Plasmon-assisted energy transfer near metal nanostructures

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Abstract

A unified theory of plasmon-assisted resonance energy transfer between molecules near a metal nanostructure is developed. In a wide parameter range, transfer is dominated by plasmon-enhanced radiative transfer mechanism.

1. Introduction

Resonance energy transfer [1] (RET) between spatially separated molecules plays an important role in diverse phenomena across physics, chemistry and biology. During past decade, significant advances were made in RET enhancement and control by placing molecules near metal films and nanoparticles (NP) supporting surface plasmons [2–8]. Coupling of molecular dipole to SP in nanostructure opens up new energy transfer channels. Quantum efficiency of RET is governed by the interplay between several processes: excited donor's energy can either be radiated, dissipated, or absorbed by the acceptor, and each of these channels is affected by the nearby metal in its own way. In a closely related phenomenon, plasmon-assisted fluorescence, radiation quantum efficiency strongly depends on distance between molecule and metal surface, d, and measured fluorescence from single molecules attached to a metal NP shows, with decreasing d, emission enhancement followed by quenching [9, 10]. Similarly, when a donor *and* an acceptor molecules are placed nearby a plasmonic nanostructure, energy transfer between them should be affected by dissipation in metal and by plasmon-enhanced radiation. However, traditional model by Gersten and Nitzan [11, 12] and its extensions to planar and composite systems [13–15] incorporate new plasmon-mediated energy transfer channels, but do not account directly for the aforementioned energy loss processes. As a result, these models yield enormous (up to 10^5) RET enhancement that contrasts sharply with a much more modest (~ 10) increase [3–5, 7, 8] and even reduction [2, 6] of measured RET rates. In the paper, we developed a unified theory for RET near metal nanostructures that accounts accurately for the *full* energy flow in the system. We also show that, in a wide parameter range, the dominant RET mechanism is plasmon-enhanced radiative transfer (PERT).

2. Model

The Förster formula [1] for transferred energy, W_{ad}^{F}, between a donor and an acceptor has the form

$$\frac{W_{ad}^{F}}{W_d} = \frac{9}{8\pi} \int \frac{d\omega}{k^4} f_d(\omega) \sigma_a(\omega) \left| D_{ad}^{0} \right|^2 , \tag{1}$$

where W_d is donor's radiated energy, $f_d(\omega)$ is its spectral function, $\sigma_a(\omega)$ is acceptor's absorption cross-section, D_{ad}^{0} is dipoles' electromagnetic coupling at distance r_{ad} and k is the wavevector of light. In the

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near field ($kr_{ad} \ll 1$), dipoles' coupling is dominated by Coulomb interaction, $D^0_{ad} = q_{ad}/r^3_{ad}$ (q_{ad} is the orientational factor), and RET changes with distance as $(r_F/r_{ad})^6$, where r_F is Förster's radius. In the far field ($kr_{ad} \gg 1$), RET is dominated by radiative coupling $|D^0_{ad}| \propto k^2/r_{ad}$ leading to weaker r^{-2}_{ad} dependence [16]. Eq. (1) is derived from the first-order transition probability under perturbation D^0_{ad}.

For molecules near a plasmonic nanostructure, Eq. (1) must be modified. The original model by Gersten and Nitzan [11, 12] and its later extensions to planar and composite systems [13–15] incorporates plasmons into transition intermediate states, but does not account for dissipation in metal and plasmon-enhanced radiation channels. We have derived a generalization of Förster's formula for RET near metal nanostructures that accounts accurately for the full energy flow in the system:

$$\frac{W_{ad}}{W_d} = \frac{9}{8\pi}\int \frac{d\omega}{k^4}\frac{\gamma_d}{\Gamma_d(\omega)}\tilde{f}_d(\omega)\tilde{\sigma}_a(\omega)\left|\tilde{D}_{da}(\omega)\right|^2, \tag{2}$$

where γ_d is donor's free space radiative decay rate, Γ_d is its full decay rate, $\tilde{f}_d$ and $\tilde{\sigma}_a$ are modified spectral function and absorption cross section, respectively, and the coupling $\tilde{D}_{da}$ includes high-order SP-assisted transitions. While the latter is enhanced due to plasmon-mediated channels, the factor γ_d/Γ_d accounts for RET quenching due to donor's energy transfer to the metal and plasmon-enhanced radiation. Note that the absence of this factor leads to spuriously large RET rates [11–14]. Importantly, when donor and acceptor separations from a nanostructure differ substantially, RET is dominated by plasmon-enhanced radiative transfer (PERT) due to the following process [17]: a donor first radiatively excites a SP in the metal which then nonradiatively transfers its energy to the acceptor.

3. Numerical results

Calculations were performed for a donor and acceptor molecules near spherical Ag NP in water with normal dipole orientations relative to NP surface. The near field coupling matrix D_{jk} ($j,k = a,d$) is obtained from the Mie's theory Green's dyadic as $D_{jk} = D^0_{jk} + D^r_{jk} + D^{nr}_{jk}$, where

$$D^r_{jk} = -i\frac{2}{3}k^3\left[1+2\alpha_1\left(\frac{1}{r_j^3}+\frac{1}{r_k^3}\right)+\frac{4|\alpha_1|^2}{r_j^3 r_k^3}\right](\hat{\mathbf{r}}_j\cdot\hat{\mathbf{r}}_k), \qquad D^{nr}_{jk} = -\sum_l \frac{\alpha_l(l+1)^2}{r_j^{l+2}r_k^{l+2}}P_l(\hat{\mathbf{r}}_j\cdot\hat{\mathbf{r}}_k), \tag{3}$$

are, respecyively, the radiative and nonradiative terms, $\alpha_l = R^{2l+1}\frac{l(\epsilon-\epsilon_0)}{l\epsilon+(l+1)\epsilon_0}$ is NP l-pole polarizability, $P_l(x)$ is the Legendre polynomial, $D^0_{ad} = (1+\sin^2\theta/2)/r^3_{ad}$ is free-space coupling, $\hat{\mathbf{r}}_a\cdot\hat{\mathbf{r}}_d = \cos\theta$ is angle between molecules, and angular momenta up to $l = 50$ were included in calculations. Molecules' full decay rates are $\Gamma_j = -\left(3/2k^3\right)\gamma_j D''_{jj}$. We considered a high-yield donor with a broad emission band due to vibrational modes. Molecules' optical bands were modeled by Lorentzians of width 0.05 eV centered at 2.95 eV and 3.2 eV with maximal overlap at about SP energy of 3.08 eV.

In Fig. 1 (left panel), we plot W_{ad} vs. molecules' distance d from the $R = 30$ nm NP surface at $\theta = \pi/3$ with equal $d_a = d_d = d$ and with changing $d_d = d$ at fixed d_a. Three models—the full Eq. (2), its nonradiative part only, and the Gersten-Nitzan model [11, 12]—are compared to Förster's transfer Eq. (1). For $d_d = d_a$, W_{ad} is about three times larger than W^F_{ad} and rapidly decays with d, while for $d/R \ll 1$ it is quenched by metal. There is no enhancement if only the nonradiative channel is included in Eq. (2). In contrast, the Gersten-Nitzan model yields much greater enhancement (up to 10^5) for $d/R \ll 1$ since it includes no quenching effects. However, at fixed d_a and $d_d/R > 1$, the full W_{ad} is the largest one due to the dominant role of the PERT mechanism, as discussed above.

The relative rates of SP-assisted RET and Förster's transfer are highly sensitive to the system's geometry, as illustrated in Fig. 1 (right panel). RET is quenched if both molecules are close to the NP surface but it becomes enhanced if donor-NP distance increases. For $\theta = \pi/3$ RET is enhanced if $d_d > R$, but for $\theta = \pi$ it is strongly enhanced for nearly all d. In fact, NP acts as a hub that couples equally well nearby and remote molecules with different θ while Förster's transfer drops for large r_{ad}. For smaller NP sizes, the role of PERT becomes less pronounced yet remains dominant for larger donor-NP distances.

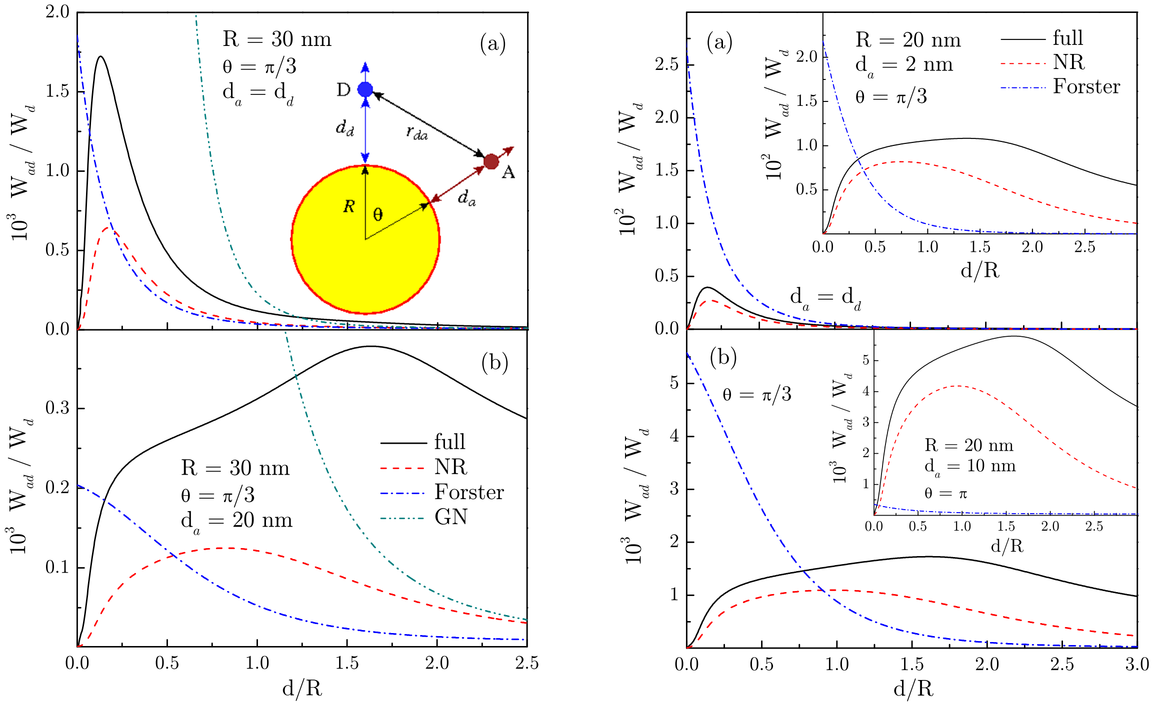

Fig. 1: **Left panel**: RET vs distance for $R = 30$ nm Ag NP is shown at $\theta = \pi/3$ with (a) $d_a = d_d = d$ and (b) $d_a = 20$ nm, $d_d = d$ using the full Eq. (2), the nonradiative (NR) channel only, Förster's transfer Eq. (1), and the Gersten-Nitzan (GN) model. **Right panel**: RET vs distance for $R = 20$ nm Ag NP is shown (a) at $\theta = \pi/3$ with $d_a = d_d$ and $d_a = 2$ nm (inset) and (b) with $d_a = 10$ nm at $\theta = \pi/3$ and $\theta = \pi$ (inset) using full, nonradiative (NR), and Förster models.

4. Conclusion

In summary, a theory of resonance energy transfer between donors and acceptors near a plasmonic structure is presented which maintains a correct balance between transfer, dissipation, and radiation that is essential for interpretation of experimental data. The plasmon-enhanced radiative transfer is shown to be the dominant mechanism in a wide parameter range. This work was supported by the NSF under Grants No. DMR-0906945 and No. HRD-0833178.

References

[1] T. Förster, Ann. Phys., vol. 437, p. 55, 1948.
[2] A. Leitner and H. Reinisch, Chem. Phys. Lett., vol. 146, p. 320, 1988.
[3] J. R. Lakowicz *et al.*, J. Fluoresc., vol. 13, p. 69, 2003.
[4] P. Andrew and W. L. Barnes, Science, vol. 306, p. 1002, 2004.
[5] J. Zhang, Y. Fu, and J. R. Lakowicz, J. Phys. Chem. C, vol. 111, 50 (2007).
[6] F. Reil, U. Hohenester, J. R. Krenn, and A. Leitner, Nano Lett., vol. 8, p. 4128, 2008.
[7] K. Y. Yang, K. C. Choi, and C. W. Ahn, Opt. Express, vol. 17, p. 11495, 2009.
[8] K. H. An, M. Shtein, and K. P. Pipe, Opt. Express, vol. 18, p. 4041, 2010.
[9] P. Anger, P. Bharadwaj, and L. Novotny, Phys. Rev. Lett., vol. 96, 113002, 2006.
[10] S. Kuhn, U. Hakanson, L. Rogobete, and V. Sandoghdar, Phys. Rev. Lett., vol. 97, p. 017402, 2006.
[11] J. I. Gersten and A. Nitzan, Chem. Phys. Lett., vol. 104, p. 31, 1984.
[12] X. M. Hua, J. I. Gersten, and A. Nitzan, J. Chem. Phys., vol. 83, p. 3650, 1985.
[13] S. D. Druger, S. Arnold, and L. M. Folan, J. Chem. Phys., vol. 87, p. 2649, 1987.
[14] H. T. Dung, L. Knöll, and D.-G. Welsch, Phys. Rev. A, vol. 65, p. 043813, 2002.
[15] M. Durach, A. Rusina, V. I. Klimov, and M. I. Stockman, New J. Phys., vol. 10, p. 105011, 2008.
[16] D. L. Andrews and G. Juzeliunas, J. Chem. Phys., vol. 96, p. 6606, 1992.
[17] V. N. Pustovit and T. V. Shahbazyan, Phys. Rev. B, vol. 83, p. 085427, 2011.