k_{\text{rad}}(R_F/d)^\sigma, \quad (1)$$

where $\sigma=6$ gives the usual Förster expression, k_{rad} is the radiative rate of the donor dye molecule in the absence of the acceptor molecule and R_F is Förster radius expressed in terms of an overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor.^{8,9} At large separation between donor and acceptor, Förster expression has been found to be fairly reliable.¹⁰ At short separation, however, Förster expression has been known to overestimate the rate of energy transfer,¹⁰ primarily due to the inadequacy of the point dipole approximation. Thus, if the separation between D-A system is smaller than the size of the either donor or acceptor, one should expect a deviation from $1/d^6$ distance dependence of the rate. The value of the expo-

nent σ in Eq. (1) thus becomes a subject of considerable interest and importance.

However, this conventional FRET technique employing only dye molecules as donor and acceptor suffers from several limitations, prominent among them is the restriction on the upper limit of separation of only 80 Å. Beyond this distance, the energy transfer becomes too weak to be useful.¹¹ This limitation has motivated a novel use of metallic nanoparticles having prominent absorption spectrum in the visible region as either the acceptor, or more recently, as both donor and acceptor in the FRET.¹² The absorption of light by metal nanoparticles is mainly dominated by surface plasmon (SP) resonance.^{13,14} In such RET systems, separations up to 700 Å can be monitored, which is about 10 times larger than the Förster distances, R_F . This unique feature makes a metal nanoparticle potentially an extremely useful marker in many applications.

A large number of theoretical and experimental studies exist on the rate of radiative and nonradiative energy transfer from a dye to a metal surface.¹⁵⁻²¹ Most of these studies start from a dielectric function of the metal and are essentially based on Mie's well-known theory of surface plasmons. Nevertheless, the distance dependence of RET in such systems remains unsettled. Several theoretical studies have considered transfer of energy from an excited dipole to a metal surface and have predicted the separation to have a d^{-4} (that is, non-Förster) dependence. A recent experimental study²² of energy transfer from a fluorescent dye to a gold nanoparticle of size 1.4 nm has also observed d^{-4} dependence. The experimental results were interpreted in terms of the existing surface excitation transfer (SET) mechanism, appealing to earlier theoretical work cited above.^{15,18}

In this Communication, we adopt a different approach. We present a quantum mechanical formalism to calculate the

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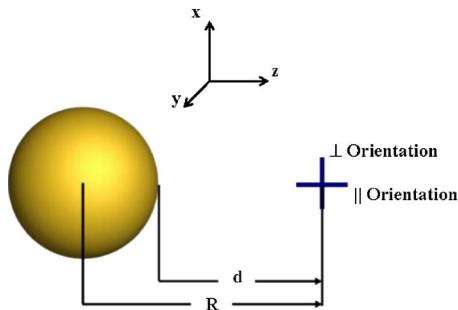


FIG. 1. A schematic illustration of the geometric arrangement of the spherical nanoparticle and the dye molecule in two different orientations, parallel and perpendicular, with respect to the distance vector \mathbf{R} . \mathbf{d} is the distance measured from the surface of the nanoparticle. The figure also shows the coordinate system employed in our calculations.

nonradiative decay rate of a dye molecule in presence of a metallic nanoparticle. The absorption spectra of metal nanoparticles over a wide range of size is dominated by surface plasmon resonance. Therefore, the formalism invokes the transfer of excitation energy to the surface plasmon modes of the nanoparticle. As already mentioned, most of the previous studies on nonradiative energy transfer use Mie's theory²³ which involve macroscopic frequency dependent material dielectric constant of the bulk metal. In this regard, the present treatment of energy transfer is more microscopic and appeals directly to the collective electronic excitations of the nanoparticle, treated quantum mechanically.

The theory makes several interesting predictions. First, we find that Coulombic energy transfer to the surface plasmonic modes indeed has the Förster d^{-6} distance dependence at large separation between the dye and the nanoparticle. However, at distances comparable to (and also for somewhat larger than) the size of the nanoparticle, the distance dependence of the rate is found to vary as $d^{-\sigma}$, with σ between 3 and 4. We also find that the rate of energy transfer depends critically on the size of the nanoparticle and the orientation of the dye molecule with respect to the separation vector \mathbf{R} (see Fig. 1). We believe this is the first detailed report of intermediate distance physics, orientation and size dependence of RET for a dye-nanoparticle system.

THEORETICAL FORMULATION

The initial, donor state of the system $|D^e; A^g\rangle$ consists of an excited dye molecule ($|D^e\rangle$) and a nanoparticle in its ground state ($|A^g\rangle$), which refers to the plasmon vacuum. The *nonradiative* energy transfer from the dye to nanoparticle involve simultaneous de-excitation of molecule and collective excitation (plasmon) of compressible electron gas in the nanoparticle. The final acceptor state of the system is, therefore, represented by $|D^g; A^e\rangle$. The rate of excitation energy transfer depends on the strength of Coulombic interactions and the spectral overlap between the emission and the absorption spectra of the dye and the nanoparticle, respectively. Within the first order time-dependent perturbation theory, the rate of energy transfer is given by Fermi golden rule. The interaction matrix elements can be separated into nuclear factors and the electronic coupling matrix elements (V_{DA}) using

the Franck-Condon principle. The rate of energy transfer within these approximations is given by

$$k_{DA} = \frac{2\pi}{\hbar} |V_{DA}|^2 \sum_{M_D, N_D} \sum_{M_A, N_A} f(E_{N_D}^e) f(E_{M_A}^g) \times |\langle \chi^{D^g}; \chi^{A^e} | \chi^{D^e}; \chi^{A^g} \rangle|^2 \delta(E_{N_D}^e - E_{M_D}^g + E_{M_A}^g - E_{N_A}^e), \quad (2)$$

where

$$V_{DA} = \langle \psi_{M_D}^g; \psi_{N_A}^e | H_I | \psi_{N_D}^e; \psi_{M_A}^g \rangle. \quad (3)$$

H_I is the interaction Hamiltonian and $\langle \chi^{D^g}; \chi^{A^e} | \chi^{D^e}; \chi^{A^g} \rangle$ matrix elements are the nuclear overlap factors, and ψ s are the electronic wave functions. The delta function satisfies the condition of energy conservation. The sum is over all the possible vibrational states of donor molecule and the various other degrees of freedom of the nanoparticle (like the interaction with phonons, electron-hole pair interactions which broadens the absorption spectrum of the nanoparticle) weighed by their initial thermal distribution, $f(E_{N_D}^e)$ and $f(E_{M_A}^g)$, respectively. We assume the Franck-Condon factors to be of the order of unity. The delta function in Eq. (2) can be written as

$$\delta(E_{N_D}^e - E_{M_D}^g + E_{M_A}^g - E_{N_A}^e) = \int_{-\infty}^{\infty} dE \delta(E_{N_D}^e - E_{M_D}^g - E) \delta(E_{M_A}^g - E_{N_A}^e + E). \quad (4)$$

In Förster's theory, the first term is eventually transformed into the donor emission spectrum while the second term gets reduced to the absorption spectrum of the nanoparticle. In the theoretical implementation of the scheme, the sharp resonance lines are replaced with Lorentzians in order to account for the broadening caused by various degrees of freedom. In this work, we take the broadening to be of width 0.025 eV uniformly.

MODELS FOR DYE AND NANOPARTICLE

We model the dye using a "particle in a box" Hamiltonian [expressed in terms of creation (c_n^\dagger) and annihilation (c_n) operators] given by

$$H_D = \sum_n E_n c_n^\dagger c_n, \quad (5)$$

where E_n are the one particle energy levels. The charge density operator of the dye system is given by

$$\rho(\mathbf{r}_D) = \frac{-2e}{L} \sum_{m,n} \psi_m^*(\mathbf{r}_D) \psi_n(\mathbf{r}_D) c_m^\dagger c_n + \frac{e}{L} \sum_m c_m^\dagger c_m, \quad (6)$$

where ψ s are the electronic wave functions which depend on \mathbf{r}_D , the position vector of a point in the dye measured from its center, e is the magnitude of electron charge and $2L$ is the length of the 1D box. The second term accounts for the uniformly distributed positive charge background and ensures the overall charge neutrality of the dye molecule.

As noted above, the most important degrees of freedom of the nanoparticle involved in the energy transfer with the

dye are collective surface modes, namely surface plasmons. Our treatment therefore will consider only the collective excitations of the electron fluid in the nanoparticle. Adapting from earlier work,²⁴⁻²⁶ where the motion of the electron density in the nanoparticle is described within an electrohydrodynamic approximation, the Hamiltonian

$$H_A = \int d^3\mathbf{r}_A \left[\frac{1}{2} \frac{m_e}{e^2 n_0} (\mathbf{j})^2 + \frac{1}{2} \rho \phi + \frac{m_e \beta^2}{2e^2 n_0} \rho^2 \right] \quad (7)$$

describes the quantum dynamics of the plasmonic excitations, where n_0 and m_e denote the mean electron number density of the nanoparticle and electron mass, respectively. Also, \mathbf{j} is the current operator, and ρ is the charge density operator, ϕ is the electrostatic potential (generated by the charge density fluctuation; hence it is dependent on ρ via the Coulomb kernel) all of which depend on the position vector \mathbf{r}_A that describes points in the nanoparticle measured from a reference point (centre, in the case of a spherical nanoparticle). Specializing to a spherical nanoparticle of radius a , the Hamiltonian is diagonalized in the “plasmon basis” and becomes

$$H_A = \sum_{l,m} \hbar \omega_{l,m} a_{l,m}^\dagger a_{l,m}, \quad (8)$$

where the Bosonic operators $a_{l,m}^\dagger(a_{l,m})$ create(destroy) plasmon modes with quantum numbers (l,m) with frequencies $\omega_{l,m}$. The plasmon frequencies of the nanoparticle are determined by obtaining the eigenvalues of the Helmholtz equation

$$\nabla^2 \rho_{l,m}(\mathbf{r}_A) + \alpha^2 \rho_{l,m}(\mathbf{r}_A) = 0, \quad (9)$$

where

$$\alpha^2 = \frac{\omega_{l,m}^2 - \omega_p^2}{\beta^2}, \quad (10)$$

and $\omega_p^2 = e^2 n_0 / m_e \epsilon_0$ is the plasma frequency of the bulk material (ϵ_0 is the permittivity of free space). The quantity β is related to the Fermi velocity (v_F) of the electrons by $\beta^2 = 3v_F^2/5 = (3\hbar^2/5m_e^2)(3\pi^2 n_0)^{2/3}$. Note that the eigenfunctions $\rho_{l,m}$ satisfy the boundary condition equivalent to the vanishing of the current perpendicular to the surface of the nanoparticle. This condition allows the frequencies $\omega_{l,m}$ to be calculated via

$$\frac{l+1}{l} \frac{j_{l+1}(\alpha a)}{j_{l-1}(\alpha a)} = 1 - \frac{\omega_p^2}{\omega_{l,m}^2}, \quad (11)$$

which are independent of the quantum number m (j_l s are the spherical Bessel functions). We note that modes with $\omega_{l,m} < \omega_p$ correspond to surface modes, while those with $\omega_{l,m} > \omega_p$ are bulk modes; our interest at present is restricted to the former. Further, in our simple model $\omega_{l,m}$ depend only on two parameters, namely the electron density n_0 and the radius a of the nanoparticle. It will be shown later that the particle radius has a strong influence on the frequencies of small nanoparticles (i.e., the plasmon frequencies depend on the radius of the particle and the electron density), while for larger particles the frequencies are fractions of the bulk

plasma frequency, essentially independent of the radius. The charge density operator $\rho(\mathbf{r}_A)$ is written as

$$\rho(\mathbf{r}_A) = \sum_{l,m} \rho_{l,m}(\alpha \mathbf{r}_A) = \sum_{l,m} A_{l,m} j_l(\alpha r_A) Y_{l,m}(\theta, \phi), \quad (12)$$

where $Y_{l,m}$ represent the spherical harmonics and $A_{l,m}$ is the “amplitude operator” given in terms of the plasmon Bosonic operators as

$$A_{l,m} = \left(\frac{\epsilon_0 \alpha^2 \hbar \omega_{l,m}}{2a^3} \right)^{1/2} \times \left[\frac{\omega_{l,m}^2}{\omega_p^2} \left(\frac{2l+1}{2} \right) j_{l+1}^2(\alpha a) - j_{l-1}(\alpha a) j_{l+1}(\alpha a) \right]^{-1/2} \times (a_{l,m}^\dagger + a_{l,m}). \quad (13)$$

CALCULATION OF THE TRANSFER RATE

To study the energy transfer between the dye and the nanoparticle, we study

$$H_I = \frac{1}{4\pi\epsilon_0} \int d\mathbf{r}_D \int d^3\mathbf{r}_A \frac{\rho(\mathbf{r}_D)\rho(\mathbf{r}_A)}{|\mathbf{R} - \mathbf{r}_A + \mathbf{r}_D|}, \quad (14)$$

which represents the Coulombic interaction between the two charge densities. We have studied the energy transfer in two different ways. First, the full Coulombic interaction Eq. (14) between D and A is used in the Fermi golden rule [Eq. (2)] to calculate the rate of energy transfer. Second, we study the interaction within the dipole approximation, where the Coulombic interaction is approximated by the dipole interactions among the charge distributions of the dye and the nanoparticle. The dipolar interaction Hamiltonian is given by

$$H_I^{dip} = \frac{1}{4\pi\epsilon_0} \left[\frac{\boldsymbol{\mu}_D \cdot \boldsymbol{\mu}_A - 3(\boldsymbol{\mu}_D \cdot \hat{\mathbf{d}})(\boldsymbol{\mu}_A \cdot \hat{\mathbf{d}})}{d^3} \right], \quad (15)$$

where $\boldsymbol{\mu}_A = \int d^3\mathbf{r}_A \mathbf{r}_A \rho(\mathbf{r}_A)$ and $\boldsymbol{\mu}_D = \int d\mathbf{r}_D \mathbf{r}_D \rho(\mathbf{r}_D)$ are the dipole operators of the nanoparticle and the dye, respectively, d is the distance between the dye and the nanoparticle surface and $\hat{\mathbf{d}}$ is the corresponding unit vector (see Fig. 1).

Standard calculation based on the dipole-dipole interaction Hamiltonian then immediately leads to Förster expression [Eq. (1)], where the Förster radius (R_F) is given by

$$R_F^6 = \frac{9c^4 \kappa^2}{128\pi^3 \epsilon_0^2 k_{rad}} \int_0^\infty \frac{d\omega}{\omega^4} I_D(\omega) \alpha_A(\omega), \quad (16)$$

where $\alpha_A(\omega)$ is the absorption cross-section of the nanoparticle, $I_D(\omega)$ is the emission spectrum of the donor molecule and c is the speed of light, κ is the orientation factor.

The rate of energy transfer is calculated for a donor dye molecule emitting at 520 nm. Specifically, we consider a transition from the first excited level ($n=2$) to the ground state ($n=1$), and this corresponds to $E_2 - E_1 = 2.39$ eV. The acceptor is a nanoparticle with plasma frequency $\omega_p = 5.7 \times 10^{15} \text{ s}^{-1}$ (after Ref. 27; this fixes the value of the electron density n_0). The plasmon frequencies for the pertinent surface modes depend on the size a of the nanoparticle and are plotted in Fig. 2. The size dependence is strong for particles

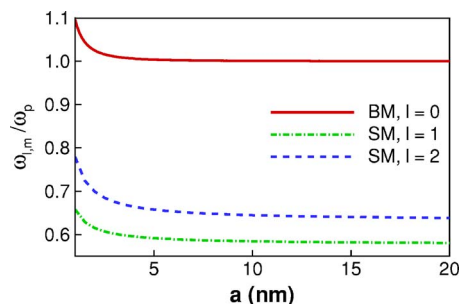


FIG. 2. Dependence of the frequencies of the surface plasmon mode (SM) and the bulk plasmon mode (BM) on the radius (a) of the nanoparticle characterized by plasma frequency $\omega_p = 5.7 \times 10^{15} \text{ s}^{-1}$. The frequencies of the bulk modes with $l=1, 2$ are larger than those for $l=0$ and hence not shown.

with $a \lesssim 7 \text{ nm}$, and asymptotically reaches a plateau value (independent of the size of nanoparticle) for larger particles

$$\omega_l = \omega_p \sqrt{\frac{l}{2l+1}}. \quad (17)$$

Thus the model used in this work reduces to Mie's theory that uses a bulk dielectric function of the form $\Re(\epsilon(\omega)) = 1 - (\omega^2/\omega_p^2)$, when the particle size is large compare to $n_0^{-1/3}$. However, we note again that in small nanoparticles which are of current experimental interest, the particle size dependence of the plasmon frequencies is important. Again, the frequencies of the surface modes are lower than ω_p ; for a nanoparticle of radius $\sim 10 \text{ nm}$, the $l=1$ surface plasmon has an absorption spectrum centered around 590 nm , while the $l=2$ mode is centered around 450 nm . Both of these shift to smaller wavelengths with reduction in the size of the nanoparticle. These considerations show that for a nanoparticle in the range of $5\text{--}30 \text{ nm}$ radius, the $l=1$ ("dipolar" mode) is the predominant accepting mode for energy transfer with a dye emitting in the visible range from $500\text{--}600 \text{ nm}$ (absorption spectrum of gold nanoparticles lie in this range). Therefore, the summation over different l, m modes in Eq. (12) is reduced to summation over different values of m for $l=1$ mode. Since the emission spectra of the dye and the absorption spectra of the nanoparticle has negligible overlap for $l=2$ mode, the rate of energy transfer to this mode can be ignored. However, we shall study the distance dependence of energy transfer to the $l=2$ "quadrupolar" surface mode to further contrast it from the $l=1$ dipolar mode.

DISTANCE DEPENDENCE OF ENERGY TRANSFER RATE

The rate of energy transfer is calculated for both: the full Coulombic interaction and the dipole approximation approach using Eq. (2) where H_I are given by Eqs. (14) and (15), respectively. Note that in the parallel orientation (when the dye is taken along the z axis, see Fig. 1) the contribution to rate is from $l=1, m=0$ mode, while for the perpendicular orientation (when dye is taken along the x - or y -axis, see Fig. 1), contribution comes from a linear combination of $l=1, m=\pm 1$ modes. Figure 3 illustrates that the rate of energy transfer (k_{DA}) is Förster-type at large separations compared to the radius of the nanoparticle. However, at small separa-

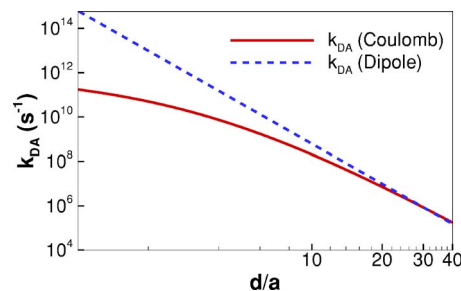


FIG. 3. The distance (d) dependence of the rate of energy transfer (k_{DA}) calculated using full Coulomb interaction (solid line) and the dipole-dipole approximation (Förster theory) (dashed line) for the parallel orientation for nanoparticle of size (a) 3 nm .

tions ($d < 20a$), it breaks down and at distances approximately $d=a$ to $d=4a$, value of σ lies between 3 and 4. Figure 4 explicitly shows the distance dependence of σ for dipolar ($l=1, m=0$) as well as quadrupolar ($l=2, m=0$) excitations. Note that asymptotically σ goes to 8 for quadrupolar surface plasmon excitations, in contrast to 6 for the dipolar mode.

ORIENTATION DEPENDENCE OF ENERGY TRANSFER RATE

Because of the spherical symmetry of the nanoparticle, the orientation dependence is markedly different from that in two-dye systems. In the latter case, depending on angle θ (defined as the angle between $\hat{\mathbf{R}}$ and dye molecule, both being in the same plane), the normalized rate $[k_{DA}/k_{DA(\max)}]$ varies from 0 to 1.¹⁰ If the dyes are oriented perpendicular to each other with the dipole of one of them oriented along $\hat{\mathbf{R}}$ (this corresponds to $\theta=0^\circ$ for one dye and $\theta=90^\circ$ for the other), then there is no energy transfer. On the other hand, when the dyes are parallel to each other, $k_{DA}/k_{DA(\max)}$ is either 1 (both $\theta=0^\circ$) or 0.25 (both $\theta=90^\circ$).

The scenario is different in nanoparticle-dye system due to the "isotropic nature" of the $l=1$ dipole operator. This is seen by noting that $Y_{1,0}(\theta, \phi) \sim \frac{z}{r}$, $Y_{1,\pm 1}(\theta, \phi) \sim (x \pm iy)/\sqrt{2}r$. We can use the "p-orbital" obtained by orthogonal linear combinations of $Y_{1,m}$ s, i.e., $p_z(\theta, \phi) \sim \cos \theta$, $p_x \sim \sin \theta \cos \phi$, $p_y \sim \sin \theta \sin \phi$ to describe the charge density operator of this mode

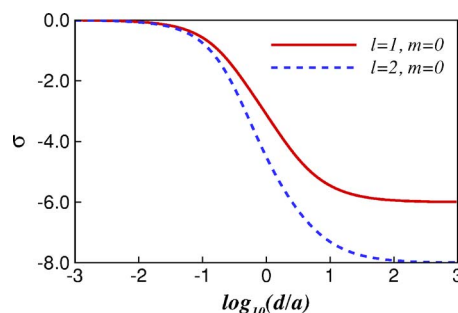


FIG. 4. The distance dependence of the rate exponent σ [see Eq. (1)] for the parallel orientation for $l=1$ (dipolar) and $l=2$ (quadrupolar) mode. Note that at large distances σ approach 6 and 8 for $l=1$ and $l=2$ mode, respectively. At smaller distances, Förster assumption of purely dipolar interaction is not valid and as a consequence the value of σ for $l=1$ mode deviates from 6. The exponent σ is obtained from the calculated rate k_{DA} [using the full Coulomb interaction Hamiltonian Eq. (14)] via $\sigma = d(\log k_{DA})/d(\log d)$.

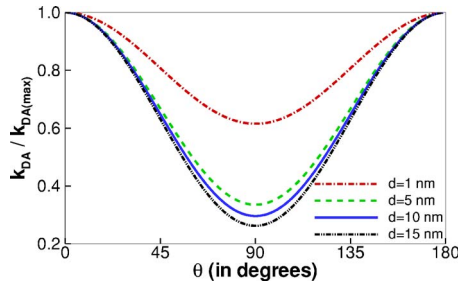


FIG. 5. Dependence of the rate of energy transfer on the orientation of the dye dipole moment μ_D with respect to $\hat{\mathbf{d}}$ [unit vector corresponding to \mathbf{d} (see Fig. 1)], i.e., $\cos \theta = \mu_D \cdot \hat{\mathbf{d}}$. The result shown is for a gold nanoparticle of radius 1 nm, calculated using the full Coulombic interaction Eq. (14).

$$\rho_{l=1}(\mathbf{r}_A) \sim j_1(ar_A)(p_x(\theta, \phi)(a_x^\dagger + a_x) + p_y(\theta, \phi)(a_y^\dagger + a_y) + p_z(\theta, \phi)(a_z^\dagger + a_z)), \quad (18)$$

where a_x^\dagger , etc. replace the $a_{1,m}^\dagger$ operators. The corresponding dipole operator therefore reduces to

$$\mu_A = \mu_A(\mathbf{e}_x(a_x^\dagger + a_x) + \mathbf{e}_y(a_y^\dagger + a_y) + \mathbf{e}_z(a_z^\dagger + a_z)), \quad (19)$$

where \mathbf{e}_i ($i=x, y, z$) are the basis vectors, and

$$\mu_A = \left(\frac{2\pi^3 \epsilon_0 \alpha^2 \hbar \omega_1}{3a^3} \right)^{1/2} \times \left(\frac{3\omega_1^2}{2\omega_p^2} j_2^2(\alpha a) - j_0(\alpha a) j_2(\alpha a) \right)^{-1/2} \int dr_A r_A^3 j_1(ar_A) \quad (20)$$

is the “quantum unit of dipole moment” of the nanoparticle corresponding to the $l=1$ surface plasmon excitation with frequency ω_1 (note the \hbar !). Clearly, under the influence of the Coulombic interaction from the dipole of the dye, the matrix element of $\mu_D \cdot \mu_A$ will reduce to $\mu_D \mu_A$ since μ_D is an “isotropic” operator. This result may also be seen physically by noting that the “ p -orbital” like dipolar surface plasmon that is excited will have its axis in the same direction as the dipole moment of the donor dye, this renders the matrix element of $\mu_D \cdot \mu_A$ direction independent. Therefore, at large d ($d \gg a$), where the dipolar interaction Eq. (15) is accurate, the orientation dependence of the transfer is governed solely by the second term ($\mu_D \cdot \hat{\mathbf{d}})(\mu_A \cdot \hat{\mathbf{d}})$. Since, the matrix element of μ_A is parallel to that of μ_D , it follows that this orientation dependence of the rate is determined solely by the angle between the donor dipole μ_D and the vector $\hat{\mathbf{d}}$. Further, it follows that, in contrast to the conventional FRET, there is no orientation that forbids energy transfer, and at large separation the ratio of the largest rate of transfer to the smallest rate of transfer approaches 4. Interestingly, the orientation dependence becomes weaker at smaller distances (see Fig. 5).

DEPENDENCE OF THE ENERGY TRANSFER RATE ON THE SIZE OF THE NANOPARTICLE

As is evident from the above discussion, the energy transfer rate from a nanoparticle to a given dye is governed by three factors. First is the Coulombic overlap integral

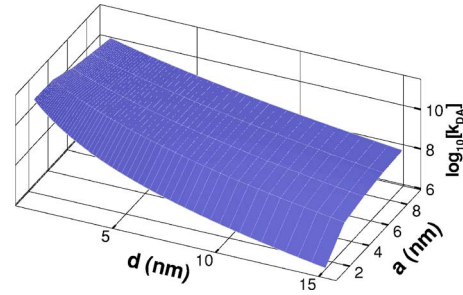


FIG. 6. Energy transfer rate as a function of the radius (a) of the nanoparticle and the distance (d) between the nanoparticle and the dye.

Eq. (3), the other two are the position (surface plasmon frequency) and width (inverse surface plasmon lifetime) of the absorption spectrum of the nanoparticle relative to those of the dye. For a given dye, all three are, in general, functions of the nanoparticle size. We discuss the size dependence at large separation distances ($d \gg a$). Further, the analysis is simpler for large nanoparticles since their plasmon frequencies (see Fig. 2) are, to a very good approximation, independent of the size. Thus the size dependence of the energy transfer rate at large distances for large nanoparticles is determined entirely by the Coulombic overlap integral which is in turn proportional to the quantum unit of dipole moment. For a large nanoparticle we have [from an asymptotic analysis of Eq. (20)]

$$\mu_A \approx \left(\frac{4\pi^3 \epsilon_0 \hbar \omega_p}{9\sqrt{3}} \right)^{1/2} a^{3/2}. \quad (21)$$

It follows that for particles greater than ~ 7 nm, the transfer rate at large distances depends on the volume of the particle. For small nanoparticles both the plasmon frequency and lifetime depend on the size of the particle, hence the overlap of the absorption spectrum of the particle with the emission spectrum of the dye also contributes to the size dependence. We have not studied the plasmon lifetime (inverse width of the absorption spectrum) in this work. Approximating the width of absorption spectrum to be size independent (size dependence of the absorption spectrum has been studied using a time dependent density functional theory, for example, in Ref. 28), we have calculated the size dependence of the transfer rate at various distances as a function of nanoparticle size (see Fig. 6). These results agree with the asymptotics discussed above. Moreover, we find, interestingly, that at small separation distances, the energy transfer rate can even be nonmonotonic with respect to particle size (for small particle sizes). Clearly, a more detailed study including the size dependence of plasmon lifetimes is necessary to uncover the complete picture.

In brief, the present work addresses the important issues of distance and orientation dependence of the rate of excitation energy transfer from a dye to a metal nanoparticle. The results presented here show that for most applications of FRET involving metal nanoparticle, the energy transfer shall involve surface plasmons and the asymptotic distance

dependence remains Förster-type, although $1/d^6$ dependence breaks down at separations $\leq 20a$. The orientation factor varies from 1 to 4 as the dye molecule is rotated along the dye-nanoparticle axis from the perpendicular to the parallel orientation. The formalism adapted uncovers the quantum unit of dipole moment for nanoparticle plasmon excitations and predicts an asymptotic a^3 size dependence of the rate of energy transfer. The present formalism remains unchanged when the nanoparticle is the donor and a fluorescent dye is the acceptor. In addition, our formalism can be easily extended to address the problem of energy transfer between two nanoparticles of different sizes or different metals.

In a recent experimental study, Strouse *et al.* found that the rate of energy transfer from a dye, a FAM moiety, to a Au-nanoparticle (diameter=1.4 nm) can be fitted to a $1/d^4$ distance dependence.²² These authors have suggested that this result may be understood as energy transfer from the dye to the surface modes of the nanoparticle: surface energy transfer (SET).^{15,18} We point out that these theoretical studies^{15,18} are mainly for the interaction of a dye with a large metallic surface: surface of a metallic “half-space”. The d^{-4} dependence, in that context, arises from a large (thermodynamic) degeneracy of surface plasmonic/particle-hole excitations. Our work uncovers that energy transfer from the dye to the surface plasmonic modes of a nanoparticle do not have such large degeneracies giving rise to an asymptotic Förster-type dependence. Moreover, at distances comparable to or even somewhat larger (~ 4 times) than the size of the nanoparticle, this dependence looks apparently as d^{-3} to d^{-4} . All these predictions can be experimentally tested.

The present work unambiguously shows that the transfer to the surface plasmon modes of the nanoparticle can only lead to an asymptotic d^{-6} dependence. We note, however, that one cannot really rule out the involvement of other excitations (such as particle-hole excitations) in the nanoparticle as the cause of the observed d^{-4} distance dependence. Indeed, it is reported that the nanoparticles with size < 2 nm cannot support the surface plasmons,²⁹ as a result for such small particles other energy transfer routes like particle-hole excitations attain importance. We are currently exploring the possibility of multiple particle-hole excitations in the nanoparticle giving rise to a $1/d^4$ dependence.

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