Abstract

For emitters embedded in media of various refractive indices, different macroscopic or microscopic theoretical models predict different dependencies of the spontaneous emission lifetime on refractive index. Among those models are the two most promising models: the virtual-cavity model and the real-cavity model. It is a priori not clear which model is more relevant for a given situation. By close analysis of the available experimental results and examining the assumptions underlying the two models, we reach a consistent interpretation of the experimental results and give the criteria which model should apply for a given situation.

Keywords: local-field effect; radiative lifetime; virtual-cavity model; real-cavity model; refractive index

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It has long been known that the spontaneous-emission rates of emitters can be modified by changing the surrounding dielectric media. The theory on this subject continues to attract considerable attentions due to its fundamental importance and its relevance to various applications in low-dimensional optical materials and photonic crystals. Various macroscopic (see Ref. 2 for a recent review) and microscopic theoretical models have been developed to model the dependence of the spontaneous emission rates (or lifetimes) on refractive index. Among those models are the real-cavity model (also referred to as empty-cavity model), where emitters (usually ions) are assumed to create tiny cavities when replacing host ions, and the virtual-cavity model, which is based on the Lorentz local field. Different models predict substantially different dependences of radiative lifetime on the surrounding media. There are also some measurements intended to discriminate these models, with most experimental results tend to agree with the real-cavity model. Especially, recent measurements on the radiative lifetime of Eu$^{3+}$ ion embedded in glass of varying refractive index also tend to agree with the real-cavity model, in contrary to the general belief that the virtual-cavity model should be more relevant. Duan and Reid pointed out that $4f \rightarrow 4f$ electric dipole radiative relaxation, which is due to mixing in $4f^N$ states with states of opposite parity, depends strongly on the environment and does not serve as a good examination of the two models. To overcome the problem in $4f \rightarrow 4f$ transitions, Duan and Reid analyzed the lifetimes of $5d \rightarrow 4f$ transitions of Ce$^{3+}$ ions in hosts of different refractive indices and the results maintained the text-book virtual-cavity model. However, they did not try to answer the questions why most other experimental results agree with the real-cavity model, and which model should apply for a given situation.

In this Letter, we examine those reported experimental results on various emitters in various surrounding media that appear to support different models. We point out why they support certain model in some cases and why they need to be reinterpreted with other models. Finally we answer the titled question by our consistent explanation of the experimental results and state the rule to choose the proper model for a given situation.

Measurements on the radiative lifetime of Eu$^{3+}$-hfa-topo complex emitter in a series of apolar hydrocarbons was reported by Rikken et al. in 1995. Experimental results show that the emissions are from $5D_0$ levels and dominated by electric dipole transitions to $7F_2$ levels, and the radiative quantum yield is close to unity. Fig. 1 is the plot of the
measured lifetimes together with the best fitting using the real-cavity model:

$$\tau_{\text{real}} = \tau_0 \frac{1}{n \left(\frac{3n^2}{2n^2+1}\right)^2},$$

where $\tau_0$ is the lifetime of the emitter in vacuum, the factor $n$ is due to the reduction of speed of light in the media and $\left(\frac{3n^2}{2n^2+1}\right)^2$ is the ratio of the electric field in the cavity (local field) to the macroscopic field in the media. $\tau_0$ is taken to be an adjustable parameter independent of the refractive index in the fitting.

It is well-known from Fermi’s golden rule that $\tau_0$ is proportional to the square modulus of the electric dipole moment and the cubic of the emission photon energy. In general, the $4f - 4f$ emission photon energy does not change substantially in different surrounding media, but the electric dipole moment of $4f - 4f$ transitions depends strongly on the arrangement of ligand ions. In the experiment, Eu$^{3+}$ ions are embedded in organic ligand cages which remain almost the same when the surrounding media are changed. Therefore the electric dipole moments and emission photon energies do not vary, and hence the unknown $\tau_0$ does not vary with the surrounding media and can be treated as an adjustable parameter.

It can be explained why the radiative lifetime of Eu$^{3+}$-hfa-topo complex supports the real-cavity model. The complex expels the solvent from the volume occupied by the complex and create a real tiny cavity of the dielectric, and the relatively large and rigid Eu$^{3+}$ complex leads to a region of small polarizability and hence small refractive index, which in the limiting case, is close to that of the vacuum. The ratio of the average electric field of the complex to the macroscopic electric field in the surrounding media obeys the real-cavity model. The ratio of the electric field “felt” by the Eu$^{3+}$ ion to the average electric field of the complex is a constant that does not depend on the surrounding media. Therefore the radiative lifetime for a given complex in various surrounding media can be described with the real-cavity model.

The real-cavity model is also confirmed by the measurements on Eu$^{3+}$(fod)$_3$ embedded in a dense supercritical CO$_2$ gas, where the refractive index changes from 1.00 to 1.27 when the pressure varies between 1 and 1000 bars.

Other similar cases have been reported by Lavallard et al. in 1996 and later by Lamouche et al. in 1998 with the sulforhodamine B molecules as emitters. In those experiments, the sulforhodamine B molecules are dissolved in water droplets (with refractive index $n_w$) which are stabilized by a surfactant (with refractive index $n_s$) and then suspended in
solutions of different refractive index \( n \). Theoretical modeling for this case is slightly more complicated and more general than the real-cavity model. It has been given based on the same principle as the real-cavity model as:

\[
\tau_{\text{real}} = \tau_0 \frac{1}{nB^2},
\]

\[
B = \frac{9n^2n_s^2}{(n_s^2 + 2n_w^2)(n_w^2 + 2n_s^2) + 2\left(\frac{2}{n}\right)^3(n_w^2 - n_s^2)(n_s^2 - n^2)},
\]

where \( a \) is the total radius and \( b \) is the radius of the water core. The special cases where \( n_w \approx n_s \) and \( a \approx b \) reduce to the real-cavity model (by replacing the \( n \) in Eq.(1) with \( n_r = n/n_w \)). The measurements confirm the more general equations Eq.(2) than the real-cavity model Eq.(1).

**Measurements on the radiative lifetime of Ce\(^{3+}\) ions** in hosts of different refractive indices have been summarized by Duan and Reid. The transition involved is the \( 5d \rightarrow 4f \) electric dipole allowed emission whose electric dipole moment is proportional to the radial integral \( \langle 5d | r | 4f \rangle \), which is mainly determined by the localized orbitals of Ce\(^{3+}\). Assuming \( \langle 5d | r | 4f \rangle \) to be constant, the results do not agree with the real-cavity model and are much better described by the virtual-cavity model, i.e.

\[
1/\tau_{\text{virtual}} = \frac{64\pi^4 e^2 | \langle 5d | r | 4f \rangle |^2}{5h\lambda^3} \chi
= \frac{4.34 \times 10^{-4} | \langle 5d | r | 4f \rangle |^2}{\lambda^3} \chi,
\]

where \( \lambda \) is the the average emission wavelength for Ce\(^{3+}\) in a given host, and

\[
\chi = n \left( \frac{n^2 + 2}{3} \right)^2
\]

is the refractive-index dependent factor. Note that \( \lambda \) can be substantially different for Ce\(^{3+}\) ions in different hosts. From the measured lifetime \( \tau_{\text{exp}} \) and emission wavelength \( \lambda \), we can obtained “experimental” values

\[
\frac{1}{[| \langle 5d | r | 4f \rangle |^2 \chi]_{\text{exp}}} = \frac{4.34 \times 10^{-4} \tau_{\text{exp}}}{\lambda^3}.
\]

Those “experimental” values can be compared to calculated values by considering the the unknown \( | \langle 5d | r | 4f \rangle | \) as a fitting parameter. In Fig.2 the “experimental” values \( 1/[| \langle 5d | r | 4f \rangle |^2 \chi]_{\text{exp}} \) are plot as a function of \( n \) together with the best least square fitting using the virtual-cavity model (\( \chi = n[(n^2 + 2)/3]^2 \)). For comparison, the least square fitting using the real-cavity model (\( \chi = n[3n^2/(2n^2 + 1)]^2 \)) is also plot.
On the other hand, we can calculate $\langle 5d | r | 4f \rangle$ for each Ce$^{3+}$ in each host for both virtual- and real-cavity models. For the virtual-cavity model, the obtained values show no systematic dependence on refractive index $n$ as expected, but there is for the real-cavity model. This also means that the virtual-cavity model describes the radiative lifetime of Ce$^{3+}$ in various hosts better than the real-cavity model.

The results can also be understood. In all those hosts, the low-polarizability ions Ce$^{3+}$ replace cations with low polarizability. These replacements do not create (tiny) cavities of the dielectric media, substantially different from the real-cavity cases. Hence the ratio of the local field to the macroscopic field can be calculated using the Lorenz model, i.e. the virtual-cavity model.

**The radiative lifetime of $Y_2O_3$:Eu$^{3+}$ nanoparticles embedded in media of various refractive indices** were measured in 1999. The experimental results were originally interpreted with the virtual cavity model. Since the nanoparticles (with constant refractive index $n_{Y_2O_3}$) expel, as has been pointed out by Duan and Reid, the media (with effective refractive index $n_{\text{eff}}(x)$) and create real cavities in the media, the real-cavity model should apply instead, with the refractive index in Eq. (1) replaced with the effective refractive index $n_r$ for the media relative to the nanoparticle:

$$n_r = \frac{n_{\text{eff}}(x)}{n_{Y_2O_3}}$$

$$= \frac{n_{Y_2O_3} + (1-x) \cdot n_{\text{med}}}{n_{Y_2O_3}},$$

where $n_{\text{med}}$ is refractive index of the media without embedding $Y_2O_3$ particles, and $x$ is the 'filling factor' showing what fraction of space is occupied by the $Y_2O_3$ nanoparticles surrounded by the media. At the same time, the $\tau_0$ should be replaced with the lifetime of a $Y_2O_3$:Eu$^{3+}$ nanoparticle in the media such that $n_r = 1$. One such case is when the $Y_2O_3$:Eu$^{3+}$ nanoparticle is part of the bulk $Y_2O_3$:Eu$^{3+}$, whose lifetime is denoted as $\tau_{\text{bulk}}$. The variation of the lifetime with $n_r$ can be written as:

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

(9)

Fig. 3 plots the radiative lifetime as a function of the media. It can be seen that Eq. (9) with filling factor $x = 0.15$ fits the measurements very well. The filling factor is not explicitly measured, but this value is consistent with the TEM pictures of these samples.

**The lifetimes of CdTe and CdSe quantum dots** in media have been measured very recently and interpreted with the fully microscopic model of Crenshaw and Bowden. This
model predicts a much weaker dependence of radiative lifetime on refractive index and does not separate the coefficients due to photon density of states and due to local-field effect. More recently, Berman and Milonni\textsuperscript{5} studied the corrections to radiative lifetime theoretically using a slightly different but more realistic approach of fully microscopic many-body theory and obtained a theoretical result compatible with macroscopic models. They also pointed out the problem with the fully microscopic model given by Crenshaw and Bowden. As pointed out by Duan and Reid\textsuperscript{15}, since the media are expelled from the space occupied by the quantum dots, the real-cavity model should apply. The relaxation in the quantum dots is partly due to nonradiative relaxation, which shall not depend on the refractive index of the media. We assume that the nonradiative relaxation rate $1/\tau_{\text{NR}}$ is constant and obtain:

$$\frac{1}{\tau(n)} = \frac{1}{\tau_{\text{R0}}} \left( \frac{3n^2}{2n^2 + 1} \right)^2 n + \frac{1}{\tau_{\text{NR}}}.$$  

Fig. 4 plots the total lifetime of the quantum dot CdSe as a function of the refractive index of the media. Using the experimental quantum efficiency of 55%, the model fits the experimental lifetimes very well. We notice that there is an argument in Ref.\textsuperscript{14} that the effective quantum efficiency is higher than 55% and hence plot an alternative simulated lifetime using a quantum efficiency 90%. It is also compatible with the experimental lifetimes within experimental errors. This means that, although not conclusive, the lifetimes of CdTe and CdSe quantum dots in media can also be explained by the real-cavity model.

The lifetimes of Eu$^{3+}$ ions in the glass system $x$ PbO + $(1-x)$ B$_2$O$_3$ ($x = 0.7-1.0$) have been measured in 2003 and interpreted with the real-cavity model. It has previously been pointed out by Duan and Reid\textsuperscript{8} that the electric dipole moment for Eu$^{3+}$ ions $f - f$ transitions strongly depends on the local structure, which may change when the composition of the glass changes, and so the lifetime may not serve as a good examination of different models. However, they did not intend to explain why the experimental results come out to follow the prediction of the real-cavity model. Clearly, if the virtual-cavity model is employed to calculate the electric dipole moment, there will be a correlation in the trend of the electric dipole moment with the refractive index in that when the refractive index increases, the electric dipole moment decreases in a systematic way. Another problem we try to answer is: if Ce$^{3+}$, whose emission is $f - d$ transition, is used instead of Eu$^{3+}$ in the glass system, then which model should best describe the measurements.

From a recent study of the network structure of B$_2$O$_3$-PbO\textsuperscript{16} it can be seen that the bond
length B-O is less than 0.15 nm, while Pb-O is between 0.25 to 0.3 nm, comparable with the usual bond length between a rare-earth ion and O ion. Therefore a rare-earth ion can only substitute a Pb ion in the glass. When $x$ decreases from 1.0 to 0.7, the rare-earth ion remains in Pb position and hence the local structure does not change substantially. Therefore, when $x$ decrease the emission energy does not change, and it is very likely that the electric dipole line strength of Eu$^{3+}$ in the glass do not change substantially either. Hence the variation of experimental lifetime with $x$ reflects the effect of changing refractive index, which favor the real-cavity model.

In factor, We notice that Pb is different from light cations in that it has a very large polarizability and is often used as additives to glass to increase the index of refraction. The substitution of Pb with a low-polarizability rare-earth ion creates a tiny cavity of the dielectric in the media. Hence the real-cavity become more relevant than the virtual-cavity model. If $f − d$ transition of Ce$^{3+}$ ion is used instead of $f − f$ transiton of Eu$^{3+}$, we predict that the radiative lifetime will also close to the real-cavity model and provide an even better test for our analysis.

In summary, All the experimental results for emitters embedded in dielectric media have been successfully interpreted with either real-cavity model or virtual-cavity model in a consistent way. From the interpretation, the titled question is now clear: when the emitter expels the dielectric media and create a real (tiny) cavity in the media (including the case of ions of high polarizability being replaced with ionic emitters of low polarizability), the spontaneous emission lifetime obeys the real-cavity model. When the emitters substitute ions of low polarizability, they do not create a real cavity in the media, and then the emission lifetime obeys the virtual-cavity model.

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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 C. K. Duan and M. F. Reid, to be published on Current Applied Physics.
9 G. L. J. A. Rikken and Y. A. R. R. Kessener, Phys. Rev. Lett **74**, 880 (1995).
10 P. Lavallard, M. Rosenbauer, and T. Gacoin, Phys. Rev A **54**, 5450 (1996).
11 G. Lamouche, P. Lavallard, and T. Gacoin, J. Lumin **76&77**, 662 (1998).
12 R. S. Meltzer, S. P. Feofilov, B. Tissue, and H. B. Yuan, Phys. Rev B **60**, R14012 (1999).
13 C. K. Duan and M. F. Reid (2005), to be presented on the 24th international rare-earth research conference, Keystone, Colorado, June 26-30.
14 S. F. Wuister, C. de M. Donega, and A. Meijerink, J. Chem. Phys **121**, 4310 (2004).
15 C. K. Duan and M. F. Reid, J. Chem. Phys **122**, 094714 (2005).
16 H. Ushida, Y. Iwadate, T. Hattori, S. Nishiyama, and et al., J. Alloys Compd. **377**, 167 (2004).
FIG. 1: Radiative lifetime of Eu$^{3+}$-hfa-topo as a function of the solvent refractive index. The dots are measured lifetimes and the curve is fit to Eq. (1).
FIG. 2: Variation of $1/(\langle |5d| r |4f\rangle_{\text{eff}}^2 \chi)$ with refractive index. The experimental values are plotted as ‘*’ with a 10% error bar. The solid curve is calculated with virtual-cavity model using best least-square-fitting value $\langle |5d| r |4f\rangle_{\text{eff}} = 0.0291$, and the dashed curve is for real-cavity model with best least-square-fitting value $\langle |5d| r |4f\rangle_{\text{eff}}' = 0.0404$. 
FIG. 3: 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. (9) using $x = 0.15$; dots: experimental values as given in FIG. 2 of Ref. 12.
FIG. 4: The dependence of the lifetime of excitons in GdTe quantum dots on the refractive index of solvent. Squares: experimental data taken from FIG. 4 of Ref. 14; stars and crosses: simulated with real-cavity model using best-fitted $\tau_{NR} = 58$ns (giving the experimental quantum efficiency $\sim 55\%$ at $n = 1.44$) and a much higher $\tau_{NR} = 260$ns (giving a quantum efficiency $\sim 90\%$ at $n = 1.44$), respectively.