COOPERATIVE FLUORESCENCE OF MOLECULES NEAR A METAL NANOPARTICLE

Tigran V. Shahbazyan,[a] *Vitaliy N. Pustovit*[a,b]
[a] *Department of Physics, Jackson State University, Jackson, MS 39217, USA*
[b] *Laboratory of Surface Physics, Institute of Surface Chemistry, Kyiv 03164, Ukraine*
tigran.shahbazyan@jsums.edu

Radiation of a dipole near a metal nanoparticle (NP) supporting localized surface plasmon (SP) is currently attracting renewed interest due to possible biosensing applications. The emission of a photon by a dipole-NP complex involves two competing processes: resonance energy transfer (RET) from excited dipole to SP before a photon is emitted, and decay into optically-inactive excitations in the metal (Ohmic losses). These channels are characterized by radiative, Γ^r, and non-radiative, Γ^{nr}, decay rates, respectively, and their balance is determined by separation, d, of the emitter from the metal surface. The emission is most enhanced at some optimal distance, and is quenched when the dipole is close to the NP surface due to the suppression of quantum efficiency, $Q = \Gamma^r/\left(\Gamma^r + \Gamma^{nr}\right)$, by prevalent non-radiative processes. Both enhancement and quenching were observed in fluorescence experiments on Au and Ag nanoparticles [1–5]. Furthermore, in recent *single-molecule* measurements [4, 5], the distance dependence of fluorescence rate was found to be in a good agreement with *single-dipole-NP* models [6].

Here we identify a novel mechanism in the emission of light by an *ensemble* of dipoles located near a nanostructure supporting localized SP. A typical setup would involve, e.g., dye molecules or quantum dots attached to a metal NP via DNA linkers. Namely, we demonstrate that RET between individual dipoles and SP leads to a *cross-talk* between the emitters. As a result, the emission of a photon becomes a *cooperative* process involving all the dipoles in the ensemble. This *plasmonic* mechanism of cooperative emission is somewhat analogous to the Dicke effect for N radiating dipoles in free space, confined within a volume with characteristic size smaller than the radiation wavelength λ [7]. In that case, the cooperative emission is due to photon exchange between emitters that gives rise to super-radiant states with enhanced radiative decay rate $\sim N\Gamma_0^r$, where Γ_0^r is the decay rate of an *isolated* dipole. In contrast, in plasmonic systems, the dominant coupling mechanism between dipoles is *SP exchange*, i.e., excitation of SP in a NP by an excited dipole followed by its absorption by another dipole, rather than direct radiative coupling. Such SP-induced coupling leads to the formation of *plasmonic super-radiant* states that dominate the emission of a photon. Importantly, because the NP acts as a *hub* that couples nearby and remote dipoles with about equal strengths, the SP-induced cross-talk is more uniform throughout the ensemble, as compared to the Dicke radiation coupling, resulting in a more efficient hybridization.

Specifically, we show that for an ensemble of N dipoles distributed in a solid angle around a metal NP, there are just *three* plasmonic super-radiant states, each with radiative decay rate $\gamma_\mu^r \simeq N\Gamma^r/3$. Furthermore, in a wide range of dipole-NP distances, their *non-radiative* decay rates also scale as $\gamma_\mu^{nr} \simeq N\Gamma^{nr}/3$, hence the *quantum efficiencies* are essentially the *same* as those of individual dipoles near a NP. As a result, we find that the total energy *radiated* by an ensemble, W, is only *thrice* that radiated by a single dipole near a NP, W_0:

$$W \simeq 3(\hbar kc/4)Q = 3W_0, \tag{1}$$

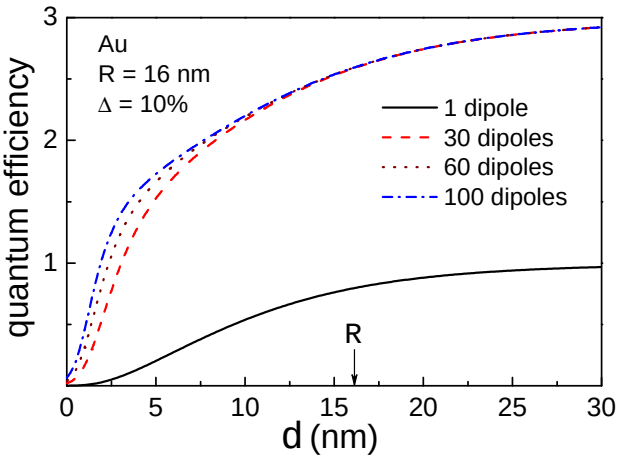

Figure 1: Quantum efficiencies for ensembles of 30, 60, and 100 dipoles vs. average (with 10% fluctuations) distance compared to that for an isolated dipole near Au NP.

where k and c are wavevector and speed of light, and the remaining energy is dissipated in a NP via sub-radiant states [8].

In Fig. 1, we compare distance dependence of quantum efficiencies for ensembles of 30, 60, and 100 molecules, randomly distributed in a solid angle, to the single-molecule Q near a $R = 16$ nm gold NP. For average distances $d \gtrsim R/2$ (8 nm), all ensemble dependences collapse into single curve with magnitude about thrice that of single-dipole curve, indicating that the emission is dominated by super-radiant modes. Even closer to NP surface, up to $d \approx 5$ nm, the emission largely remains cooperative, although deviations from $3Q$ behavior appear. For smaller distances, the eigenstates are no longer super- and sub-radiant modes, and cooperative emission is destroyed by non-radiative processes.

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