Microcavity effect of dyes adsorbed on a levitated droplet

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The fluorescence spectra and lasing behavior of dye molecules adsorbed on a droplet levitated in an electrodynamic trap have been studied. A simple classical model describes the dye–cavity-mode interaction quantitatively well when the homogeneous linewidth of the dye is wider than the free spectral range of the cavity. When the free spectral range becomes comparable with the homogeneous linewidth, the prediction of the model systematically deviates, indicating that stochastic fluctuations of the radiating dipoles need to be taken into account. [S1050-2947(99)04909-4]

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I. INTRODUCTION

The interest in microsphere optical resonators [1] is derived both from the fundamental study of the photon confinement with its quantum-electrodynamical consequences and from the application in electro-optics. The basic effect of a microcavity on the matter inside is enhancement or suppression of the radiative decay rate. The phenomenon has been generally discussed on the basis of the mode volume consideration [2]. Some further arguments for the case of a spherical dielectric cavity have also been presented along the same line [3]. One outstanding issue, however, is a *quantitative* understanding of the enhancement or inhibition of the radiative transition due to the cavity mode. In order for the quantitative study, it is of prime importance that the system under study be as simple as possible so that a theoretical model can be applied in a most straightforward manner. A levitated droplet with dye molecules selectively adsorbed on the surface is an ideal system; one has a perfect sphere without any support that disturbs the mode structure and with the light-matter interaction localized at a well-defined position in the cavity. Here we present experimental results on a systematic study of fluorescence spectroscopy of dye monolayers adsorbed on a levitated droplet. We found in a dilute dye system that a simple classical theory describes the spectra quite accurately when the homogeneous width Γ_{homo} of the dye is larger than the free spectral range (FSR) of the cavity modes. However, when the FSR is comparable with Γ_{homo}, a systematic deviation was found, a sign that the dynamics of the radiating molecule must be taken into account. The lasing property was also studied.

II. THEORY

The optical resonance-mode analysis of a dielectric sphere, the so-called morphology-dependent resonance (MDR, or whispering-gallery mode), has been the subject of continuing studies [4]. Furthermore, a variety of microscopic treatments of a radiating dipole interacting with the resonant modes have appeared [5,6]. In the following, we will use the treatment by Druger *et al.* [6], based on a classical model in which a point dipole interacts with a classical electromagnetic field. The validity of the classical approach, for the case in which the coupling between light and matter is weak, has been shown in the seminal work by Kuhn [7].

We will not repeat the derivation of the formula here but only summarize it as follows: Consider a classical point dipole embedded in a dielectric microsphere. The dipole emits light into various resonance modes of the sphere. The coupling strength with each mode is calculated from the overlap of the mode with the dipole radiation pattern. These modes in turn form a radiation field at the location of the dipole, which is felt by the transition moment as a reaction field. Depending on the phase of the reaction field, the dipole transition is suppressed or enhanced. This is the classical description of the cavity quantum electrodynamics.

When the molecule is located on the surface (but *inside* [8]) of the sphere, the effect of the reaction field can be calculated in a relatively simple closed form. Expressed in terms of the modulation of the radiative decay rate relative to the decay rate in the free space, it is written as

$$\frac{\gamma(\theta,\omega)}{\gamma}=1+\frac{3}{2}\sum_{l=1}^{\infty}(2l+1)\left\{\mathrm{TM}_l\left[l(l+1)\left(\frac{j_l(mX)}{(mX)}\right)^2\times\cos^2(\theta)+\frac{1}{2}\left(\frac{[(mX)j_l^2(mX)]'}{(mX)}\right)^2\sin^2(\theta)\right]+\frac{1}{2}\mathrm{TE}_l j_l^2(mX)\sin^2(\theta)\right\}, \tag{1}$$

where TM_l and TE_l are given by

$$\mathrm{TM}_l=\frac{h_l^{(1)}(X)[mXh_l^{(1)}(mX)]'-m^2h_l^{(1)}(mX)[Xh_l^{(1)}(X)]'}{m^2j_l(mX)[Xh_l^{(1)}(X)]'-h_l^{(1)}(X)[mXj_l(mX)]'}, \tag{2a}$$

$$\mathrm{TE}_l=\frac{h_l^{(1)}(X)[mXh_l^{(1)}(mX)]'-h_l^{(1)}(mX)[Xh_l^{(1)}(X)]'}{j_l(mX)[Xh_l^{(1)}(X)]'-h_l^{(1)}(X)[mXj_l(mX)]'}, \tag{2b}$$

and j_l and $h_l^{(1)}$ are the spherical Bessel function and Neuman function of the first kind of lth order, respectively. The prime implies differentiation with respect to the respective argument. Here, θ is the angle of the dipole moment with respect to the surface normal, m is the index of refraction of the dielectric sphere (outside is vacuum), and X is the size parameter, i.e., $X=2\pi a/\lambda$ (a=the radius of the sphere and λ=the wavelength of light in a vacuum).

It has been shown that Eq. (1) gives semiquantitative agreement with the experimental observation as far as the orientational (θ) dependence of the dipole moment is concerned [9]. One important aspect of Eq. (1) is its ω dependence through X, which gives the cavity enhancement or suppression of the radiative transition probability. Although others have obtained qualitative agreement with Eq. (1) [10], with efforts to reduce background noise, we are able to obtain a quantitative agreement.

III. EXPERIMENT

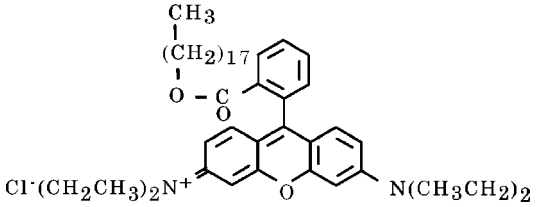
The basic experimental procedure is similar to the one presented previously [11]. It consists of a spherical void electrodynamic levitator trap (SVELT) [12] with a picopipette injecting a droplet whose radius is in the range 4–10 μm. The droplet is illuminated with either a pulsed laser light (second harmonic of a pulsed Nd:YAG laser, $\lambda=532.7$ nm, pulse rate $\sim$10 kHz, pulse width = 1 ns) or a cw laser light [all line (488–515 nm) Ar laser]. In order to achieve uniform illumination over the central volume of the trap, the laser beam was not focused tightly ($\sim$100 μm diameter). At the focal point, the pulse energy was less than 4 mJ/cm^2 (corresponding to the peak power density of 4 MW/cm^2). The cw energy was less than 20 W/cm^2.

The fluorescence was collected at right angle of the incident light. The image of the sphere was formed at the entrance slit of a 30-cm monochromator equipped with a liquid-N_2-cooled charge-coupled device (CCD) camera. The spectral resolution [full width at half maximum (FWHM)] of about 0.2 nm was determined using line spectra from a low-pressure gas discharge tube.

Photobleaching limited the total observation time to be less than 1 min. Exchanging the air in the trap with N_2 gas from a liquid N_2 boiloff extended this time by a factor of 5. A more serious limiting factor, however, is the slow evaporation from the droplet. The initial composition of the droplet contains water (see below). The time needed for the water to evaporate completely and the final water content in equilibrium varies depending on the relative humidity in the trap. This time can be long since prolonged injection to find a droplet of the desired size increases the water vapor concentration.

The residual water in the droplet has two effects: (a) it lowers the index of refraction and (b) it slows the rate at which the droplet diameter decreases. From the spectral shift observed after repeated data collection on a single droplet, we judged that the data collection time of 1–5 s is short enough to avoid the broadening of the line shape due to the slow change in the droplet size.

(A) ODRB



(B) Rhodamine 6G

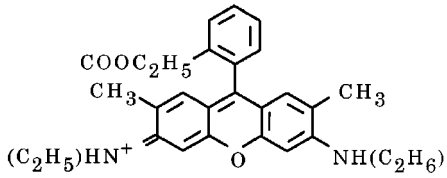


FIG. 1. Molecular structures of the dyes. Dye *A*: ODRB= octadecyl rohdamine B. Dye *B*: rohdamine 6G, which is electrostatically adsorbed onto the stearic acid monolayer on the surface of the droplet.

The sample consists of methanol solution of a dye and stearic acid mixed with glycerol in 3:1 volume ratio. The dyes used are listed in Fig. 1. After being injected into the trap, methanol evaporates quickly, leaving a monolayer on the surface of the droplet. The dye concentration was such that the average distance between dye molecules is 50 nm. This dilute concentration avoids Förster-type energy transfer which becomes active at a distance less than 10 nm. Just enough stearic acid was added to form a monolayer on the droplet surface. This acts as a ''filler'' for dye *A* and provide the surface adsorption site [13] for dye *B* which is not surface active by itself.

The mixture was drawn into a capillary of the picopipette. Since the driving fluid of the pipette is purified water, the water inevitably gets into the solution to varying degrees. All experiments were done at room temperature.

IV. RESULTS AND DISCUSSION

A. Reproducibility

In order for a quantitative study, the reproducibility and reliability of data were first examined. In Fig. 2 are shown three fluorescence spectra of dye *A*. The mode asignment (TE, TM, mode number *n*, and order number *s*) was done using fitting parameters described below. Figures 2(a) and 2(b) [=(b1) and (b2)] are from two different droplets formed and detected under nominally identical conditions. The similarity of the spectral shape indicates that the diameters of the two droplets matches within 0.4%. Two spectra (b1) and (b2) were taken from the same droplet several minutes apart with-

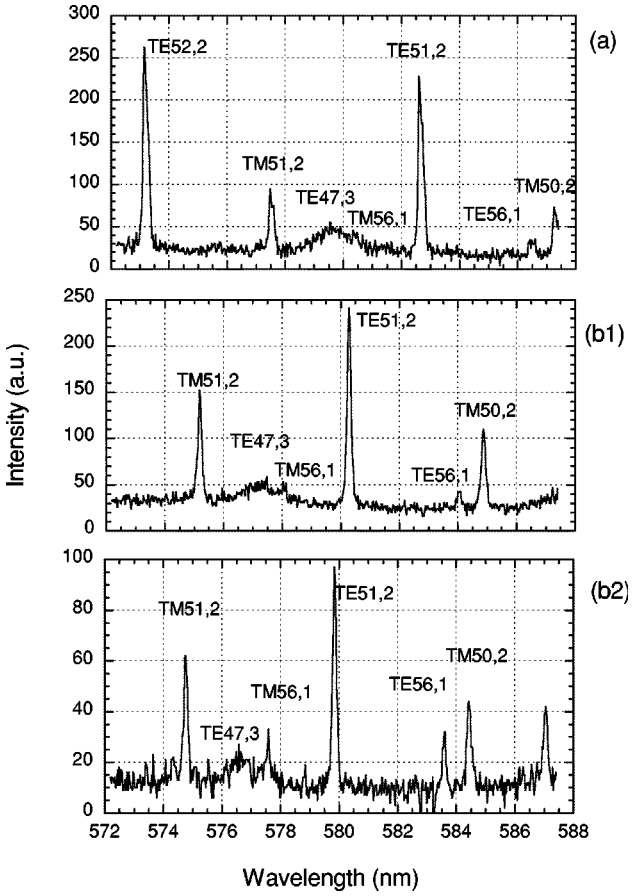


FIG. 2. Reproducibility of the fluorescence spectra. (a) and (b) [= (b1) and (b2)] are two droplets formed under nominally identical conditions. (b2) was taken several minutes after (b1), showing a slight reduction in the droplet size due to evaporation.

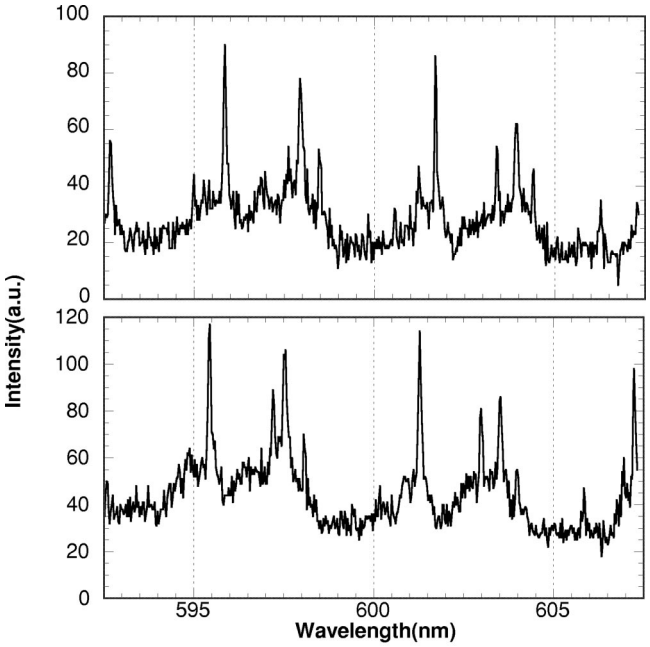


FIG. 3. Excitation polarization dependence of the fluorescence spectra. Incident light is polarized parallel (top panel) and perpendicular (bottom panel) to the plane of incidence. Two spectra are essentially identical (the relative peak hights of different modes and peak heights with respect to the nonresonant background level) except for the slight overall shift due to evaporation.

out the laser illumination. The shift of the spectra and reduction in intensity from (b1) to (b2) are due to the gradual decrease in the size of the droplet and the photobleaching of the dye, respectively. Although the overall spectral shapes are fairly stable despite the photobleaching, the $s=1$ modes tend to fluctuate from spectrum to spectrum. This point will be discussed later. Since the period for a stable trapping for the majority of droplets is scores of minutes, it turned out to be not practical to allow a waiting period for a droplet to reach a stable size after the complete water evaporation. Therefore, in a multiple exposure experiment, a small shift of the size could not be avoided.

Figure 3 shows two spectra with the incident light polarized parallel (a) and perpendicular (b) to the plane of incidence. Since they are similar, we judge that the polarization dependence does not affect the discussion below. All data were taken with the laser light polarized at 45° with respect to the plane of incidence. Figures 2(b1) and 2(b2) and Figs. 3(a) and 3(b) represent the quality of the reproducibility of our data.

B. Case for a larger droplet

When the droplet is large such that Γ_{homo} is wider than the FSR of the MDR, the application of Eq. (1) is most straightforward. Because the homogeneous width covers many FSR, the relative transition probability for a molecule giving off a photon at a particular ω is determined solely by Eq. (1).

In Fig. 4 are shown fluorescence spectra of dyes *A* and *B*. The dashed line is a fit using Eq. (1). The fitting parameters are the radius (a) and index of refraction (m) of the droplet and the tilt angle (θ) of the dye chromophore. There are further factors to be considered. (1) The quantum yield of these dyes in dilute solutions is high [14] enough so that the nonradiative decay is ignored. (2) The instrumental resolution is convoluted in Fig. 4. This is the limiting factor of the resolution in Fig. 4 and actual peaks should be much narrower and taller. (3) The background absorption coefficient (mostly attributed to the glycerol) [15] is estimated to have an effective Q value (Q_{abs}) of 10^7. Varing Q_{abs} in the range of 10^6–10^8 does not significantly affect the quality of the fit (see below).

The fit to the data in Fig. 4 is quite good within the reproducibility of the data (Fig. 3). Note that this is the first time that the relative contribution of the off-resonance part (the background fluorescence corresponding to the suppression of the transition) and resonance part (enhancement) is quantitatively compared with the theory. The dyes *A* and *B* have essentially the same chromophore. The difference in the orientation (θ) of the dye chromophores of the two reflects the difference in the adsorption mechanism: one is surface active while the other is electrostatically adsorbed to the stearic acid monolayer.

The $s=1$ modes are systematically missing in Fig. 4. In a lossless medium, the inherent Q values of $s=1$ modes are much larger than 10^7 (of the order of 10^{10}). The low instrumental resolution does not wipe out these lines since the

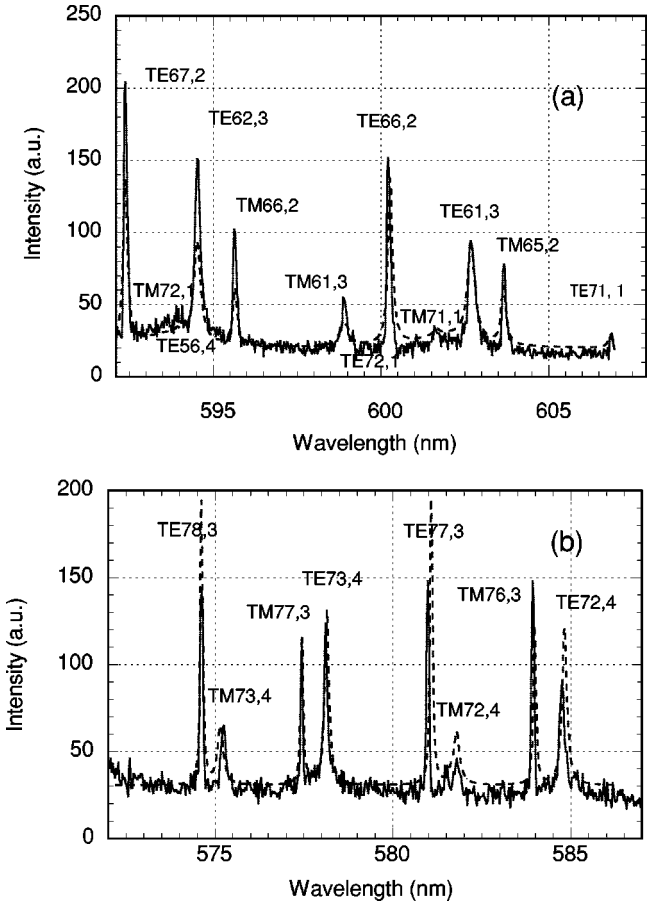


FIG. 4. Fluorescence spectra of (a) dye *A* and (b) dye *B*. The surface density is about 1 molecule/(50 nm)^2. The dashed line is a fit using Eq. (1). The fitting parameters are as follows: (a) $a=5.2475\ \mu$m, $m=1.435$, $\theta=\pi/2$ and (b) $a=6.0475\ \mu$m, $m=1.460$, $\theta=\pi/3$.

integrated intensity of all modes is nearly equal. The low instrumental resolution would simply reduce the peak height of the $s=1$ modes to the level of other resonance peaks. However, the absorption affects the spectrum in a different manner. The photon of high-Q mode stays much longer in the cavity so that it has much better chance to be absorbed while trapped. Due to this mechanism, any mode having $Q \gg Q_{abs}$ *disappears* from the fluorescence [16]. The relatively large uncertainty of Q_{abs} simply reflects the fact that in these droplets Q values for the $s=1$ modes (Q_1) and $s=2$ modes (Q_2) satisfy the inequality $Q_2 \leqslant 10^6 < Q_{abs} < 10^8 \leqslant Q_1$.

The actual Q values of the high-Q mode are also very sensitive to the state of the droplet and can be easily spoiled, e.g., by the deviation from a perfect sphere due to surface ripples or by scattering by impurity. Whenever the Q values of $s=1$ modes are spoiled and become comparable to or lower than Q_{abs} the peaks *reappear* in the spectrum. This is the reason for the rather unstable appearance of the $s=1$ modes in Fig. 2.

C. Lasing property

The effect of inherently high Q values of $s=1$ modes relative to Q_{abs} can be further seen in a lasing experiment. Figure 5 shows the emission spectra of dye *A* with a pulsed excitation (a) and with a cw excitation (b), respectively. Be-

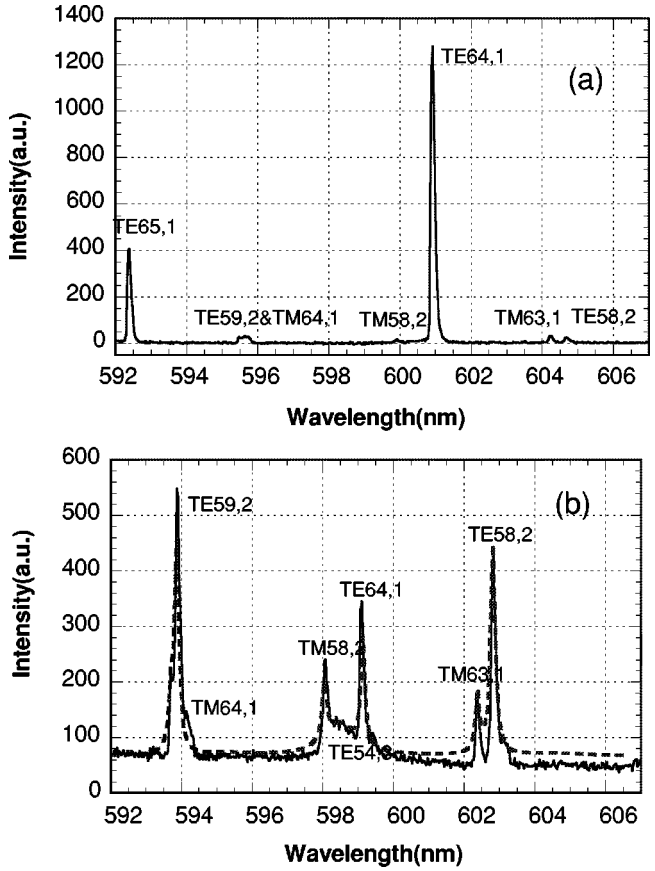


FIG. 5. Emission spectra of a droplet with dye *A*. (a) Pulsed excitation and (b) cw excitation. $a=4.7975\ \mu$m, $m=1.405$, $\theta=\pi/2$. (b) was recorded after (a) so that (b) is smaller.

cause the droplet is smaller, the inherent Q values for $s=1$ modes (slightly above 10^8) are lower than those in Fig. 4 and thus they become visible in Fig. 5(b). When excited by light with a stronger peak power from a pulsed laser, lasing occurs [Fig. 5(a)]. Note that only the TE, $s=1$ peaks are lasing. Since the molecules are lying flat, the TE modes have larger gain. With a stronger excitation, TM, $s=1$ modes can also lase but at much lower intensity compared with the TE modes. In all cases, however, lasing was observed only from $s=1$ modes. As has been discussed, the Q values of the $s=1$ modes should be larger than those of other modes, despite their apparent lower peak heights in the fluorescence spectra. Since the absorption affects all modes equally in the lasing condition, the modes with higher Q values (larger density of states) are favored for stimulated emission, the $s=1$ modes as observed.

D. Case for a smaller droplet

The FSR gets larger as the droplet size shrinks. Figure 6 shows the emission spectra of dye *A* on progressively smaller droplets. Only $s=1$ modes are now dominant, in strong contrast to Fig. 4. The Q values of the $s=1$ modes are less than 10^4 in this size range and the peak width of the smallest sphere clearly exceeds the instrumental resolution. Note that the fit [shown in dashed line, calculated using Eq. (1)] is quite poor. (The overall intensity variation across the spectrum is due to the fluorescence profile of the dye. The fit does not take this factor into account.) The peak height with re-

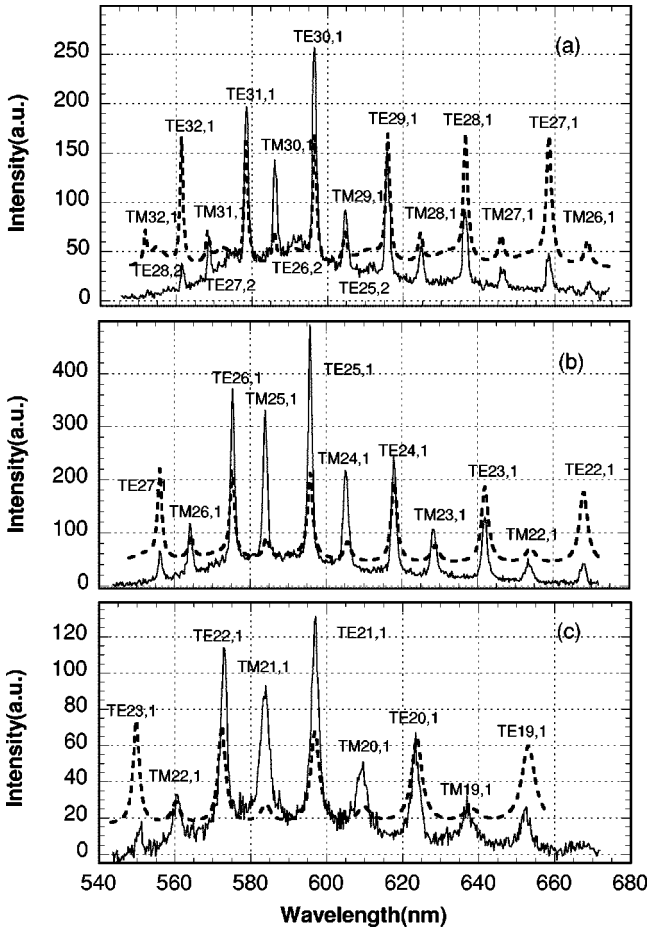


FIG. 6. Emission spectra of smaller droplets. (a) $a=2.3175$ μm, (b) $a=1.9656$ μm, and (c) $a=1.6670$ μm. In all cases, $m=1.435$ and $\theta=\pi/2$. The dashed line is the calculated spectrum using Eq. (1) assuming a flat fluorescence intensity profile.

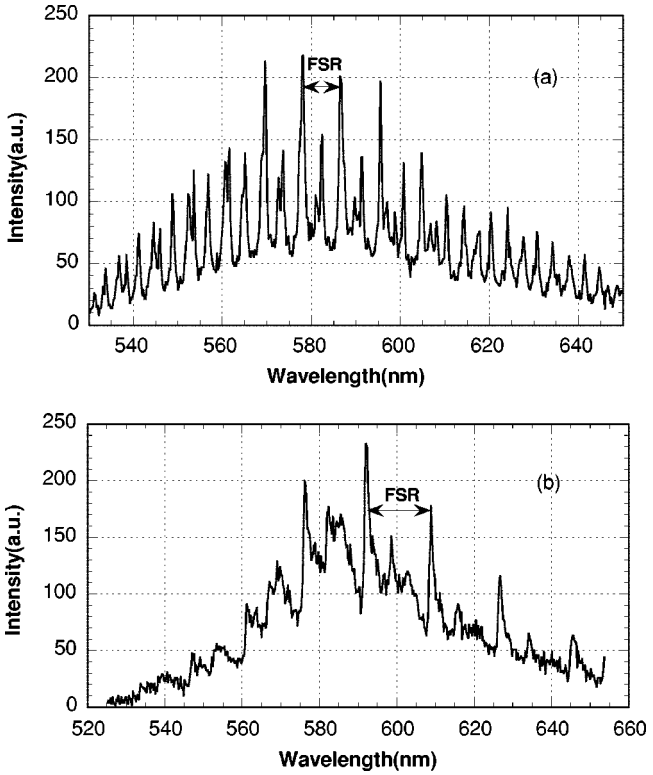


FIG. 7. Emission spectra of dye *A* on glass spheres of diameter ~ 9 μm (a) and ~ 5 μm (b).

spect to the background is much larger than the calculated value, or conversely, the background is quite suppressed. The relative peak heights of the TE and TM modes are also grossly off the mark. Both modes tend to become of equal height.

The homogeneous width of a dye in solution at a room temperature is not well understood but is probably in the range of ~ 100 cm^{-1} corresponding to ~ 5 nm [9,17,18]. The FSR of the droplets shown in Fig. 6 is, therefore, equal to or larger than Γ_{homo}. In this case, Eq. (1) cannot be used in a straightforward manner to interpret the data as has been done above.

Let us consider a case in which Γ_{homo} is small compared with the FSR. What has been calculated in Eq. (1) is the effect on the radiative transition rate by the cavity resonance modes at a particular frequency ω. Suppose that the fluorescence spectrum is inhomogeneously broadened. Then, depending on the environment, some molecules with matching frequency with the resonance modes feel the strong enhancement and radiatively decay back to the ground state quickly while others which are off resonant feel suppression and the lifetime is prolonged. (This distinction is absent when $\Gamma_{homo} \gg$ FSR because no net effect remains after the integration of the emission profile of individual molecules over Γ_{homo}.) Therefore, with time-resolved fluorescence spectroscopy, one would see initial resonance peaks followed by a rapid decay of these peaks into the slowly decaying background. An indication of such a phenomenon has been indeed observed previously [19]. The appearance of the fast decay component has also been observed in the energy-integrated fluorescence lifetime measurement [18]. However, all molecules of high quantum yield will emit photons of their respective energies sooner or later. Therefore, under a weak excitation in which the molecules spend most of the time in the ground state so that the number of photons absorbed per unit time is independent of the radiative enhancement or suppression factor, the *time integrated* fluorescence spectrum should show *no* peaks.

The observation (enhanced peaks and/or suppressed background) is just the opposite of the above expectation. Clearly, the consideration of FSR and Γ_{homo} alone is not adequate to interpret the data. One possible mechanism that can account for the observation is the spectral diffusion [20]. The spectral diffusion is the shift of the central frequency of the dye fluorescence spectral profile due to the fluctuating environment. Of course, a clear boundary between physical processes that lead to Γ_{homo} and the spectral diffusion may be difficult to draw especially in the case of molecules in liquid solution at room temperature. But in the case under consideration, any fluctuating behavior occurring in the time scale between subpicosecond to the fluorescence lifetime ($\sim$ ns) can be identified as spectral diffusion not Γ_{homo}. When the molecular emission (i.e., Γ_{homo}) falls between the resonance modes, the fluorescence is suppressed and the molecule remains excited. Through the spectral diffusion, however, the molecule has a chance to come into resonance

with the MDR mode. The ehnanced decay rate in this case makes the fluorescence at the MDR mode more likely. The process thus favors the fluorescence on the MDR mode at the expense of the reduced fluorescence off the resonance. Based on this scenario, it is also easily understood that the distinction between different modes (TM and TE) tends to be reduced. Note that this effect starts to show up when the diameter of the droplet is less than ~ 5 μm, which coincides nicely with the size of the droplet with which the cavity-enhanced decay rate becomes noticeable in the time-resolved experiment [18].

Spectral diffusion is strongly dependent on the matrix in which the dye is embedded. It is expected to be as large as the inhomogeneous width in the case of the liquid solution at room temperature. The effect should be less pronounced for a more rigid matrix. For comparison, we have performed a reference experiment using glass spheres. Glass spheres were dispersed in ethanol and dye-stearic acid solution and injected into the levitator in the same way as the glycerol droplet. The number density of the spheres in the solution was chosen such that, on the average, much less than one sphere was contained in an ejected droplet from the picopipette. If the droplet contains a sphere, the sphere stays in the trap coated with a monolayer of dye or stearic acid after evaporation of methanol. In Fig. 7 are shown the fluorescence spectra of dye *A* on glass spheres. The one from the larger sphere (diameter ~ 9 μm) has a similar peak to background ratio as one from a glycerol droplet of comparable size (e.g., Fig. 4). On the other hand, the spectrum from the smaller sphere (diameter ~ 5 μm), shows much smaller peak to background ratio in strong contrast with Fig. 6. Although many aspects such as the surface roughness and sphericity of the glass spheres make the straightforward comparison difficult, the trend in going from Fig. 7(a) to 7(b) seems clearly in agreement with the above explanation.

V. CONCLUSIONS

We have shown that Eq. (1) based on a simple classical model quantitatively describes the modification of the emission spectrum of a dye molecule embedded in a microsphere in the regime $\Gamma_{homo} > \mathrm{FSR}$. It deviates systematically for the case $\Gamma_{homo} \leqslant \mathrm{FSR}$. We propose that in the latter regime, the consideration for the dynamics of the molecule in the excited state has to be taken into account explicitly.

ACKNOWLEDGMENTS

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