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## On the Concentration Dependence of Metallic Nano-Particles in Enhanced Forster Resonance Energy Transfer

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# On the concentration dependence of metallic nano-particles in enhanced Forster resonance energy transfer

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**Abstract.** The enhanced Forster resonance energy transfer is obtained in recent experiments. One of the most important experimental facts is the observed strong enhancement of donor fluorescence with increasing concentration of metallic nanoparticle acceptors in the first stage. We propose three types of energy transfer mechanisms (Forster FRET, surface SET, and Coulomb CET) and predict simple relations for their dependencies on the concentration of metallic nano-particles. The competition of these mechanisms leads to the transfer intensity dependence on the concentration dependence of metallic nano-particles. Using these assumptions, we expect and argue about the compatibility between the experimental results.

## 1. Introduction

Plasmon effects of metal nanoparticles have many applications for a variety of application areas such as: chemical analysis and catalysis, detection of biomolecules, pharmaceuticals, diagnosis, imaging and therapy, discovering the contamination by heavy metal ions, analyzing food additives and contamination [1-10].

The Foster Resonance Energy Transfer (FRET) is a process of energy transmission through dipole-dipole interaction, from a chemical molecule (donor - D) to the acceptor molecule (acceptor - A), but here the donor emission band must overlap the acceptor's absorption bands. Currently, FRET effects are widely applied in the fields of chemistry, biology such as stem cell research, as well as studies of proteins, and biometric applications.

In recent decades, metal nanostructures are famous by the attractive optical properties of the electromagnetic spectrum from UV to MIR spectral region. For example, they are used to enhance the optical signal in the fluorescence, Raman spectrum, IR spectrum, and increase the contrast in nuclear magnetic resonance (MRI). Its nature is fundamentally enabled by the surface plasmon resonance-based localized collective oscillations of electron cloud with metal nanoparticles.



FRET between two molecular donors (D - usually a fluorophore) and acceptor, in which used acceptor is a metal nanoparticle is an important physical method for investigation biological systems with applications in medical treatment and drug discovery today [12,13].

Within the limits of the distance between A and D equal to 10 nm, we have given a new reasonable model with mixing mechanism: FRET-mechanism for small size and SET-mechanism for large size metal nanoparticles. Even with a research by electronic excitation transfer (CET) from a segment of polyfluorene to tetraphenyl porphyrin, Bagchi et al. have show the  $R^{-2}$  dependence rule [16].

We propose a GRET model [22] with three types of energy transfer mechanisms (Forster FRET, surface SET, and Coulomb CET) and predict simple relations for their dependencies on the concentration of metallic nano-particles. The competition of these mechanisms leads to the transfer intensity dependence on the concentration dependence of metallic nano-particles.

In this paper we examine this General resonance energy transfer (GRET) model and plasmonic effects of nanoparticles for more recently obtained experimental data. We will show that our GRET model gives a quite good agreement with experimental data, and could explain the enhanced fluorescence intensity in the presence of gold particles with their concentration dependence.

## 2. Theoretical Model

The first paragraph after a heading is not indented (Bodytext style). We propose three types of energy transfer mechanisms (Forster FRET, surface SET, and Coulomb CET) and predict simple relations for their dependencies on the concentration of metallic nano-particles [22].

Denote the FRET, SET, and CET efficiencies as given by

$$E_{\text{FRET}} = \frac{1}{1 + (R/R_{\text{FRET}})^6}, \quad (1)$$

$$E_{\text{SET}} = \frac{1}{1 + (R/R_{\text{SET}})^4}, \quad (2)$$

$$E_{\text{CET}} = \frac{1}{1 + (R/R_{\text{CET}})^2}, \quad (3)$$

where  $R_{\text{FRET}}$ ,  $R_{\text{SET}}$  and  $R_{\text{CET}}$  are the FRET, SET and CET radii, respectively.  $R = |\vec{r}_A - \vec{r}_D|$  is the distance between the A and the D. At  $R=R_{\text{FRET}}$ ,  $R=R_{\text{SET}}$ , and  $R=R_{\text{CET}}$ , half of excitation energy of D is transferred to nano-metallic particle A.

Denote  $D(\vec{r}_A, \vec{r}_D; \omega)$  the Green function. The function  $M$  is defined as

$$M(\omega) = |\vec{G}_D(\omega) \cdot D(\vec{r}_A, \vec{r}_D; \omega) \cdot \vec{G}_A(\omega)|^2. \quad (4)$$

We have [17,20]

$$M(\omega, \langle R \rangle) = \frac{1}{(4\pi\epsilon_0)^2} K^2 G_A(\omega)^2 G_D(\omega)^2 \left[ \frac{3}{\langle R \rangle^6} + \frac{(\omega/c)^2}{\langle R \rangle^4} + \frac{(\omega/c)^4}{\langle R \rangle^2} \right] \quad (5)$$

where  $K^2 = [0,1]$  is the orientation factor of effective dipoles and  $\langle R \rangle$  is the average D-A distance. In the equation (5) there are just 3 contributions given by FRET, SET, and CET-mechanisms respectively.

We assume a simple relation between the average donor-acceptor distance  $\langle R \rangle$  and NPs concentration  $n$  as  $\langle R \rangle \sim (n_A + n_D)^{-1/3} \approx n^{-1/3}$ .

We have

$$M(\omega, \langle R \rangle) = \frac{1}{(4\pi\epsilon_0)^2} K^2 G_A(\omega)^2 G_D(\omega)^2 [A n^2 + B n^{4/3} + C n^{2/3}], \quad (6)$$

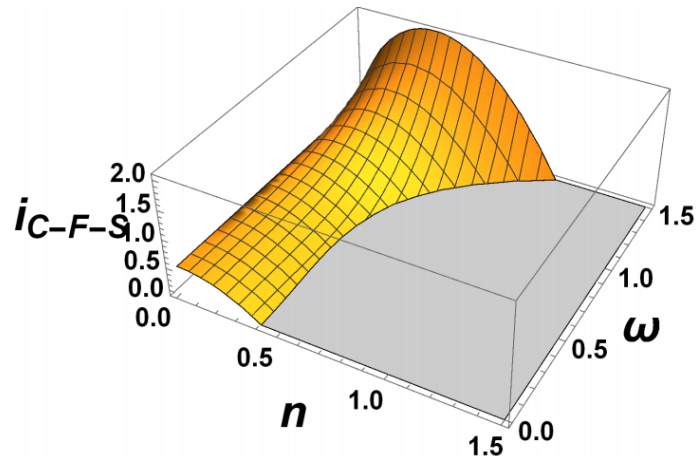
where  $A, B$ , and  $C$  are some constants and  $n_A, n_D$  are concentration of A and D, respectively.

The competition of these mechanisms: give more energy to the donor via CET mechanism ( $c > 0$ ) and take the energy from a donor via FRET and SET mechanisms ( $a < 0, b < 0$ ). With the usual linear optic condition  $(G_A G_D)^2 \sim n$ , the normalized intensity  $I$  is

$$I(n) = I_0 + a n^3 + b n^{7/3} + c n^{5/3}, \quad (7)$$

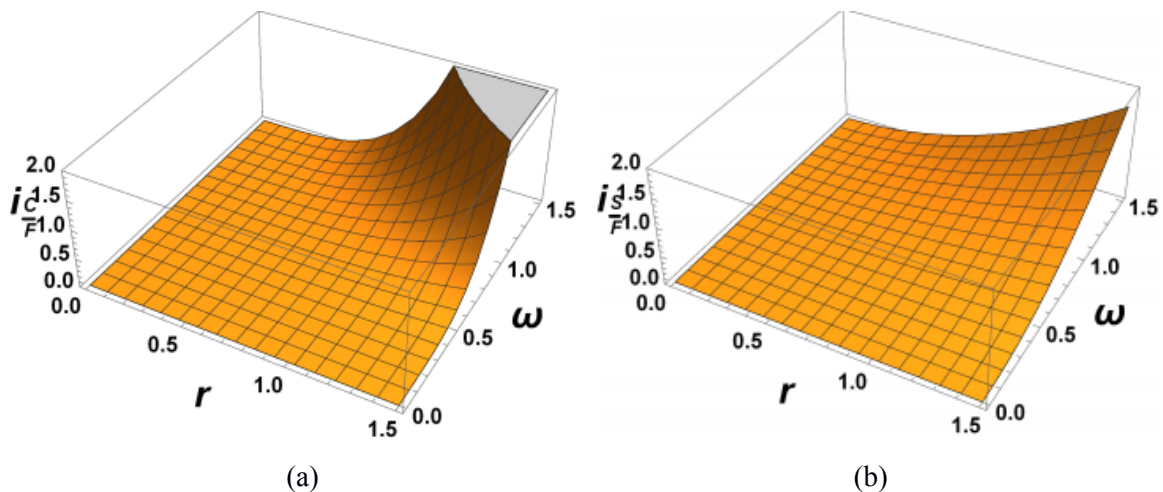
where  $a, b$ , and  $c$  are some constants,  $I_0$  is the normalized intensity at  $n \approx 0$ .

The form of normalized luminescence intensity  $I$  (C-F-S) is plotted in Figure 1 with the assumption that the contribution of CET is positive ( $c > 0$ ), the contributions of FRET and SET are negative ( $a < 0, b < 0$ ). At small frequency  $\omega$ , the intensity always decreases with increasing the density of NPs concentration  $n$ . At high frequency  $\omega$ , the intensity first increases with increasing  $n$  until some certain value  $n_{\max}$ , then decreases after this point. This behavior of the luminescence intensity  $I$  versus the density of NPs concentration  $n$  was observed in the experiment.



**Figure 1.** The form of normalized luminescence intensity  $I$  (C-F-S) with the assumption that the contribution of CET is positive ( $c > 0$ ), the contributions of FRET and SET are negative ( $a < 0, b < 0$ ). This behavior of the luminescence intensity  $I$  versus the density of NPs concentration  $n$  is the same as in experimental observations.

The average distance  $r$ -dependence and frequency  $\omega$ -dependence of the ratio of CET contribution versus FRET contribution are presented in Figure 2a, and the ratio of SET contribution versus FRET contribution is presented in Figure 2b.

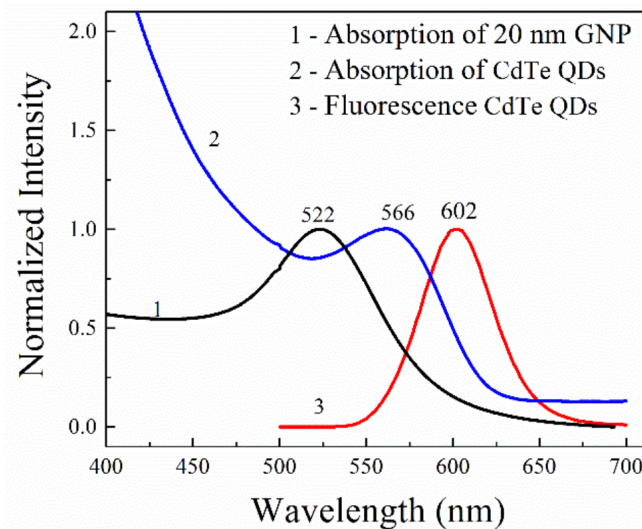


**Figure 2.** The ratio of CET contribution versus FRET contribution (a), and the ratio of SET contribution versus FRET contribution (b).

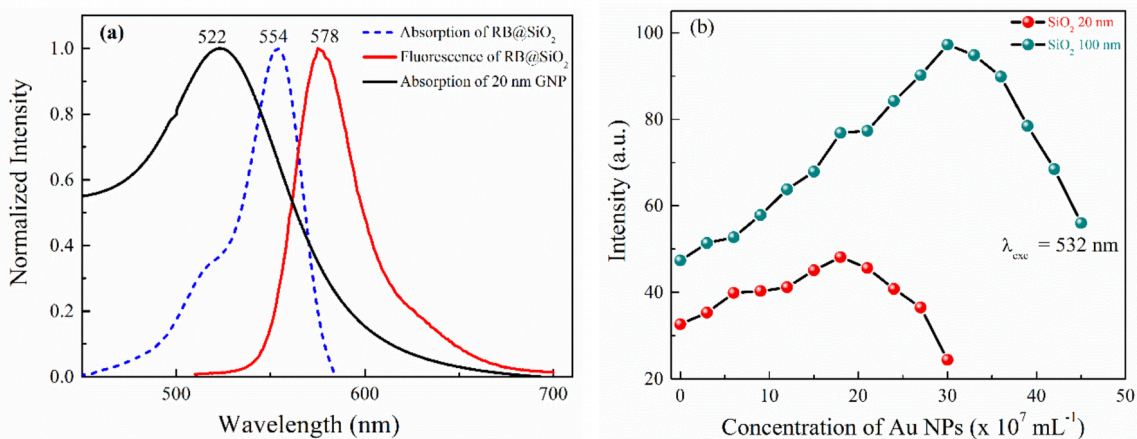
This is entirely consistent with our theoretical models given above.

### 3. Comparison with experiment

We investigated the resonance energy transfer between fluorophores (D) and the metal nanoparticles (A). As a result, it caused the extinction or fluorescence enhancement. The experiments were conducted at room temperature and at 532 nm excitation for a mixture of D-A pairs in aqueous solution. Using the JASCO-V570-UV-Vis-NIR spectrometer were measured absorption spectra, a Cary Eclipse spectrofluorometer were recorded. The fluorescence spectra, transmission and scanning electron microscopes (TEM, JEM 1011 and SEM, Hitachi S-480) were used to determine the shape, size of particles. The energy transfer experiments were carried out for two types of D-A pairs: CdTe QDs – GNPs, RBDSNPs – GNPs (20 nm and 100 nm GNPs).



**Figure 3.** Absorption and fluorescence spectra for CdTeQDs-GNPs.

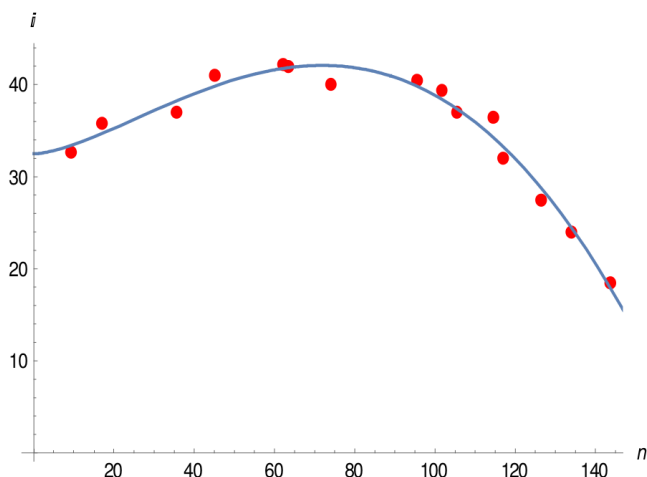


**Figure 4.** Absorption, fluorescence spectra (a) and donor fluorescence intensity vs acceptor concentration of D-A pair (b) between RBDSNPs – (20 and 100) nm GNPs.

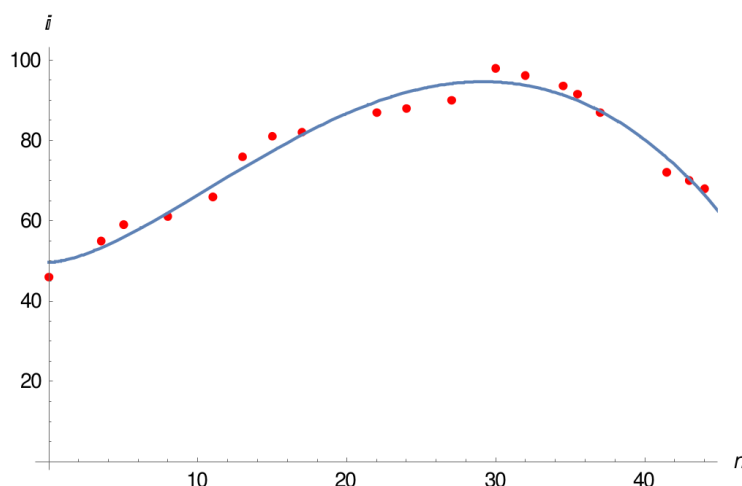
Using the model developed in the previous part, we calculate the fluorescence dependence on the concentration of gold nanoparticles. The theoretical fitting results have a quite good agreement with the above experiments. This model has also been tested in previous report [22].

From Figures 3 to 6 we can see that at a small frequency  $\omega < \omega_0$ , where  $\omega_0$  is some certain frequency, the luminescence intensity always decreases with increasing the density of NPs concentration  $n$ . At higher frequency  $\omega > \omega_0$ , the intensity first increases with increasing  $n$  until

some certain value  $n_{\max}$ , then decreases after this point. That behavior was mentioned in the above our model theory and also was observed in the experiment.



**Figure 5.** Results of theoretical models. The blue curve is a fit with parameters:  $a = -8.2785 \times 10^{-7}$ ,  $b = -1.088 \times 10^{-3}$ ,  $c = 2.6794 \times 10^{-2}$ ,  $I_0 = 32.48$ , and the experiment data are shown in red cycles.



**Figure 6.** Results of theoretical models with GNPs (Au 20 nm). The blue curve is a fit with parameters  $a = -3.9947 \times 10^{-4}$ ,  $b = -3.5438 \times 10^{-3}$ ,  $c = 0.5343$ ,  $I_0 = 49.6958$ , and the experiment data are shown in red cycles.

So we can confirm the mode of general resonance energy transfer is a mix of 3 mechanisms FRET, SET and CET. The dependence of each mechanism depends on the distance between D and A that we have surveyed.

#### 4. Conclusion

Resonance energy transfer between fluorescent and fluorescent metal surface enhanced fluorescence has many applications in various fields. The results of this paper propose a theoretical model for calculating the fluorescence intensity versus concentration of gold nanoparticles.

We propose a GRET model with three types of energy transfer mechanisms (Forster FRET, surface SET, and Coulomb CET) and predict simple relations for their dependencies on the concentration of metallic nano-particles. The competition of these mechanisms can be explained as: giving more energy



to donor via CET mechanism ( $c > 0$ ) and taking the energy from donor via FRET and SET mechanisms ( $a < 0$ ,  $b < 0$ ) lead to the transfer intensity dependence on the concentration dependence of metallic nano-particles.

This results is quite important contribution in the study of fluorescent enhancement. Our model succeeds in explaining how the fluorescence intensity depends on the concentration of gold particles in experiments with CdTeQDs-GNPs, 20 and 100 nm RBDSNPs-GNPs. In the future, we can develop antenna models describing the transeiver enhanced fluorescence signal between D and A.

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### References

- [1] Xie W and Schlücker S 2004 *Reports on Progress in Physics* **77** 116502
- [2] Chen X-J, Cabello G, Wu D-Y and Tian Z-Q 2014 *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **21** 54-80
- [3] Schlücker S 2014 *Angew. Chem. Int. Ed.* **53** 4756-4795
- [4] Cialla D, Pollok S, Steinbrücker C, Weber K and Popp J 2014 *Nanophotonics* **3** 383-411
- [5] Ma W, Kuang H, Xu L, Ding L, Xu C, Wang L and Kotov N A 2013 *Nat. Commun.* **4** 2689
- [6] McAughtrie S, Faulds K and Graham D 2014 *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **21** 40-53
- [7] Dinh T V, Liu Y, Fales A M, Ngo H, Wang H-N, Register J K, Yuan H, Norton S J and Griffin G D 2015 *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology* **7** 17-33
- [8] Li D-W, Zhai W-L, Li Y-T and Long Y-T 2014 *Microchim. Acta* **181** 23-43
- [9] Alvarez-Puebla R A and Liz-Marzán L M 2012 *Angew. Chem. Int. Ed.* **51** 11214-11223
- [10] Zheng J and He L 2014 *Comprehensive Reviews in Food Science and Food Safety* **13** 317-328
- [11] Keller E L, Brandt N C, Cassabaum A A and Frontiera R R 2015 *Analyst* **140** 4922-4931
- [12] Hussain S A. et al 2009 *Introduction to FRET*, arXiv preprint arXiv:0908.1815
- [13] Chen G, Song F, Xiong X, Peng X 2013 *Ind. Eng. Chem. Res* **52** 11228-11245
- [14] Wong K F, Bagchi B, Rossky P J 2004 *J. Phys. Chem. A* **108** 5752
- [15] Vincent R, Carminati R 2011 *Phys. Rev. B* **83** 165
- [16] Singh H, Bagchi B 2005 *Curr. Sci.* **89** 1710
- [17] Breshike C J, Riskowski R A, and Strouse G F 2013 *J. Phys. Chem. C* **117** 23942
- [18] Ha C V, Nga D T, Viet N A, Nhung T H 2015 *J. Opt. Comm.* **353** 4955
- [19] Wong, K F, Bagchi B, and Rossky, P J 2004 *J. Phys. Chem. A* **108** 5752-5763
- [20] Tuncay O, Pedro L H, Evren M, Onur A Sedat N, Ilkem O, Qing Z, Qihua X, and Hilmi V D 2013 *Nano Lett.* **13** 3065-3072
- [21] Andrews D L, Bradshaw D S 2004 *Eur. J. Phys.* **25** 845858
- [22] Hoa N M, Ha C V, Nga D T, Lan N T, Nhung T H, and Viet N A 2016 *J. Phys.: Conf. Ser.* **726** 012009