Report on ESF short visit 5231

Cooperative plasmon-mediated fluorescence of gain dyes near plasmonic nano structures. Application to biomolecular nanosensing.

Date: 15.10.2012-30.10.2012
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1. Work program

The time of this short visit was 15 days. The aim of short visit has been establishment of future collaboration. For this purpose I gave a talk "Cooperative Plasmon-mediated effects of fluorescent dyes near a metal nanoparticle". Besides the talk, a detailed discussion about obtained theoretical results as well as planned collaboration work with group of Dr. Arkadiy Chipouline has been initiated. Several improvements to the nonlinear model of plasmonic nanoresonator based on metal and gain compensation fluorescent materials have been proposed as a result of intense discussions and analytical derivations. Therefore, the main target of visit, which was to establish basis for a future collaboration, has been reached.

2. Summary of the talk

Fluorescence detection is now a central technology for research in medicine, biology and biotechnology. As examples, DNA sequencing by fluorescence was first reported in 1987 [1-2], resulting in near completion of the sequence of the human genome by 2001 [3-4]. Fluorescence detection has replaced radioactivity in most medical testing [5-6]. More recently, fluorescence methods have been extended to high throughput studies of gene expression using the so-called gene chips which can contain over 30 000 individual DNA sequences [7-8]. These applications rely on the free-space spectral properties of the fluorophores. To date all the fluorescence observables, including spectral shifts, anisotropies, quantum yields, and lifetimes, have all been utilized in basic and applied uses of fluorescence. The possibility to modify the emission of fluorophores or chromophores by increasing or decreasing their radiative creates a new opportunity in fluorescence, radiative decay engineering (RDE). An opportunity to control the radiative rates arises from the interactions of fluorophores with nearby metallic surfaces or particles. The electric field felt by a fluorophore is affected by interactions of the incident light with the nearby metal surface and also by interaction of the fluorophore oscillating dipole with the metal surface. Additionally, the fluorophore-oscillating dipole induces a field in the metal. These interactions can increase or decrease the field incident on the fluorophore and increase or decrease the radiative decay rate. The proposed is a mechanism [9-11] of the collective emission for fluorophore-oscillating dipoles exposed to the light near a nanostructure. In our works it is demonstrated that resonance energy transfer between fluorophore-oscillating dipoles and surface plasmon of nanoparticle (NP) becomes a cooperative process involving all dipoles in the ensemble and the NP. This plasmonic mechanism of cooperative emission represents an extension, to plasmonic systems, of the Dicke effect for N radiating dipoles in free space. A new plasmonic Dicke mechanism developed in [9-11] creates possibilities to manipulate and control decay rates of fluorophores in vicinity of metallic nanostructures, i.e. is a new step in RDE.

3. **Improvements to theoretical description**

The key element of the proposed research a) - d) is the Maxwell's equation for the local electric field $\mathrm{E}(r)$. As an example of cooperative Plasmon-mediated system we may consider an aggregate that consists of metal nanoparticle (NP) and layer of N fluorescent dyes located at positions r_j (see Fig.1)

$$\varepsilon(r)\frac{\omega^2}{c^2}\vec{E}(r) - \nabla \times \nabla \times \vec{E}(r) = 4\pi\frac{\omega^2}{c^2}\sum_{j=1}^{N}\vec{p}_j\delta\left(r - r_j\right), \tag{1}$$

with $j = 1,2, \dots N$ (we set origin $r = 0$ at NP center). We also assume that the aggregate is illuminated by an external incident field $\vec{E}_{inc}$.

Accurate description of the dynamics of interacting classical systems is a fundamental task. Indeed, quantum structures represented by gain material atoms or molecules, or their

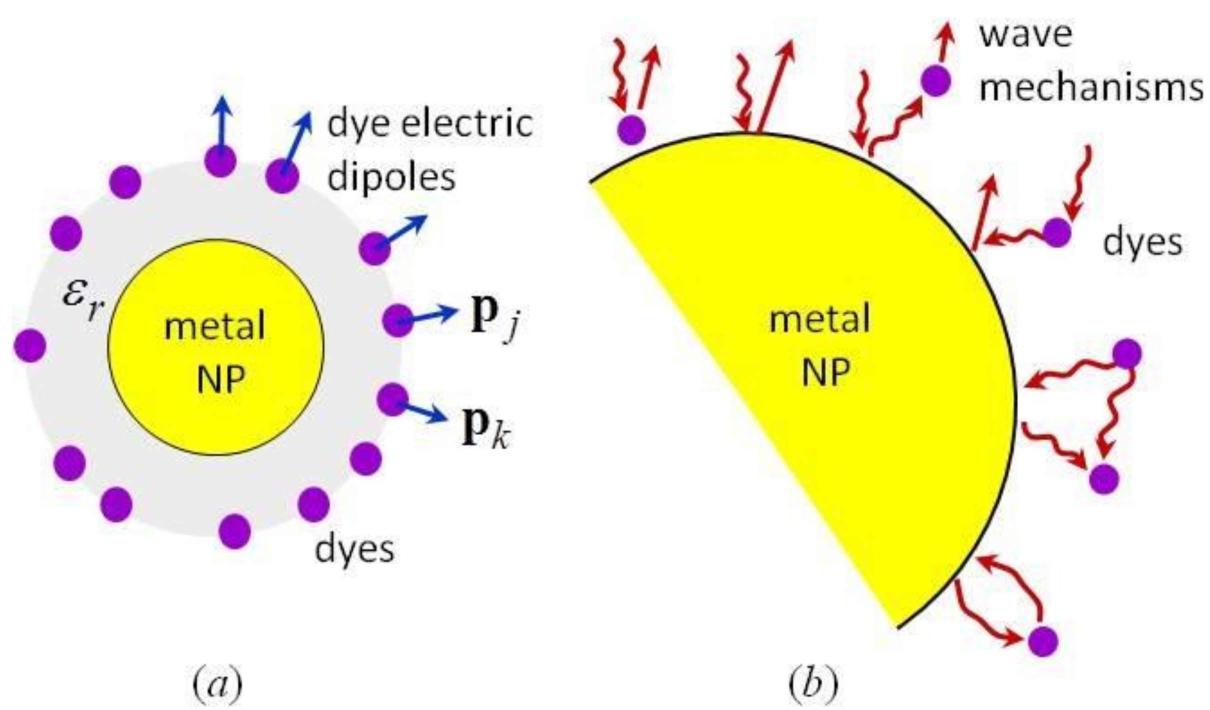

Fig. 1: (a) the system with one nanoparticle and layer of N dyes, (b) radiative and non-radiative mechanisms of the plasmonic coupling.

aggregates can be accurately modeled only with use of quantum approach. The initial Maxwell-Bloch equation in density matrix formalism for dye molecule can be formulated as

$$\frac{d\rho_{12}^{(j)}}{dt} - i\omega_{12}\rho_{12}^{(j)} + \gamma_{12}\rho_{12}^{(j)} = i\frac{\mu\, G\, E(r,t)}{\hbar}, \tag{2}$$

where $G = \rho_{22}^{(j)} - \rho_{22}^{(j)}$ and $p_j = \mu_j\rho_{12}^{(j)}$, μ_j is a the matrix element of the dipole moment of the working transition and p_j is a dipole moment of the j-th gain molecule. Solution of this equation will give us

$$\vec{p}_j = \alpha_d\vec{E}(r,\omega) = \frac{\mu^2 G}{\hbar}\frac{\vec{E}(r,\omega)}{(\omega_{12}-\omega)-i\gamma_{12}}, \tag{3}$$

where population inversion parameter G has in general nonlinear dependence from the local field in the system. An accurate description of nonlinearities appeared from the analysis of Maxwell-Bloch equations was a subject of discussion with Dr. Arkadiy Chipouline. It have been decided to provide more extended quantum-classical dynamics description for the case of individual plasmonic nano-resonators in form of the radiating fluorescent dyes or metamaterials (i.e. assemblies of such resonators) combined with various quantum systems. That all can find potential application in the new types of the nanobiomolecular sensors, comprised of metal nanoparticles and biomolecules, Forster resonance energy transfer (FRET), colorimetric sensing, and surface-enhanced Raman scattering (SERS).

4. Conclusion

The target of short visit 5231 on October 15th, 2012 has been initiation of the future collaboration of Dr. Vitaliy Pustovit and group of Dr. Arkadiy Chipouline from University of Jena, Germany. For this purpose applicant has held a talk "Cooperative Plasmon-mediated effects of fluorescent dyes near a metal nanoparticle" on his recent results in plasmonic nanoscience. It has been agreed that nonlinear effects in optical response of metal-molecular aggregates have to be properly taken into account. It have been proposed a general plan of further collaboration work in this project for next year, responsibilities and tasks, including joint publication in state of art scientific journals.

References

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