

A close look at the Förster energy transfer in the vicinity of a metallic nanoparticle

Una examinación de la transferencia de energía Förster en la cercanía de una nano-partícula metálica

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ABSTRACT

The energy of an excited molecule (donor) can be transferred to a nearby molecule (acceptor) in ground state (Förster energy transfer). This mechanism, due to intermolecular electromagnetic interaction, depends on the environment in which the donor-acceptor pair is embedded. We closely examine the influence of a gold nanosphere on the Förster energy transfer rate K_F including the impact of excitation of surface plasmons. When the intermolecular distance R is $\lesssim 3$ nm, the influence by the metallic nanosphere on K_F is weak. However, when the donor-surface separation is a few nanometers from the surface and R is $\gtrsim 3$ nm, K_F is modified by the presence of the nanoparticle. The excitation of surface plasmons causes a stronger perturbation of K_F . In the aforementioned region ($R \gtrsim 3$ nm), K_F can be enhanced with respect to K_{F0} (Förster energy transfer rate without nano-sphere).

RESUMEN

La energía de una molécula excitada (donador) puede ser transferida a una molécula cercana (aceptor) en estado base (transferencia de energía Förster). Este mecanismo, debido a la interacción electromagnética intermolecular, depende del entorno en el cual el par donador-aceptor es embebido. Se examina detalladamente la influencia de una nano-esfera de oro sobre la rapidez de transferencia de energía Förster K_F , incluyendo el impacto de la excitación de plasmones de superficie. Cuando la distancia intermolecular es R es $\lesssim 3$ nm, la influencia de la nano-esfera metálica sobre K_F es débil. Por otro lado, cuando la separación donador-superficie es de unos cuantos nanómetros y la distancia intermolecular R es $\gtrsim 3$ nm, K_F es modificada por la presencia de la nano-partícula; la excitación de plasmones de superficie causa una perturbación más fuerte de K_F . En la mencionada región ($R \gtrsim 3$ nm), K_F puede aumentar con respecto a K_{F0} (rapidez de transferencia de energía Förster sin nano-esfera).

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INTRODUCTION

Förster energy transfer occurs when an excited molecule (donor) D^* transfers its energy to a nearby molecule (acceptor) A in ground state (Förster, 1946). Typically, this process occurs when the intermolecular separation R is close to, or less than 10 nm. This energy transfer mechanism is due to donor-acceptor electromagnetic interaction. Commonly, Förster energy transfer is associated with plant photosynthesis; because of the Förster process, the energy absorbed by chlorophyll molecules is transported long distances until it reaches the cell reaction centers. However, Förster energy transfer also has a very important practical use in measuring nanometric displacements of the conformational folding of proteins. Consequently, Förster energy transfer can be applied as a tool for studying biological processes. For

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example, this tool enabled the observation of the myosin motion (muscular contraction) that works as a lever arm acting on an actin filament (nanomotor) (Suzuki, Yasunaga, Ohkura, Wakabayashi, Sutoh, 1998).

Current technology has the capability to grow, manipulate and observe nanostructures, including the synthesis of new molecular probes. In particular, the confinement of light in a subwavelength region can be attained by exciting plasmonic resonances of metallic nanoparticles, which are collective oscillations of electrons. The aforementioned light focussing capability has generated interest in understanding how light can be manipulated by such metallic nanoparticles; promising applications are currently in development such as biosensors, photovoltaics and efficient emitters (nano-antennas).

Since, as mentioned, the Förster energy transfer is mediated by electromagnetic interaction, it is influenced by the environment in which the molecules are embedded. Recently, we have clearly illustrated until what extent a metallic nanosphere modifies the Förster energy transfer rate K_F (the rate of change of the acceptor probability of being in excited state), including the effect of the excitation of surface plasmons (Gonzaga-Galeana & Zurita-Sánchez, 2013) (an extended list of references about this topic is contained therein). We have shown that K_F is practically unperturbed by the nanosphere when the molecular pair is separated at most a few nanometers (~ 3 nm); the direct donor-acceptor interaction is dominant in this region. On the contrary, when the intermolecular distance is larger than about 3 nm, the Förster energy transfer rate K_F is greatly perturbed by the presence of the nanosphere; the perturbation is greater when surface plasmons are excited. This effect arises from the fact that the strength of scattering field in the aforementioned region is strong enough to compete with the direct field.

We present new results of the influence of K_F by a spherical nanoparticle. These results extend our very recent and detailed study that deals with such perturbations of K_F . We particularly delve into the modification of K_F by a gold nanosphere. To examine the impact of the excitation of surface plasmons on K_F , two specific donor-acceptor pairs are analyzed: the first (second) pair considers that the plasmonic resonant frequencies are outside (inside) the spectral overlap of the donor-emission and acceptor-absorption spectra, namely, the off(on)-resonance case.

This work is organized as follows. The next section describes the characteristics of the particular case that is analyzed including the geometry and dielectric properties of the environment (a gold nanosphere embedded in a background medium). This section also presents the spectral properties of the two donor-acceptor pairs that were selected for our analysis and how Förster energy transfer K_F can be calculated. The following section shows the results of the influence on Förster energy transfer K_F by the metallic nanosphere, including the discussion of these results. In the last section, the conclusions are presented.

THEORY

Consider a gold nanosphere (centered at the origin) with radius a . Without loss of generality, the donor molecule is located along the z -axis and outside the sphere, namely $\mathbf{r}_D = z_0 \mathbf{n}_z$ ($z_0 > a$ and \mathbf{n}_z is the Cartesian unit vector along the z -axis). While \mathbf{r}_A is the position of the acceptor. This setup is illustrated in figure 1.

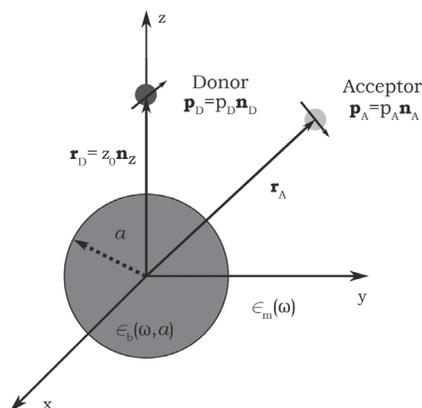


Figure 1. Förster energy transfer in the vicinity of a nanoscale metallic sphere. The donor molecule and acceptor are located outside the sphere. Source: Authors own elaboration.

Consider two pairs of fluorophores (light-emitting organic molecules): the first (second) pair is composed of *Alexa Fluor 660 (Fluorescein)* as donor and *Alexa Fluor 700 (Eosin)* as acceptor. The spectral overlap between the emission and absorption spectra of the former (latter) pair forbids (allows) the excitation of the plasmonic resonances of the gold nanosphere. Figure 2(a) plots the emission (absorption) spectra of *Alexa Fluor 660 (Alexa Fluor 700)* as a function of the free-space wavevector k_0 ; whereas, figure 2(b) depicts the emission and absorption spectra of *Fluorescein* and *Eosin*, respectively.

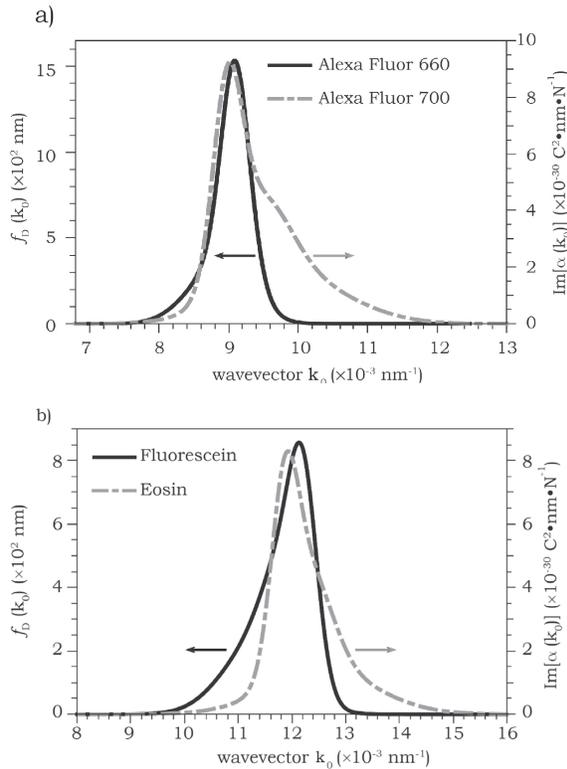


Figure 2. The spectra f_D (emission) and $\text{Im}[\alpha]$ (absorption) as function of the wavevector k_0 . (a) Alexa Fluor 660 (donor) and Alexa Fluor 700 (acceptor). (b) Fluorescein (donor) and Eosin (acceptor). We consider $\text{Im}[\alpha(k_0)] = \pi |\mathbf{p}_A|^2 f_A(k_0) / (ch)$ where $f_A(k_0)$ is the absorption spectrum (normalized to unit area); an acceptor dipole electronic transition $|\mathbf{p}_A| = 1.602 \times 10^{-29}$ Cm was assumed.

Source: Authors own elaboration.

The dielectric function of the nanosphere is $\epsilon_b(\omega, a)$, which is size-dependent and different from that of the bulk. This is due to the nanoscale confinement of the free-electrons of the metal as well as the interaction of these electrons with the surface atoms of the background medium. It turns out that $\epsilon_b(\omega, a) = 1 + \chi_i(\omega) + \chi_d[\omega; \omega_p, \gamma(a)]$ where $\chi_i(\omega)$ is the susceptibility arising from interband transitions (bounded electrons) and χ_d is the Drude-model susceptibility with plasma frequency ω_p and size-dependent collision rate $\gamma(a) = \gamma_0 + Av_F/a$ (γ_0 is the bulk collision rate, v_F is the Fermi velocity, and A is a dimensionless factor that depends on the material of the background medium (Hövel, Fritz, Hilger, Kreibig & Vollmer, 1993)). $\chi_i(\omega)$ can be found by subtracting the bulk dielectric function $\epsilon_b(\omega)$ and bulk Drude susceptibility $\chi_d[\omega; \omega_p, \gamma_0]$. For gold, the experimental data of $\epsilon_b(\omega)$ is encountered in (Pallik, 1998), $\omega_p = 1.37 \times 10^{16}$ rad/s, $\gamma_0 = 4.05 \times 10^{13}$ rad/s,

$v_F = 1.4 \times 10^{15}$ nm/s, and we choose $A = 0.9$ (an intermediate value with respect to measured A -values (Hövel *et al.*, 1993)). Fluorophores are usually prepared in either water or a buffer solution, thus consider that the molecules and the nanosphere are embedded in an aqueous medium with dielectric constant $\epsilon_m = 1.77$ (water for optical frequencies).

We assume that the donor and acceptor are in the vicinity of a nanoscale metallic sphere (see figure 1) and their corresponding emission and absorption spectra, respectively, lie in the visible range. Consequently, the molecules and the sphere are enclosed in a volume $V \ll \lambda_0^3$ (λ_0 is the free-space wavelength). Therefore, by taking into account the aforementioned assumptions, the Förster energy transfer rate K_F can be obtained by using quasi-static approximation. It turns out that, in the quasi-static limit, the Förster energy transfer rate is given by (see supplementary material of (Gonzaga-Galeana & Zurita-Sánchez, 2013)).

$$K_F = \frac{2 |\mathbf{p}_D|^2}{\hbar} \int_0^\infty f_D(\omega) \text{Im}[\alpha(\omega)] \times |\mathbf{n}_A \cdot \overleftrightarrow{\mathbf{Q}}(\mathbf{r}_A, \mathbf{r}_D) \cdot \mathbf{n}_D|^2 d\omega. \quad (1)$$

Here, \mathbf{p}_D is the dipole moment of electronic transition of the donor (\mathbf{n}_D is the unit vector that indicates its polarization), \hbar is the reduced Planck constant, f_D is the donor emission spectrum normalized to unit area, (ω is the angular frequency), $\text{Im}[\dots]$ denotes the imaginary part, and $\overleftrightarrow{\alpha} = \alpha \mathbf{n}_A \mathbf{n}_A$ is the acceptor polarizability (acceptor is only polarizable along the unit vector \mathbf{n}_A). $\overleftrightarrow{\mathbf{Q}}$ is the static Green tensor which is related to the electric field \mathbf{E} generated by an electric dipole, that is,

$$\mathbf{E}(\mathbf{r}) = \overleftrightarrow{\mathbf{Q}}(\mathbf{r}, \mathbf{r}_0) \cdot \mathbf{p}, \quad (2)$$

(\mathbf{p} is an arbitrary dipole that is located at \mathbf{r}_0 (source point), and \mathbf{r} is the field point). The static Green tensor $\overleftrightarrow{\mathbf{Q}}$, so the Förster energy transfer rate K_F (see (1)), depends on environment in which the dipole is embedded. Also, notice from (1) that, K_F depends on the overlap between the emission (donor) and the absorption (acceptor) spectra as well as the dipole orientations of the molecules. The components of the static Green tensor $\overleftrightarrow{\mathbf{Q}}$ can be straightforwardly linked to the static potential Φ created by the dipole \mathbf{p} when the dipole is specifically near a dielectric sphere; the explicit expression for Φ is found in supplementary material of (Gonzaga-Galeana & Zurita-Sánchez, 2013).

RESULTS

We consider

$$\tilde{K}_F(\mathbf{r}_A) \equiv K_F(\mathbf{r}_A, \mathbf{r}_D = z_0 \mathbf{n}_z) / K_{D0}, \quad (3)$$

that is, the normalized Förster energy transfer rate $K_F(\mathbf{r}_A, \mathbf{r}_D = z_0 \mathbf{n}_z)$ (donor placed at the z -axis and outside the sphere) with respect to the donor decay rate *without sphere* (K_{D0}). K_{D0} is given by

$$K_{D0} = \frac{|\mathbf{p}_D|^2}{3\pi\epsilon_0\hbar c^3} \int_0^\infty f_D(\omega)\omega^3 \sqrt{\epsilon_m(\omega)} d\omega, \quad (4)$$

where c is the vacuum speed of light and ϵ_0 is the vacuum permittivity.

Figure 3 shows the contour plots of $\log[\tilde{K}_F(\mathbf{r}_A)]$ ($\log[\dots]$ denotes the base 10 logarithm and $\mathbf{r}_A \in xz$ -plane) for donor and acceptor dipoles oriented in the z -direction in which the left (right) column corresponds to the off(on)-resonance case; the contour plots of the top, for comparison purposes, exhibit the case without sphere, while the other ones consider the presence of a particle with radius $a = 7.5$ nm, and donor-surface separations $s \equiv z_0 - a = 1.5$ nm as well as 8 nm.

When the donor-acceptor separation is $s = 1.5$ nm (figures 3(b)-(B)), the contour lines $\log[\tilde{K}_F(\mathbf{r}_A)] = 1, 2, 3$, remain almost unchanged with respect to the case without a sphere, excepting the bottom lobes near the nanosphere. While, on the contrary, the lobes of $\log[\tilde{K}_F(\mathbf{r}_A)] = -3, -2, -1, 0$ are strongly modified by the presence of the nanosphere. The area enclosed by any of these low-value contour lines is greater than its corresponding K_F -value for the case in which the sphere is absent. Consequently, if the acceptor is placed inside the region between $\log[\tilde{K}_F(\mathbf{r}_A)] = -3$ and 0, the energy transfer rate K_F is enhanced with respect to K_{F0} (Förster energy transfer rate *without* a nanosphere). By comparing figures 3(b) and (B), we notice that the contour lines $\log[\tilde{K}_F(\mathbf{r}_A)] = -3, -2, -1, 0$ are more distorted for on-resonance than for the off-resonance due to the excitation of surface plasmons.

Now the donor is placed at 8 nm from the surface (figures 3(c) and (C)). The patterns of $\log[\tilde{K}_F(\mathbf{r}_A)] = 1, 2, 3$, are practically unperturbed by the nanosphere, as well as the lateral and top lobes of $\log[\tilde{K}_F(\mathbf{r}_A)] = -3, -2, -1, 0$. Conversely, the bottom lobes of $\log[\tilde{K}_F(\mathbf{r}_A)] = -3, -2, -1, 0$ are perturbed by the nanosphere, but not as strongly as in the case where $s = 1.5$ nm; even in this case there is a weak influence on K_F due to the excitation of surface plasmons (compare figures 3(c) and (C)).

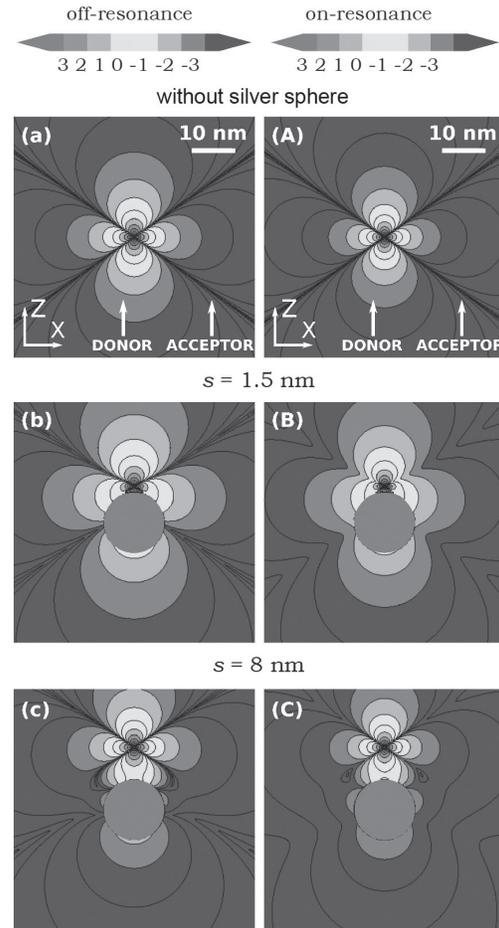


Figure 3. Contour plots of $\log[\tilde{K}_F(\mathbf{r}_A)]$ (\mathbf{r}_A belongs to the xz -plane) for $a = 7.5$ nm, and both acceptor and donor dipoles oriented in the z -direction. Off-resonance: (a) without sphere, (b) $s = 1.5$ nm, (c) $s = 8$ nm: (A) without sphere, (B) $s = 1.5$ nm, (C) $s = 8$ nm. We recall that $s \equiv z_0 - a$ (the donor-surface separation) and that the coordinate system origin is placed at the sphere center.

Source: Authors own elaboration.

If the donor is moved further away from the surface, then the patterns of the contour plots of \tilde{K}_F corresponding to the case without nano-sphere should be recovered.

In Gonzaga-Galeana & Zurita-Sánchez (2013), we examined in detail the influence on K_F by a *silver* nanosphere. Similarly to the silver nanoparticle, the high-value contour curves of $\tilde{K}_F(\mathbf{r}_A)$ are barely perturbed by the nanosphere because the direct electromagnetic interaction is dominant, whereas the low-value contour curves of $\tilde{K}_F(\mathbf{r}_A)$ are modified by the presence of the sphere since the scattering field contribution becomes comparable or weaker than the aforementioned direct

interaction. However, for the on-resonance response and the donor position a few nanometers (~ 2 nm) from the surface, the contour lines of $\log[\tilde{K}_F(\mathbf{r}_A)]$ are more distorted for a nanoparticle made of *silver*. This effect can be attributed to the fact that the strength of field scattered (on-resonance) by the silver nanoparticle is larger than that by the gold nanosphere because the collision rate $\gamma(a)$ is larger for gold than for silver.

CONCLUSION

We studied the influence of a gold nanosphere on the Förster energy transfer rate K_F . Our contour plots of $\tilde{K}_F(\mathbf{r}_A)$ exhibit neatly how K_F is modified when the molecular donor-acceptor pair is near the nanosphere, including the impact of the excitation of surface plasmons. The high-value contour lines of $\log[\tilde{K}_F(\mathbf{r}_A)]$ suffer slight changes with regard to the case when the sphere is absent. On the contrary, the contour lines of $\log[\tilde{K}_F(\mathbf{r}_A)]$ corresponding to low-values are more strongly perturbed as the donor-surface separation decreases. These low-value contour lines are resized (the area enclosed by them is larger than that for the case without sphere, implying an enhancement of the factor K_F / K_{F0}) and distorted (the deformation of them is more noticeable if surface plasmons are excited). Our results could be exploited to extend the potential of the aforementioned tool for detecting the dynamics of the motion of proteins.

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