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Cavity-enhanced fluorescence decay rates from microdroplets

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We show that enhanced fluorescence decay rates in microdroplets due to weak coupling to Mie resonances should not follow an inverse radius dependence, $1/a$, as has been assumed in several publications, but should contain both $1/a$ and $(1/a)^2$ components. The correspondence with experiment is very good. © *1997 American Institute of Physics.* [S0021-9606(97)02119-3]

Recently there has been a great deal of general interest in fluorescence from spherical microdroplets (μ-drops).[1] This interest has been generated from a host of applications, such as the detection of single solute molecules,[2] and the enhancement of intermolecular energy transfer,[3] to name a few. In particular, it has been demonstrated that the fluorescence decay rate for micron sized aerosol particles shows a pronounced dependence on radius, a, which is properly attributed to the interaction between excited states and Mie resonances (a.k.a. whispering gallery modes, or Morphology Dependent Resonances).[4,5] Although existing theory for one-dimensional (1D) cavities predicts that the rate of decay should follow an inverse size dependence, researchers in both Refs. 4 and 5 point out that the experimental decay rates appear to increase more rapidly with decreasing size. In this paper we revisit the problem of fluorescence decay from μ-drops. By using specific properties of spherical resonances we show that the size dependence of the optimal volume averaged fluorescence decay rate, in the simplest case, should contain both $1/a$ and $(1/a)^2$ components. The theory is found to be in good correspondence with the reported experimental data.

We start our analysis by recognizing that the rate of decay in cavity in a weak coupling limit is governed by a Fermi golden rule,

$$\Gamma_c(\omega) = \frac{2\pi}{\hbar^2} |M|^2 \rho_c(\omega), \tag{1}$$

where M is the matrix element representing the atom-field interaction, and $\rho_c(\omega)$ is the volume averaged density of photon states, associated with the emission process. Yokoyama and Brorson[6] have shown that the application of this equation to an emission process associated with a spectrum $h(\omega)$, gives a rate of decay relative to that in bulk of

$$\frac{\langle \Gamma_c \rangle}{\Gamma_0} = \frac{\int_0^\infty h(\omega)\rho_c(\omega)d\omega}{\int_0^\infty h(\omega)\rho_0(\omega)d\omega}, \tag{2}$$

where Γ_0 and ρ_0 are the decay rate and density of states in bulk, respectively. Within the particle, the density of states is redistributed according to the sum rule

$$\int_{\Delta\omega} \rho_c(\omega)d\omega \approx \int_{\Delta\omega} \rho_0(\omega)d\omega, \tag{3}$$

where $\Delta\omega$ in the interresonance separation (a.k.a. "free spectral range").[7] Figure 1 shows a pictorial representation of all of the relevant spectra associated with Eq. (2). We have separated the density of states within the particle ρ_c into resonant and background contributions;

$$\rho_c = \rho_r + \rho_b. \tag{4}$$

The resonant contribution is made up of a sum of modes, i.e., $\rho_r(\omega) = \Sigma_s \rho_{r,s}(\omega)$, for which the strength of each is controlled by a second sum rule,[7]

$$\int \rho_{r,s}(\omega)d\omega \approx \frac{D_s}{V_p}, \tag{5}$$

where D_s is the mode degeneracy and V_p is the particle volume.

By choosing a normalized Lorentzian line shape for $h(\omega)$, i.e., $h(\omega) = (\Gamma_h/2\pi)/(\omega^2 + \Gamma_h^2/4)$, and centering it on a resonance (Fig. 1), we are now in a position to evaluate Eq. (2) for optimal volume averaged effect.

We assume that the resonant modes are much narrower than the homogeneous line width and use the periodicity of the modes to replace the integration over all frequency by integration over one free spectral range, i.e., the range of integration becomes $\omega_s - \Delta\omega/2 < \omega < \omega_s + \Delta\omega/2$. Using Eq. (5) the integral over the resonant contribution in the numerator of Eq. (2), $\int h(\omega)\rho_{r,s}(\omega)d\omega = 2D_s/\pi\Gamma_h V_p$. The nonresonant contribution to the numerator is obtained by determining ρ_b. Here we are aided by the sum rule in Eq. (3). The background density of states is the average level left behind after "carving out" the resonant contribution, i.e., $\rho_b = \rho_0 - (D_s/\Delta\omega V_p)$. Together, the numerator in Eq. (2) becomes $\int h(\omega)\rho_c(\omega)d\omega = \rho_0 + (D_s/V_p\Delta\omega)((2\Delta\omega/\pi\Gamma_h) - 1)$. The denominator in Eq. (2) is $\int h(\omega)\rho_0(\omega)d\omega = \rho_0$, and the quotient

$$\frac{\langle \Gamma_c \rangle}{\Gamma_0} = 1 + \frac{D_s}{\rho_0 V_p \Delta\omega}\left(\frac{2\Delta\omega}{\pi\Gamma_h} - 1\right). \tag{6}$$

In arriving at Eq. (6) we have effectively assumed that $\Gamma_h \leqslant 2\Delta\omega/\pi$.

Equation (6) is different than the 1D result in Ref. 6. For 1D, $\langle \Gamma_c \rangle/\Gamma_0$ is proportional to the free spectral range $\Delta\omega$, $\langle \Gamma_c \rangle/\Gamma_0 = 2\Delta\omega/\pi\Gamma_h$,[6] and therefore inversely proportional

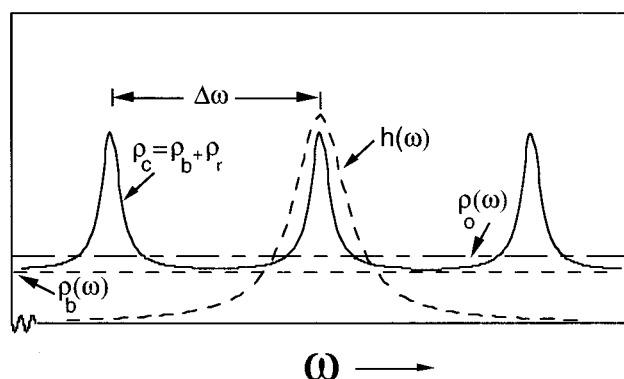[a)]Telephone: 718 260 3085, Fax: 718 260 3139, electronic mail: arnold@photon.poly.edu

FIG. 1. Relevant spectra for evaluating Eq. (2).

FIG. 2. Comparison between the experimental decay rate data vs. diameter in Ref. 5, the $1/a$ hypothesis based on Ref. 6 ($\Gamma_h = 100$ cm^{-1}) as presented in Ref. 5, and the size dependence as calculated from Eq. (6) ($\Gamma_h = 160$ cm^{-1}, $f = 20$ μm).

to the cavity size. This result can be recovered from Eq. (6) with $D_s/\rho_0 V_p \Delta\omega = 1$. The latter condition essentially says that the degeneracy would have to be the same as the total number of states in a free spectral range. This is not surprising. For a 1D analysis $D_s = 1$, and this is the same as the number of states in one free spectral range. This situation is quite different for a spherical particle containing Mie resonances (a.k.a. whispering gallery modes, or Morphology Dependent Resonances). The degeneracy of a whispering gallery mode $D_s = 2l + 1$, where l is the angular momentum quantum number of the mode. The angular momentum quantum number l is essentially equal to the number of interior wavelengths which can wrapped around the circumference, and therefore for $l \gg 1$, D_s is proportional to the radius a. Since the free spectral range between whispering gallery modes in a dielectric particle of refractive index n, $\Delta\omega \approx c/(n\,a)$, and the volume is proportional to a^3, $D_s/\rho_0 V_p \Delta\omega \propto 1/a$. Therefore the enhancement, $(\langle\Gamma_c\rangle/\Gamma_0) - 1$, from Eq. (6) is seen to contain a sum of terms which vary as $1/a$ and $(1/a)^2$.

The spatial distribution of excited molecules within a spherical particle irradiated by a plane wave is highly non-uniform, and the enhancement will be dependent on the radial position of the excited states. To account for this we replace $D_s/\rho_0 V_p \Delta\omega$ in Eq. (6) by f/a, where f depends on the radial distribution of the excited states. On this basis the size dependence of the enhancement takes the form

$$\frac{\langle\Gamma_c\rangle}{\Gamma_0} - 1 \approx \frac{f}{a}\left(\frac{2c}{\pi n \Gamma_h} \cdot \frac{1}{a} - 1\right). \qquad (7)$$

As we will see, in what follows, Eq. (7) provides a very good fit to experimental data in comparison to the $1/a$ dependence arrived at from 1D analysis.

Equation (7) has been derived for the optimal situation; the case in which resonances within an emission spectrum are symmetrically straddled by homogeneous lines. Data exists only for the most rapid rate of decay within a particle as a function of size.[5,8] This data is reduced from inhomogeneous decay curves by using a Laplace inversion technique.[5] Results for rhodamine 6G (R6G) in glycerol are displayed in Fig. 2. Comparison of the data with the $1/a$ hypothesis, as it appeared in Ref. 5 is also shown. The latter curve required
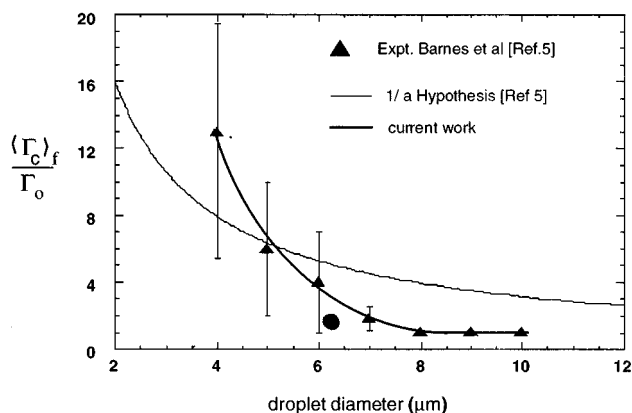
fixing the relative decay rate at a diameter of 5 μm and using $\Gamma_h = 100$ cm^{-1}. Displayed also in Fig. 2 is a fit to Eq. (7) by fixing the same point at a diameter of 5 μm and using a value of $\Gamma_h = 160$ cm^{-1}; f is assumed constant and equal to 20 μm. As one can see Eq. (7) is much better agreement with the experimental data than the $1/a$ hypothesis.

Although the coefficient $D_s/\rho_0 V_p \Delta\omega$ in Eq. (6) should to be less than one, our fit value for f in Eq. (7) at a radius $a = 2.5$ μm gives a value of f/a at this radius of 8. Clearly this value can be as small as 2 considering the large error bars in the data, however, a fit value less than 1 at this radius is improbable. The elevation of the coefficient above 1 is principally the result of fitting rates of decay for the fastest decaying molecules; molecules which are not only spectrally optimized, but also at a radius and orientation for which the projection of the transition dipole moment onto the density of states is a maximum. Our numerical calculations show that the maximum density of states (i.e., the density of states at the optimal radius within the active region near the surface) after averaging over all orientations exceeds the volume averaged density of states for a particle 2.5 μm in radius by a factor of approximately 4. A further enhancement can be credited to those molecules which are optimally oriented (i.e., the optimal orientation is expected to be radial, leading to coupling to only TM modes[9]). Overall, our numerical calculations indicate that the size dependence of f should go $\sim a^{1/2}$. Although this dependence for f is considerably weaker than either $1/a$ or $1/a^2$, we anticipate from Eq. (7) that the fastest rate of decay should go like $a^{-3/2}$ at the smallest sizes in Fig. 2. A more discriminating data set (i.e., a data set with smaller error bars) is that for R6G in ethylene glycol.[8] Indeed, in this case the size dependence of the fastest rate of decay is consistent with an $a^{-3/2}$ dependence near the smallest sizes. This dependence also agrees with numerical density of states calculations.

In summary, by using the specific properties of Mie resonances in microdroplets, we have shown that the size dependence of the optimal volume averaged fluorescence de-

cay rate, contains a sum of components which vary as $1/a$ and $(1/a)^2$. Within the bulk of the droplet $\langle \Gamma_c \rangle / \Gamma_0$ is expected, on the basis of Eq. (6), to saturate near 1 for $a > 2c/\pi n \Gamma_h$ (''saturation region''). The theory is in good agreement with experiment.

The above analysis of enhanced R6G fluorescence decay rates in glycerol and ethylene glycol microdroplets assumes that there is only one significant mode (i.e., a mode narrower than the homogeneous line width whose projection onto the transition dipole moment is maximum) which the homogeneous line overlaps within a free spectral range. It is clearly the simplest case. If the homogeneous line overlaps other significant modes within a free spectral range, our calculation would have to be modified.

Finally, it should be noted that a density of states approach to the analysis of recent fluorescence decay rate data from surfactant fluors[10] on glycerol microdroplets may prove more challenging. The problem is that the sum rules [Eqs. (3) and (5)] are not as valid in this region, due to the leakage of cavity states into free space modes at the surface. Although the problem has recently been attacked numerically by using a semiclassical approach,[11] even in this case we find that the experimental decay rate data increases more rapidly with decreasing size than $1/a$.

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