High-Q whispering gallery modes of doped and coated single microspheres and their effect on radiative rate

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Fluorescence spectra of two organic dyes doped in polymer beads as well as coated on single microparticles of silica exhibit whispering gallery modes (WGMs). For doped microspheres, theoretical simulations on WGMs have been carried out based on the Lorentz–Mie theory by varying the refractive index and the diameter of the microparticle. Similarly, for a coated microsphere, an Aden and Kerker model of the Lorentz–Mie theory has been used to simulate WGMs. For diameters $\geq 8\, \mu m$, low-resolution simulations of scattering efficiency fail to show modes of higher-quality factors $(Q \sim 10^8)$. A new procedure of identifying these modes is given here that does not require use of high-performance computing. Effects of WGMs on decay rates have also been studied. It has been found that, while doped microparticles exhibit no effect on the radiative rate, coated microparticles show inhibition of the decay rate for smaller sizes. Decay rates of single-coated microspheres are found to be distinctly different from those of randomly shaped single microcrystals. © 2009 Optical Society of America

1. INTRODUCTION

Spherical or cylindrically symmetric, nearly transparent microparticles containing fluorescent molecules act as high-quality factor (Q) resonators [1]. Given a microsphere of radius $r_1$ and relative refractive index $m$, the critical angle for an internal ray is given as $\theta_0 = \sin^{-1}(1/m)$. If such a ray hits at an angle larger than the critical angle, it gets totally internally reflected within the cavity. This results in the natural modes of oscillations of the cavity to occur at specific frequencies. These modes are known as whispering gallery modes (WGMs) or morphology-dependent resonances (MDRs) [2]. The wavelength locations of these modes are extremely sensitive to the changes in the refractive index and the size of the microcavity [3]. Applications of such studies include low-threshold lasing [4], enhanced energy transfer [5–9], and biosensing [10,11].

Each WGM is described by its polarization, e.g., transverse electric (TE) or transverse magnetic (TM), and a set of three numbers associated with it—a radial number $n$, which gives the number of maxima in the radial dependence of a mode; an angular mode number $l$ (roughly giving the number of wavelengths in a round trip inside the spherical cavity); and an azimuthal mode number $p$, which can take the values of $-l$ to $+l$. The azimuthal mode number $p$ describes the azimuthal spatial distribution of the mode. For the perfect sphere, WGMs are degenerate with respect to $p$ [12]. For a given microsphere, resonances occur at specific values of $x_{n,l}=2\pi m_{med}/\lambda$ where $r$ is the radius of the microsphere, $m_{med}$ is the refractive index of the medium, and $\lambda$ is the wavelength of the light [13].

The radiative rates of the atoms or molecules are expected to change in the presence of the microcavity environment. This is due to cavity quantum electrodynamic effects [14,15]. There are two qualitatively different regimes in the microcavities: (i) the weak coupling regime and (ii) the strong coupling regime. The weak coupling regime is characterized by monotonous exponential decay, the decay rate being enhanced or inhibited compared to the free-space value depending on whether the atomic transition frequency lies on a cavity resonance or not [14,15]. The strong coupling regime, in contrast, is characterized by reversible Rabi oscillations, where the energy of the excited atom is periodically exchanged between the atom and the field [16].

Existence of WGMs and their effect on the decay rate in polymer beads has been reported earlier [11,14,15,17]. Work on coated microspheres and microcrystals is scarce in the literature [18–23]. Large diameter beads possess high-Q modes that are very sharp and clustered. To reproduce the experimentally observed modes through simulations, there is a need of high-performance computing. Therefore, in this article we report (i) a procedure to locate the high-Q peaks in the scattering efficiency spectrum with low memory computation and (ii) the effect of WGMs on the radiative rates of molecules doped in polymer microspheres and coated on silica microspheres. We have selected two standard laser dyes, rhodamine 6G (R6G) and rhodamine B (RB), due to their high photostability. Additionally, due to their high quantum yield values, the radiative rate is close to their decay rates.

This paper is organized as follows. Section 2 gives the experimental details. Theoretical aspects of WGMs of coated and doped microspheres are given in Section 3. The results and discussion (Section 4) has been divided
into six parts (A–F). Section 4.A gives the theoretical simulations on doped and coated microspheres at smaller size parameters. Section 4.B gives the comparison of theoretical simulations and experimentally observed spectra for larger-sized beads by using low-resolution calculations. Section 4.C gives the problems of resolution at higher size-parameters. The method of resolving the high-Q modes is given in Section 4.D. Analysis of the time-resolved decay measurements for coated and doped microspheres as well as microcrystals is given in Section 4.E. In Section 4.F the effect of coating thickness on the quality factor and the radiative rate is discussed. Conclusions are given in Section 5.

2. EXPERIMENT

The standard laser dyes R6G and RB (Aldrich, 98%) were used as received. The solvent (methanol) obtained from Qualigens Fine Chemicals was of spectrograde quality. 100 mg of polymethyl methacrylate (PMMA) (MR 10 G, Soken Kagaku) microspheres were immersed in the R6G solution (10⁻⁴ M) for more than 20 h for doping. These particles were then washed with methanol and dried under ambient conditions. Similarly, glass microspheres (Duke Scientific Corp.) were coated using the RB solution (10⁻⁴ M). After completely drying, the microparticles were transferred to a slide glass for measurement.

Single microparticles were chosen with the help of the epifluorescence microscope (NIKON Eclipse E-400) equipped with a G-2A bandpass filter (510–560 nm). The excitation source was a He–Ne laser (543.5 nm). The emission was collected with a barrier filter of 590 nm with the help of a 40× objective lens and was passed through a combination of a PC-controlled spectograph (Spectrapro 2750, PI ACTON) and a CCD detector (PIXIS, PI ACTON). Decay time measurements for single microparticles and microcrystals were done with the technique of a time-correlated single-photon counting technique (TC-SPC) [14,15,17]. Analysis of the decay profiles was done by using a software program (FAST, Edinburgh Instruments). The fitting of the decay curves was judged by the value of reduced chi square ($\chi^2$) and weighed residuals [24]. For a good fit, the value of the $\chi^2$ is around 1, and the residuals are evenly distributed about the fitted curve. Theoretical simulations were performed by sharing the server (AMD Opteron, 1.80 GHz) with the help of the subroutine of Bohren and Huffman [25].

3. THEORETICAL ASPECTS

Figure 1 shows the schematic of the microcavities studied in this work. According to the Lorenz–Mie scattering theory, the separation between the adjacent WGMs (or free spectral range, FSR) for a homogeneous sphere is approximated by [23]

$$\Delta \lambda = \frac{\lambda^2}{2 \pi m_{med} r_1} \tan^{-1}\left[\frac{(m_1/m_{med})^2 - 1}{1/2}\right].$$

where $\lambda$ and $r_1$ represent the wavelength of the light and the radius of the microsphere, respectively. $m_1$ is the refractive index of the core.

For the case of the coated sphere, the refractive index of the surrounding medium is replaced by the refractive index of the mantle relative to the medium, and $m_1$ is replaced by the refractive index of the core relative to the medium [26]. Aden and Kerker [27] solved the problem of scattering from a layered sphere by using the Mie–Debye theory. The scattering cross section is given by

$$Q_s = \frac{2 \pi}{|k|^2} \sum_{n=1}^{\infty} (2n + 1)(|a_n|^2 + |b_n|^2),$$

where $k$ is the complex propagation constant. $a_n$ and $b_n$ are the scattering coefficients given by

Fig. 1. Schematic of (a) a doped and (b) a coated microsphere. $r_1$ is the radius, and $m_1$ is the refractive index of the core of the uncoated (homogeneous) microsphere. $r_2$ is the radius of the coated microsphere. $m_2$ is the refractive index of the coated layer (or the mantle).

Fig. 2. (a) Fluorescence spectrum of R6G-doped ~6 μm diameter single PMMA bead sitting on a glass plate. (b) Calculated scattering efficiency for a bead of $r=2.9685$ μm and $m=1.495$. The size parameter range is 31.72–32.61.
Here \( x_1 = 2\pi r_1 / \lambda \) and \( x_2 = 2\pi r_2 / \lambda \) in the air, \( r_2 \) is the radius of the mantle. \( \psi_n(s) \), \( \chi_n(s) \), and \( \zeta_n(s) \) are the Riccati–Bessel functions and have the following relations with the spherical Bessel \( (j_n(s)) \), Neumann \( (n_n(s)) \), and Hankel \( (h_n^{(1)}(s)) \) functions:

\[
\psi_n(s) = sj_n(s), \quad \chi_n(s) = -sn_n(s) \quad \text{and} \quad \zeta_n(s) = sh_n^{(1)}(s).
\]  

(5)

Prime denotes the differentiation with respect to the argument. The value of \( A_n, B_n \) in equations (3) and (4) are given by the following expressions:

\[
A_n = \frac{m_2\psi_n(m_2x_1)\psi_n'(m_1x_1) - m_1\psi_n'(m_2x_1)\psi_n(m_1x_1)}{m_2\chi_n(m_2x_1)\psi_n(m_1x_1) - m_1\chi_n'(m_2x_1)\psi_n(m_1x_1)},
\]  

(6)

\[
B_n = \frac{m_2\chi_n(m_2x_1)\psi_n(m_1x_1) - m_1\chi_n(m_2x_1)\psi_n'(m_1x_1)}{m_2\chi_n(m_2x_1)\psi_n(m_1x_1) - m_1\chi_n'(m_2x_1)\psi_n(m_1x_1)}.
\]  

(7)

If \( m_1 = m_2 \) or \( r_1 = 0 \), then \( A_n \) and \( B_n = 0 \) and the coefficients \( a_n \) and \( b_n \) reduce to those for a homogeneous sphere [28].

4. RESULTS AND DISCUSSION

A. WGM at Small Size Parameters

The fluorescence spectrum of R6G doped in a PMMA bead of diameter \( \sim 6 \) \( \mu \)m exhibits WGMs as shown in Fig. 2(a). Figure 2(b) shows the theoretical simulations for this bead. The following asymptotic expressions [13,29] have been used to locate the WGMs:

\[
\frac{[mxj_n(mx)]'}{m^2j_n(mx)} = \frac{[xh_n^{(1)}(x)]'}{h_n^{(1)}(x)} \quad \text{(For a TE case),}
\]

(8)

\[
\frac{[mxj_n(mx)]'}{m^2j_n(mx)} = \frac{[xh_n^{(1)}(x)]'}{h_n^{(1)}(x)} \quad \text{(For a TM case).}
\]

(9)

Here prime denotes the differentiation with respect to the argument. \( m \) is the relative refractive index of the sphere with respect to the surrounding medium. From simulations the Q values for the first- and second-order modes are found to be of the order of \( 10^3 \) and \( 10^5 \), respectively. It is noted here that a resolution in size parameter of \( 10^{-4} \) is sufficient to reproduce all of the WGMs observed in the experimental spectrum. The experimentally observed modes show lower Q values.

Similarly, for a sphere of \( \sim 8 \) \( \mu \)m diameter coated with another dye RB, the experimentally observed spectrum matches reasonably well with that obtained from the simulations, as indicated in Fig. 3. The simulations in this case have been carried out by taking the value of the refractive index of coated dye as 1.40 [23]. It is to be noted that the simulations were extremely sensitive to the refractive index and the thickness of the mantle. However, a coating thickness of \( \sim 50 \) nm was obtained from the simulation of Fig. 3.

In order to identify the modes, we made typical simulations for a homogeneous silica microsphere of a nearby size \( (r_1 = 4.141 \) \( \mu \)m) surrounded by air. It can be seen that the observed modes [Fig. 3(c)] are similar in nature to those simulated for the coated sphere [Fig. 3(b)] but deviate in their positions slightly, indicating a weak perturbation induced by the thin coating of the material. A small portion of the simulations also gives the identification of the observed modes [Fig. 3(d)]. Following are the salient features in the analysis of Fig. 3: (i) the experimentally observed modes are \( \sim 10 \) times broader than those obtained from simulations, (ii) the Q values of the first-order modes (e.g., for \( a_{521} \) mode \( Q \sim 4.3 \times 10^6 \)) for the coated sphere are smaller than for the uncoated sphere by a factor of 10 in simulated spectra; and (iii) for the coated bead the WGM peaks shift to the lower energy \( \sim 115 \) cm\(^{-1}\) as compared to that of the uncoated bead. This indicates that the perturbation is due to the imaginary part of the refractive index of the thin coating with simultaneous introduction of Qm [15] (vide infra). In addition, it is observed that in simulations the first-order modes tend to loose their intensities beyond \( 16400 \) cm\(^{-1}\). This is due to the lack of resolution employed in the simulations.

B. Fitting of Experimentally Observed Spectra of Large Diameter Beads

Figure 4(a) shows the experimentally observed fluorescence spectrum of a R6G-doped \( \sim 13 \) \( \mu \)m diameter PMMA bead. Fig. 4(b) shows a typical simulation with a resolution of \( \Delta x = 10^{-4} \).

It can be seen that, unlike in Fig. 2(b), the first-order modes are not present in the theoretical simulations at all. This is due to the fact that it requires larger memory calculations at higher resolutions and is limited by our computing facilities. In order to locate the positions of the sharp first-order modes in these low-resolution calculations we followed the following procedure.

C. Problems of Resolution at Higher X-Parameters

The calculated scattering efficiency as a function of the size parameter (1 to 50) is shown in Fig. 5 for a general
case. The resolution in the size parameter ($\Delta x$) is $3 \times 10^{-4}$. The TE and TM modes overlap in the lower-sized parameter region of 0 to 8. The insets show the well-separated TE and TM modes. The second-order modes are not significant in the size parameter range from 0 to 20. In this region, the first-order modes are built upon the broad second order peaks. A well-resolved region at size parameter range 25 to 26 on the expanded scale shows that at higher-sized parameters the modes are sharp and congested. The main features of the observed WGMs are as follows. The full width at half-maximum (FWHM) of the WGM decreases with the increase of the $n$. It in-
creases with the increase of the \( l \) for the given \( n \). In addition, it is observed that as the refractive index of the particle is increased, the position of the WGM shifts to lower-sized parameters along with the reduction in their FWHM values [30]. For large values of \( n \), the first-order peaks are missing in low-resolution calculations toward the higher-sized parameters (shown on the expanded scale in the size parameter range 43 to 44).

D. Procedure of Resolving the High-Q Modes with Low-Resolution Calculations

Locating first-order WGMs at higher \( x \) parameters becomes increasingly difficult in simulations due to their sharpness and subsequent high-Q value. The size parameter is inversely proportional to the wavelength. Therefore, it is easier to locate these peaks at lower \( x \) values (at higher wavelengths). Since we have the estimate of the FSR [Eq. (1)] for a given microcavity, it is possible to predict their locations at higher-sized parameters by extrapolating them from the region of interest.

For this purpose, we set a low-resolution limit on the simulations at the lower \( x \) values. If for a simulation a ten-fold increase in the resolution the number of peaks does not change, this spectrum can be taken as a final calculation, provided that the first-order modes are observed in this size parameter region. Figure 6 gives a typical simulation for the \( x \) value range of 39.80–40.35. By using the value of the FSR, the position of the first-order modes can be extrapolated for the region of interest at higher-sized parameters.

Initial estimates of the radius of the microspheres are done by (i) visual inspection while recording the spectrum and (ii) use of the FSR value. Figure 7(b) gives the positions of the high-Q modes (\( Q \sim 10^5 \)) marked by extrapolat-

Fig. 4. (a) Experimentally observed spectrum of R6G doped single PMMA bead of 13 \( \mu \)m diameter. (b) The calculated scattering efficiency spectrum \((r=6.0605, m=1.495)\) with \( \Delta x=10^{-4} \). The size parameter range is 58.59–61.52.
ing a low-resolution \((\Delta x = 10^{-4})\) simulation. It was found that the generated peaks by the extrapolation method matched well with those obtained with a high-resolution calculation for a small portion of \(\Delta x = 0.40\) [Fig. 7(c)] (with \(\Delta x = 10^{-7}\)). Although this method does not provide the exact value of \(Q\) for the mode, it is sufficient to estimate the dimensions of the microcavity within a few nm. Table 1 gives the \(Q\) value of some of the modes in doped and coated beads. It can be seen that while the first-order modes of the large diameter beads are of the order of \(10^8\), the experimentally observed modes are broader by 4 orders of magnitude. This broadening is not limited by the resolution of the spectrometer, as the latter is sufficient to resolve the modes with an even higher \(Q\) value (inset).

E. Time-Resolved Measurements

As described in Sections 4.A and 4.B, the coated as well as doped microspheres exhibit WGMs of the microcavity. In order to look at the influence of the WGM on the decay rate, we measured the fluorescence lifetimes of the dyes for both types of microcavities.

1. Doped PMMA Microspheres

Fluorescence lifetimes of RB in PMMA beads of various sizes are given in Table 2. It is observed that the fluorescence decay intensity \((I(t))\) fits well with a single exponential scheme

\[
I(t) = A \exp(-t/\tau)
\]  

where \(A\) is the pre-exponential factor and \(\tau\) is the fluores-
cence lifetime of the dye. Figure 8 gives a typical decay profile and its fit with Eq. (10).

Klimov et al. [31] have done the simulations for cavities of low size parameters and different refractive indices. Chew et al. [32] have made simulations for the cavities of a lower refractive index (1.47) for a higher size parameter range of 47–155. It was observed that for refractive indices up to about 1.5, the rates for both polarizations exhibit smooth oscillatory functions of the radial distances \( r_1 \) for size parameter up to 10. A higher value of refractive index or size parameter tends to magnify the amplitudes of the oscillations by a factor of a few hundred. In the present experiments, the radiative rate is not affected by the cavity environment for the case of doped microparticles. This indicates that under the present parameters of the cavity there exists a large number of interacting modes within the homogeneous linewidth of the dye inside the microsphere [33,34]. Since no effect was observed for the microspheres of size up to 6 \( \mu m \), the FSR value corresponding to this (400±5 cm\(^{-1}\)) indicates the lower limit of the homogeneous linewidth. This indicates the dephasing time \( T_2 \) to be smaller than 13±2 fs in a polymer matrix for RB at room temperature.

Barnes et al. have reported a 60% increase in the decay rate of octadecyl RB contained in glycerol microdroplets [35]. The enhancement factor decreased rapidly with the increase in the droplet diameter, and no modification was observed for droplet diameters larger than 10 \( \mu m \). In the present case, however, the low number density of dye molecules that are fixed in the PMMA bead do not give scope for any other possibility of diffusion-controlled rates that might lead to nonradiative deactivation due to dipole–dipole interactions [36,37]. Similar effects were observed earlier for low concentration beads of other dyes [3].

2. Coated Silica Microspheres and Microcrystals
It is well known that the effect of first-order modes is dominant in spectra as well as in decay rates [3]. First-order WGMs appear at the surface of the spherical cavity. In order to look at their effect on decay rates, it is essential to place fluorescent molecules at the surface of the microcavity. This can be done easily by coating the microparticles with fluorescent dyes. We have chosen silica microspheres for this purpose as the dye is unable to penetrate the particle and remains at the surface.

As shown in Section 4.A, the coated microspheres exhibit WGMs. We have recorded the decay profiles of RB coated with two different concentrations (10\(^{-3}\) M and 10\(^{-4}\) M). The observed fluorescence decay intensity \( I(t) \) in this case exhibits biexponential behavior

\[
I(t) = B_1 e^{-t/t_1} + B_2 e^{-t/t_2},
\]

where \( B_1 \) and \( B_2 \) are the amplitudes of the fluorescence intensity.

---

### Table 1. Q Values Observed in Doped and Coated Beads

<table>
<thead>
<tr>
<th>Bead diameter (( \mu m ))</th>
<th>Mode</th>
<th>( ^aQ_{\text{the}} )</th>
<th>( ^bQ_{\text{exp}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 (Fig. 2)</td>
<td>( a_{42.1} )</td>
<td>3.2 \times 10^4</td>
<td>1.1 \times 10^3</td>
</tr>
<tr>
<td>13 (Fig. 7)</td>
<td>( a_{76.1} )</td>
<td>3.0 \times 10^4</td>
<td>5.0 \times 10^4</td>
</tr>
<tr>
<td>8 (Fig. 3)</td>
<td>( a_{52.1} )</td>
<td>4.3 \times 10^6</td>
<td>3.0 \times 10^4</td>
</tr>
</tbody>
</table>

\(^aQ_{\text{the}}\): Theoretical Q value

\(^bQ_{\text{exp}}\): Experimental Q value

---

### Table 2. Fluorescence Lifetimes of RB-doped Single PMMA Beads of Various Sizes

<table>
<thead>
<tr>
<th>Bead diameter (( \mu m ))</th>
<th>( \tau(\pm0.1) ) ns</th>
<th>( \chi^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>3.5</td>
<td>1.17</td>
</tr>
<tr>
<td>10</td>
<td>3.5</td>
<td>1.09</td>
</tr>
<tr>
<td>8</td>
<td>3.5</td>
<td>1.07</td>
</tr>
<tr>
<td>5</td>
<td>3.5</td>
<td>1.11</td>
</tr>
</tbody>
</table>

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**Fig. 7.** (a) Portion of the experimental spectrum shown in Fig. 4. (b) Scattering efficiency spectrum for a bead of \( r=6.0605 \mu m \) and \( n=1.495 \) with low resolution calculations (\( \Delta x=10^{-4} \)). Thick arrows indicate the generated peaks by the extrapolating procedure described in the text. (c) High-resolution calculations (\( \Delta x=10^{-7} \)) for a small region.
lifetime components $\tau_1$ and $\tau_2$, respectively. The corresponding fractional intensities ($f_1$ and $f_2$, respectively) are given by

$$f_1 = \frac{B_1 \tau_1}{B_1 \tau_1 + B_2 \tau_2} \quad \text{and} \quad f_2 = \frac{B_2 \tau_2}{B_1 \tau_1 + B_2 \tau_2}. \quad (12)$$

The fluorescence lifetimes of RB-coated silica microspheres are given in Table 3. Figure 9(a) shows the decay curves for the coated microspheres at two sizes. The fluorescence decay for a coated bead of 33 $\mu$m in diameter shows two components, viz., 1.2 ns and 3.1 ns, respectively. The fractional intensities of the slow component dominates here. On decreasing the size to 15 $\mu$m, the corresponding decay times become 1.8 ns and 3.8 ns, respectively, with approximately the same fractional intensities. This decrease in the decay time is observed only for the beads coated with a lower concentration $10^{-4}$ M. For the beads coated with a higher concentration ($10^{-3}$ M), the decay times do not change with the size. Figure 10 shows the variation in the ratio of the modified radiative rates of RB in the silica microsphere as compared to that from the largest size ($\sim 33 \mu$m) studied here. Modification factors of $\sim 0.66$ for the fast component and 0.81 for the slow component are obtained in the present case for a bead of 15 $\mu$m. The theoretical simulations are available for lower- [39] and higher- [40] sized parameters in the literature. Chew et al. [40] have given the simulations for the size parameter range of 5 to 33 for dielectric spheres. With an increase in the size parameter, it is found that while the enhancement is observed always for the perpendicular component near the surface, the parallel component experiences inhibition (of $\sim 0.9$) at the increase in the size parameters. However, for the present case of the size parameter range of 79–174 and a moderate value of the refractive index, no theoretically simulated data is available. Moreover, the present experiments are not polarization-selective, hence they are expected to exhibit an average effect.

<table>
<thead>
<tr>
<th>Table 3. Fluorescence Lifetimes of RB-coated Single Glass Beads with Different Concentrations (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bead diameter (C)</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>$C=10^{-4}$ M</td>
</tr>
<tr>
<td>33</td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>18</td>
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<tr>
<td>15</td>
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<tr>
<td>$C=10^{-3}$ M</td>
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<tr>
<td>38</td>
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<tr>
<td>23</td>
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<tr>
<td>20</td>
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<td>15</td>
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</tbody>
</table>
F. Effect of Imaginary Refractive Index on Q Values and Radiative Rates

At higher concentrations the first-order WGMs are expected to lose their intensity, as shown in Fig. 11. This is because microcrystalline dyes generally have absorption toward the longer wavelengths [21,22]. This introduces an imaginary refractive index \( n_i \) and the absorption cross section \( Q_a \) of the microcavity resulting in the disappearance of first-order modes, as seen in Fig. 11. Hence the decay rate becomes independent of the bead size. This is born of the fact that for a coated bead with higher concentrations, the biexponential fitting essentially gives the same decay rates as that for an independent single crystal of \( 8 \times 13 \) \( \mu m \) size (Table 4). We can safely say that, although for the crystalline fluorescent dye the decay profile is biexponential in nature, it is influenced by the cavity modes with low coating thickness in smaller sizes.

To work with still lower coating concentrations was not possible due to a very weak emission of the extremely thin coating of the dye. The weak emission is accompanied by the irradiation effects that further reduce the intensity for larger duration exposures. For example, Fig. 12 gives the effect of irradiation on WGMs for a coated bead with a core of \( 18 \) \( \mu m \). It can be seen that the total fluorescence intensity decreases by a factor of \( 4 \) within a 4 min exposure, although the WGMs remain there. Therefore, at the present it is not possible to clarify the slowest inhibited decay rates one can observe in this system.

5. CONCLUSIONS

The fluorescence spectra of dyes doped in polymer beads or coated on silica beads exhibit WGMs. In theoretical simulation the WGMs for large diameter beads need high resolution to reproduce the high-Q modes. These high-Q modes can be generated by using the low-resolution calculations procedure suggested here. This is a valuable tool in the absence of a high-performance computing facility. The silica beads coated with low concentrations show inhibition of the decay rate at smaller sizes, while those coated with a high concentration show the effects similar to microcrystals due to the presence of an imaginary re-
fractive index. Experimental decay rates of coated and doped microspheres are compared with the theoretical simulations.

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