Dependence of spontaneous emission rates of emitters on the refractive index of the surrounding medial

Chang-Kui Duan

Institute of Applied Physics and College of Electronic Engineering,
Chongqing University of Posts and Telecommunications,
Chongqing 400065, China.

and

Department of Physics and Astronomy,
University of Canterbury, Christchurch, New Zealand

Michael F. Reid

Department of Physics and Astronomy

and MacDiarmid Institute of Advanced Materials and Nanotechnology,
University of Canterbury, Christchurch, New Zealand

(Dated: March 31, 2005)

Abstract

For emitters in a medium, different macroscopic or microscopic theoretical models predict substantially different dependencies of the spontaneous emission lifetime on refractive index. Various measurements have been carried out on Eu$^{3+}$, Ce$^{3+}$ and Nd$^{3+}$ ions, and quantum dots in different surrounding medial. The dependence of the spontaneous emission rates on refractive index has been interpreted with different models. By closely examining some of the experimental results, we notice that some interpretations are based on implicit assumptions which are hard to justify, and some measurements contain too big uncertainties to discriminate among different models. In this work we reanalyse the available measured results and give a consistent interpretation.
I. INTRODUCTION

It is well known that the rate of spontaneous emission of emitters can be modified by changing the surrounding dielectric medium.\textsuperscript{1,2} The theory on this subject continues to attract considerable attention due to its fundamental importance and its relevance to various applications in low-dimensional optical materials and photonic crystals.\textsuperscript{3,4,5} Various macroscopic (see Ref.\textsuperscript{2} for a recent review) and microscopic\textsuperscript{5,6,7} theoretical models have been developed to model the dependence of the spontaneous emission rates (or lifetimes) on refractive index. However, different models predict substantially different dependences of radiative lifetime on refractive index. There are also some measurements intended to discriminate these models.

In this paper: firstly, we summarize main theoretical models and the corresponding underlying assumptions (Sec. II); then we examine the existing experimental results that have been claimed to support different models and give them a consistent interpretations (Sec. III).

II. MAIN THEORETICAL MODELS

Four main models for the dependence of spontaneous emission rates for emitters on the refractive index of the surrounding medium have been proposed since Purcell\textsuperscript{8} noticed that the spontaneous emission rates can be modified by changing the environment. Since most early theoretical and experimental results focus on the modification of the rate by placing the emitters inside resonant cavities\textsuperscript{9,10} and spatially inhomogeneous dielectrics including photonic band gap materials.\textsuperscript{11,12} In those approaches the spontaneous emission rate is proportionally altered when the radiation density of states is altered. By quantizing the macroscopic Maxwell’s equations, it can be seen that the density of states of radiation is proportional to the refractive index $n$. Therefore one expression for the radiative rate has been predicted by Nienhuis and Alkemade\textsuperscript{13} as

$$\Gamma_R(n) = \Gamma_0 n,$$

where $\Gamma_R(n)$ and $\Gamma_0$ are the radiative decay rate of electric dipole emitters in the dielectric with refractive index $n$ and in vacuum, respectively. The drawback of expression Eq. (1) is that the dielectric is taken to be homogeneous over the entire space, and also occupies
the place occupied by emitters, so that the electric field felt by the emitter is equal to
the macroscopic electric field (or proportional to the macroscopic electric field, with the
coefficient not depending on the surrounding medium).

In general, the field felt by emitters is different from the macroscopic electric field. Taking
this difference into consideration leads to the so-called local-field corrections, which apply to
a wide variety of physical quantities including the spontaneous emission rate of embedded
emitters. If the system is isotropic on microscopic levels, then the local field felt by the
emitter is proportional to the macroscopic field with a ratio denoted as $f$, then we have the
corrected spontaneous emission rate for electric-dipole emitters\(^2\)

$$\Gamma_R(n) = \Gamma_0 f^2.$$  \hspace{1cm} (2)

Macroscopic derivations of the local-field correction often imply the use of cavity around
the emitter. The specific choice of the cavity is subtle matter, greatly complicating the
interpretation of these models. One famous model introduced by Lorentz have been used
in many textbooks.\(^{14,15}\) A hypothetical spherical cavity filled with medium of the same
average polarizability density as the surrounding dielectric is introduced in this model, but
the contributions from the dipoles inside the cavity to the local electric field cancel. The
ratio $f$ is given as

$$f_{\text{virtual}} = \frac{n^2 + 2}{3}.$$ \hspace{1cm} (3)

The modification of radiative rate based on this ratio is usually called virtual-cavity model
or Lorentz model.\(^2\) Using the Lorentz model assumes that the polarizibility of the media is
not altered by introducing the emitters into the media. The results for Ce\(^{3+}\) in various hosts
with different refractive indices support this models.\(^{16}\)

In the case of fluorescent molecule emitters embedded in solution, the fluorescent
molecules expel the solvent from the volume where they are located and hence creat real
cavities of dielectric there. The ratio of the local electric field inside the cavity to the
macroscopic field outside the cavity was given by Glauber and Lewenstein\(^{17}\) as

$$f_{\text{real}} = \frac{3n^2}{2n^2 + 1}.$$ \hspace{1cm} (4)

The modification of electric-dipole radiative rate based on this ratio is usually called real-
cavity model\(^2\) or Glauber-Lewenstein model. There are quite a few experimental results\(^{18,19}\)
on molecular emitters that support this model.
All these models described above are based on a macroscopic description of the dielectric. One of the key features of these models is that the dielectric host are assumed to be unaffected by the presence of the embedded emitter. More recently, Crenshaw and Bowden proposed a fully microscopic model for local-field effects using quantum-electrodynamical, many-body derivation of Langevin-Bloch operator equations for two-level emitters embedded in a dielectric host. The radiative rate can be written as

\[ \Gamma_R(n) = \Gamma_0 \frac{n^2 + 2}{3} \]  

(5)

We shall refer to this model as Crenshaw-Bowden model.

Another very important result on this subject is the work by Berman and Milonni in early year 2004. They calculated the corrections to the electric-dipole decay rate by using another approach to the fully microscopic many-body theory. Their results are perfectly consistent with the macroscopic theories to the first order of dielectric density. However, to this order, their theory does not distinguish between the virtual-cavity and real-cavity models for the local-field correction. Therefore, there are still mainly four different models for the radiative rate of embedded emitters, with two models compatible with both macroscopic and fully microscopic theories.

III. EXISTING EXPERIMENTAL RESULTS AND REINTERPRETATIONS

A. Reinterpretation of the lifetime of \( \text{Y}_2\text{O}_3:\text{Eu}^{3+} \) nanoparticles in medium

Recently we analyzed the lifetimes of \( 5d \rightarrow 4f \) transitions of \( \text{Ce}^{3+} \) ions in hosts of different refractive indices and found that virtual cavity model applies. We notice in the literature that there had been experimental results on \( \text{Y}_2\text{O}_3:\text{Eu}^{3+} \) nanoparticles embedded in medium of various refractive indices which can also be interpreted with virtual cavity model. However, these two situations are very different. For the case of \( \text{Ce}^{3+} \) in different hosts, \( \text{Ce}^{3+} \) ions replace cations of small polarizability and do not change the medium itself, so that the virtual cavity model applies. However, for the case of \( \text{Y}_2\text{O}_3:\text{Eu}^{3+} \) nanoparticles embedded in medium, the medium is expelled from the space occupied by the nanoparticle, which is similar to the case of fluorescent molecules embedded in solutions. Therefore the real-cavity model should apply, with the refractive index in the equation replaced with the...
effective relative refractive index $n_r$ of the medium (with effective refractive index $n_{\text{eff}}(x)$) to the nanoparticle (assuming the bulk refractive index $n_{\text{Y}_2\text{O}_3}$), i.e., the radiative lifetime

$$
\tau_R = \frac{1}{\Gamma_R} = \tau_{\text{bulk}} \frac{1}{n_r} \left( \frac{2n_r^2 + 1}{3n_r^2} \right)^2
$$

(6)

where

$$
n_r = \frac{n_{\text{eff}}(x)}{n_{\text{Y}_2\text{O}_3}}
$$

(7)

$$
n_{\text{eff}} = x \cdot n_{\text{Y}_2\text{O}_3} + (1 - x) \cdot n_{\text{med}}.
$$

(8)

Here $n_{\text{med}}$ is refractive index of the medium without $\text{Y}_2\text{O}_3$ particles, and $x$ is the ‘filling factor’ showing what fraction of space is occupied by the $\text{Y}_2\text{O}_3$ nanoparticles surrounded by the media.

Fig. 1 plots the radiative lifetime as a function of the medium. It can be seen that Eq. (6) with filling factor $x = 0.15$ fits the measurements very well and hence provides an consistent alternative interpretation to the original interpretation based on virtual-cavity model. The filling factor is not explicitly measured and this value is also reasonable.

**B. Reinterpretation of the lifetime of CdTe and CdSe quantum dots in media**

Very recently, the lifetime of CdTe and CdSe quantum dots has been measured and compared with three of the above models. Although it is not conclusive, the fully microscopic model of Crenshaw and Bowden is suggested to best describe the measurements. There are two possible problems with the interpretation: Firstly, as mentioned above, in early year 2004 another group studied the corrections to radiative lifetime theoretically using another approach of fully microscopic many-body theory and obtained a theoretical result compatible with macroscopic models. Secondly, in the interpretation, the measurement lifetime is considered as solely due to radiative relaxation. It is likely that part of the lifetime is due to intrinsic nonradiative relaxation. Actually, the measured quantum efficiency is around 55%.

Here we give an alternative explanation of the correction to the lifetime. Since the medium is expelled from the space occupied by the quantum dots, the real-cavity model should apply. A reasonable assumption about the nonradiative relaxation rate is that it does not depend on the medium. In such a case, the lifetime due to both radiative and nonradiative relaxation
\[ \tau(n) \text{ and the quantum efficiency } \eta(n) \text{ of the quantum dots in medium can be written as} \]
\[ \frac{1}{\tau(n)} = \left( \frac{3n^2}{2n^2 + 1} \right)^2 \frac{n}{\tau_{R0}} + \frac{1}{\tau_{NR}}, \]
\[ \eta(n) = 1.0 - \frac{\tau(n)}{\tau_{NR}}. \]

Fig. 2 plots the total lifetime of the quantum dot CdSe as a function of the refractive index of the medium. Again, the real-cavity model fits the experimental lifetime very well and give an quantum efficiency 57% that is compatible with experiments.

IV. SUMMARY

In summary, experimental results for emitters in the form of nanoparticles or moleculars that expell the media and creat a real cavity, including those that are originally interpreted with other models, are compatible with the real-cavity models. This is different from the case that emitters do not change the media, such as Ce\(^{3+}\) ions replace cations with low polarizability, where the virtual-cavity model applies.

Acknowledgment

C.K.D. acknowledges support of this work by the National Natural Science Foundation of China, Grant No. 10404040 and 10474092.

1 N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965).
2 D. Toptygin, J. Fluoresc. 13, 201 (2003).
3 A. Luks and V. Perinova, in *Progress in Optics* (Elsevier, Amsterdam, 2002), vol. 43, pp. 295–431.
4 G. M. Kumar and D. N. Rao, Phys. Rev. Lett. 91, 203903 (2003).
5 P. R. Berman and P. W. Milonni, Phys. Rev. Lett. 92, 053601 (2004).
6 M. Born and E. Wolf, *Principles of Optics* (Cambridge University Press, Cambridge, 1999).
7 M. E. Crenshaw and C. M. Bowden, Phys. Rev. Lett. 85, 1851 (2000).
8 E. M. Purcell, Phys. Rev. 69, 674 (1946).
9 D. Kleppner, Phys. Rev. Lett 47, 233C236 (1981).
10 F. D. Martini, G. Innocenti, G. R. Jacobovitz, and P. Mataloni, Phys. Rev. Lett. 59 (1987).
11 E. Yablonovitch, Phys. Rev. Lett. 58 (1987).
12 S. John and T. Quang, Phys. Rev. A 50, 1764 (1994).
13 G. Nienhuis and C. T. J. Alkemade, Physica B & C 81C, 181 (1976).
14 J. D. Jackson, Classical Electrodynamics (Wiley, New York, 1975).
15 C. Kittel, Introduction to Solid state Physics -7th ed. (John Wiley & Sons Inc., New York, 1996).
16 C. K. Duan, A. Meijerink, R. Reeves, and M. Reid (2005), to appear on J. Alloys Compd.
17 R. J. Glauber and M. Lewenstein, Phys. Rev. A 43, 467 (1991).
18 G. L. J. A. Rikken and Y. A. R. R. Kessener, Phys. Rev. Lett 74, 880 (1995).
19 F. J. P. Schuurmans, D. T. N. de Lang, G. H. Wegdam, R. Sprik, and A. Jagendijk, Phys. Rev. Lett 80, 5077 (1998).
20 C. K. Duan and M. F. Reid (2005), presented on the 2nd international research conference on advanced materials and nanotechnology, Queenstown, New Zealand.
21 R. S. Meltzer, S. P. Feofilov, B. Tissue, and H. B. Yuan, Phys. Rev B 60, R14012 (1999).
22 S. F. Wuister, C. de M. Donega, and A. Meijerink, J. Chem. Phys 121, 4310 (2004).
FIG. 1: The dependence of the $^5D_0$ radiative lifetime $\tau_R$ for the Eu$^{3+}$ C site on the refractive index of the media $n_{\text{med}}$. Solid line: simulation with Eq. (6) using $x = 0.15$; dashed line: simulated with virtual-cavity model as given in FIG. 2 of Ref. 21; circles: experimental values as given in FIG. 2 of Ref. 21.
FIG. 2: The dependence of the lifetime of excitons of GdTe quantum dots on the refractive index of solvent. Squares: experimental data taken from FIG. 4 of Ref. 22; triangles: simulated with Eq. (5) as given in FIG. 4 of Ref. 22; stars (overlaped with triangles) and crosses: simulated with real-cavity model using best-fitted $\tau_{NR} = 60$ns (giving a quantum efficiency $\sim 57\%$ for $n \sim 1.4-1.5$) and a much higher $\tau_{NR} = 260$ns (giving a quantum efficiency $\sim 90\%$), respectively.