

Effect of Fabry-Perot Cavities on Concentration Quenching

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Abstract: We show that concentration quenching of emission of dye molecules – an energy transfer to quenching centers – is inhibited in subwavelength Fabry-Perot cavities (or metal-insulator-metal, MIM, waveguides). © 2019 The Author(s)

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Energy transfer between donors and acceptors is important for a range of physical phenomena and applications ranging from photosynthesis[1] to biosensing devices [2]. According to multiple studies[1], an energy transfer (as well as spontaneous emission [3]) can be affected by metallic nanostructures [1], nanoparticles [4], surfaces [1] and cavities [1]. The full spectrum of experimental results reported in the literature includes enhancement the energy transfer by non-local metal-dielectric environments [5,6], its inhibition [1,5] and indifference [7-9]. Particularly, in the study of the Förster energy transfer between donor and acceptor molecules [1], it was shown that the same environments, such as metallic surfaces or hyperbolic metamaterials, which boost spontaneous emission, inhibit energy transfer. More recently, the effect of metallic and metal-dielectric substrates on concentration quenching of HITC dye, which is an energy transfer to quenching centers, was studied in Ref. [10]. In agreement with Ref. [1], the latter quenching was also found to be inhibited by the presence of metallic surfaces and lamellar metal-dielectric structures in a close vicinity [1]. This finding poses the threefold question: (i) can energy transfer be affected by Fabry-Perot cavities (or metal-insulator-metal, MIM, waveguides), (ii) is the effect of a cavity any different than the effect of two metallic surfaces, and (iii) is the energy transfer affected by cavity resonances? Although an enhancement of the Förster energy transfer in a Fabry-Perot cavity was demonstrated in Ref. [6], the same publication reported on the enhancement of energy transfer by a single metallic surface – the result opposite to that of Refs. [1,5]. This apparent inconsistency of the reported results motivated our study reported below.

In ensembles of highly concentrated dye molecules, a Fabry-Perot cavity (or MIM waveguide) is expected to affect both spontaneous emission and concentration quenching (Förster energy transfer). On the other hand, at low dye concentrations, the energy transfer is practically non-existent and the cavity affects only spontaneous emission (Purcell effect). Therefore, we have undertaken two series of studies of (i) the effect of the cavity on a spontaneous emission at low dye concentration [10] and (ii) the effect of the cavity on both spontaneous emission and the energy transfer (concentration quenching) at high dye concentration. The effect of a cavity on the energy transfer was assumed to be independent of the dye concentration. The first series of studies is reported in Ref. [10], while the second series of experiments is presented below.

Our experimental samples in this study were Fabry-Perot cavities (or MIM waveguides) consisting of: (i) 150 nm thick Ag film deposited on glass, (ii) Poly(methyl) Methacrylate (PMMA) films of varied thickness (ranging between $d=12$ nm and $d=350$ nm), doped with HITC dye in concentration 30 g/L (in solid state), and (iii) 30 nm thick semi-transparent top Ag layer. Control samples included HITC:PMMA films deposited on glass and on 150 nm Ag films. The metallic layers were fabricated using thermal evaporation (Nano 36 from Kurt J. Lesker) and the HITC:PMMA films were deposited by spin coating (Specialty Coating System's 6800 Spin Coater Series). The film thicknesses were measured using the DektakXT stylus profilometer (from Bruker).

The absorption band of the HITC dye has a maximum at 775 nm and the emission spectrum has a maximum at 770 nm [9]. We excited the dye at $\lambda=795$ nm with ~ 150 fs pulses of a Ti:sapphire laser (Mira 900 from Coherent) and measured the emission kinetics, at $\lambda \geq 850$ nm, using the C5680 streak camera from Hamamatsu.

In the first approximation, the emission decay kinetics were nearly single exponential. The dependence of the experimental decay rates, measured in the Fabry-Perot cavities (MIM waveguides) and on top of Ag films, on the thickness of the HITC:PMMA films (cavity size) is shown in Fig. 1 (traces 1 and 2, respectively). The reduction of the emission decay rate with the reduction of the thickness of the HITC:PMMA films on top of Ag substrate is consistent with the inhibition of the concentration quenching (energy transfer) in the vicinity of metallic and metal-dielectric substrates reported in Ref. [10]. The emission decay rates in the cavities, featuring a sharp enhancement at small values of d (Fig. 1, trace 1), have contributions from both spontaneous emission and concentration quenching.

In order to extract from the overall decay rate the contribution of the concentration quenching, we subtracted the decay rates measured at the low dye concentration [9] (Fig. 1, trace 3) from those measured at the high dye concentration (Fig. 1, trace 1). The resultant curve (Fig. 1, trace 4) matches closely the one measured on top of 150 nm Ag film (Fig. 1, trace 2). This suggests the effect of Fabry-Perot cavities (or MIM waveguides) on the concentration quenching is no different than the effect of a single silver film. More tests aimed at refining the reported results are currently in progress. The complete account of the experimental results and analysis of the underlying physics will be presented at the conference.

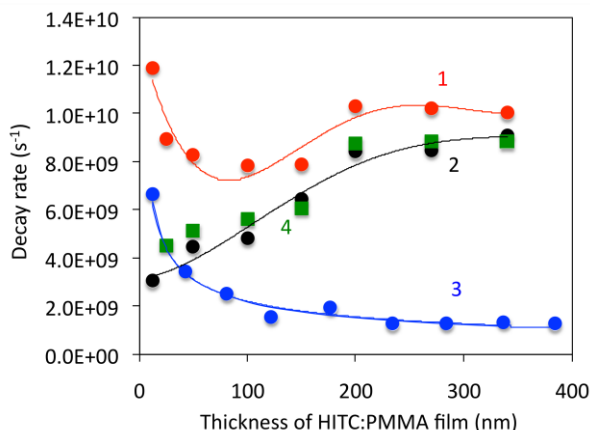


Fig. 1. Trace 1 and red circles: dependence of the emission decay rate on the thickness of the HITC:PMMA film (the cavity size d) in Fabry-Perot cavities at dye concentration 30 g/L. Trace 2 and black circles: same as above on top of Ag film. Trace 3 and blue circles: dependence of the emission decay rate on the thickness of the HITC:PMMA film (the cavity size d) at dye concentration 3 g/L [Prayakara]. Trace 4 and green squares: trace 3 subtracted from trace 1.

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