SINGLE MOLECULE FLUORESCENCE DECAY RATE STATISTICS IN NANOSCOPIC ENVIRONMENTS

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Several powerful optical imaging techniques are based on molecular fluorescence. Single emitters are also key elements in nanophotonics devices. Since the pioneering work of Purcell [1], it has been known that the spontaneous decay rate of a dipolar emitter (atom, molecule, Qdot) is dramatically affected by its environment. When a fluorescent molecule is placed in a complex environment (e.g., cluster, biological system), measurement of *statistical* properties can provide relevant information. This issue has been partially addressed in the literature [2]. In nanoscopic systems (e.g. clusters of nanoparticles) two important contributions are expected: (1) local field effects due to near-field interaction between the emitter and its environment; (2) absorption, which can substantially modify the statistics of the decay rate. In particular, the statistics of the radiative and non-radiative rates are expected to behave differently in the presence of absorption [3].

In this work, we study the fluorescence-rate statistics in a finite size (nanoscopic) random medium (cluster), made of small spherical particles. For a given configuration of the system, we calculate numerically the Green tensor of the system. We deduce the spontaneous decay rate Γ, as well the radiative and the non-radiative contributions. Repeating the calculation for the configuration distribution and performing ensemble averages allows to compute the full statistics (probability density, average value, standard deviation). These numerical experiments are used as a basis for a physical discussion.

We focus on the regime in which the statistics is determined by near field interactions, with negligible multiple scattering. The decay rate statistics is influenced by the local environment of the emitter (i.e. the interaction with the surrounding particles). In particular, we show that for moderate absorption, the non-radiative contribution is proportional to the imaginary part of the dielectric of the particles. The radiative decay rate statistics is almost independent on the level of absorption. In this regime, and for particles with uncorrelated positions (random cluster), a simple analytical model describes the average decay rates and the standard deviation within a wide range of parameters.

In summary, we study the statistics of the spontaneous decay rates in disordered nanoscopic clusters using both numerical simulations and a simple analytical model. Our results show that such statistics carry useful information about the local structure of the environment at the nanometer scale, even in the presence of absorption. This paves the way towards new imaging techniques.

[1] E.M. Purcell, *Phys. Rev.* **69**, 681 (1946).
[2] W. Guo, *Phys. Rev. A*, **69**, 043802 (2004).
[3] R. Carminati *et al*., *Opt. Comm*. **261**, 368 (2006).