Fluorescence of Oriented Molecules in a Microcavity

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Fluorescence decay rate modification has been observed for molecules in liquid microspheres (3.5 to 25 μm in diameter) where the molecular position and transition moment orientation are well defined. For small sizes (<6 μm), the decay rates scale roughly as r^{-1} and agree quantitatively with semiclassical calculations. For larger sizes (>15 μm) where the cavity storage time and fluorescence lifetime are roughly equal, an anomalous decrease in the decay rate of $\approx 30\%$ is observed which is interpreted as a consequence of intermediate molecule-cavity coupling. [S0031-9007(96)00234-7]

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Over the last several years there has been considerable interest in the properties of atomic resonance fluorescence in an optical cavity with a primary dimension comparable to the relevant transition wavelength [1]. In particular, there has been great interest in the realization of strong atom-cavity coupling [2] and the suppression of spontaneous emission into "free-space" modes. However, an important but poorly understood issue relevant to low- or zero-threshold condensed phase optical devices is the nonradiative coupling of the emitting species to a thermal bath. Unlike experiments involving dilute atomic beams where the transition is well defined and broadening is negligible, coupling to a thermal bath induces spectral broadening which is usually much larger than the cavity resonance width and may often exceed the cavity mode spacing. Interesting examples of such systems are solvated dyes whose condensed phase dynamics are well known and characterized. To date, several studies have been made on fluorescence properties of solvated dyes in microcavities [3–5]; however, additional complexities such as spatial and orientational averaging have obscured to some extent the connection between radiative and nonradiative processes in such systems. In this Letter, we report what is to our knowledge the first observation of spontaneous emission rate modification for species in a microcavity where both the molecular position *and* transition moment orientation are well defined. These experiments provide a definitive test of cavity quantum electrodynamics models in microspheres and serve as a test case of atom-cavity systems in which the emitting species are nonradiatively coupled to a thermal bath.

The experiments presented here probe the time dependence of spontaneous radiation from surfactant molecules in trapped microdroplets. Liquid microspheres have received a great deal of attention in recent years in a wide variety of optical phenomena [6]. High-Q (10^5–10^8) resonances, also called morphology dependent resonances (MDRs), in combination with high mode degeneracy can significantly enhance radiative processes in spherical microparticles [7]. For the smallest microdroplets used in this study (≈ 4 μm diam), quality (Q) factors for resonant modes are about 10^3 and roughly 40-fold degenerate, resulting in emission rate enhancement factors which may be considerably larger than in nondegenerate parallel plate resonators. Spontaneous emission rate modification has been previously observed for chelated europium ions [8] and solvated dyes [5] in microdroplets. However, factors such as spatial and orientational averaging, as well as a significant "bulk" background from fluorescence of molecules near the center of the sphere (that do not couple to high-Q MDRs) greatly complicate quantitative theoretical analysis. By controlling both the position and transition moment orientation of the fluorescent molecules, our semiclassical model could be rigorously tested in the absence of the aforementioned complications.

It has long been recognized that fluorescence decay rates in a microcavity (as well as in the vicinity of conducting surfaces) should depend strongly on the orientation of the (electric) transition dipole moment with respect to the cavity axis. If the transition moment, $\vec{\mu}$, has a fixed orientation with respect to the cavity axis, the emission rate is determined by a projection of the transition moment onto the subset of cavity modes having an electric field component along the direction of $\vec{\mu}$. The effect of transition moment orientation can be conveniently modeled using semiclassical methods where the power radiated from the excited molecule, considered as a damped oscillating dipole, is controlled by feedback from the cavity. Within a linear response formalism [9], the scattered field seen by the dipole at a given frequency ω and position $\mathbf{r}'$ is $\mathbf{E}(\mathbf{r}') = \underline{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \vec{\mu}$ where $\underline{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega)$ is the dyadic Green's function at position $\mathbf{r}$ for a dipole $\vec{\mu}$ positioned at $\mathbf{r}'$; the field scattered back to the molecule corresponds to setting $\mathbf{r} = \mathbf{r}'$ in the Green's function. The effect of driving the oscillating dipole with this "backscattered" field is to alter the molecular decay rate R (with

respect to the bulk rate, R_0) as

$$R/R_0 \approx 1 + (3/2k^3)\,\mathrm{Im}[\mathbf{n} \cdot \underline{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \mathbf{n}], \quad (1)$$

where k is the norm of the wave vector. Our numerical calculations follow closely those of Chew [10], for computing the power radiated by a dipole with position vector $\mathbf{r}$, and orientation $\mathbf{n}$ within a dielectric sphere. The principal modification is the (phenomenological) introduction of a line-shape function, $P(ka)$, where a is the particle radius and the frequency averaged decay rate is expressed as [11]

$$\left\langle \frac{R_{\perp,\parallel}}{R_0} \right\rangle = \int P(ka) \frac{R_{\perp,\parallel}(ka)}{R_0} d(ka), \quad (2)$$

where $\perp$ and $\parallel$ denote perpendicular and parallel orientation with respect to the surface *normal* of the particle.

Equation (2) is based on similar phenomenological frequency averaging as the model proposed by Yokoyama and Brorson [12], and predicts the same qualitative behavior in the fluorescence decay rate as a function of linewidth. The nature of $P(ka)$ is a central issue in understanding the magnitude of emission rate modification factors for solvated dyes. Recent photon echo experiments [13] have shown that contributions to the fluorescence emission profile can be divided roughly into two categories: a *homogeneous* width that is related to elastic (phase-destroying) interactions with the solvent, and an *inhomogeneous* width that reflects the (time-dependent) distribution of different local solvent-chromophore environments. The latter mechanism usually dominates the width of the emission spectrum with typical inhomogeneous spectral widths on the order of $\approx$1500 cm^{-1}. The former can be regarded as a transform-limited emission linewidth as a result of rapid decay of electronic polarization phase coherence ($T_2 < 100$ fs), and the contribution to the spectral width is therefore roughly $1/\pi T_2 \approx 100$ cm^{-1}. If the interactions between the fluorescent molecule and the solvent "bath" can be characterized as Markovian (i.e., the time scales for the two processes differ widely), an average over the *homogeneous* width (as opposed to the inhomogeneous width) is appropriate.

Surfactant molecules may be naturally localized at the surface of liquid droplets due to the free energy discontinuity at the liquid-air boundary. The fluorescent dye used in the experiments reported here was octadecyl rhodamine B (ODRB, Molecular Probes), a variant of rhodamine B where a long (saturated) hydrocarbon chain is attached to the chromophore effectively transforming the molecule into a surfactant. As demonstrated by Arnold and coworkers [14], polarization selective fluorescence imaging of trapped microdroplets provides information on both the spatial distribution and emission moment orientation. Figure 1(a) shows a fluorescence micrograph of ODRB in a levitated glycerol microdroplet. Circularly polarized light was used to excited fluorescence, which was imaged with a microscope viewing with appropriate filters along the axis of the laser beam. Segregation of ODRB to the surface of the droplet is illustrated by a rim of light at the particle boundary. Figure 1(b) shows an image of the same microdroplet taken through a polarization analyzer. The nearly complete attenuation of fluorescence near the droplet poles along the analyzer transmission axis indicates that the fluorescence in these regions is polarized orthogonal to the analyzer transmission axis and is clear evidence that the transition moment is oriented perpendicular

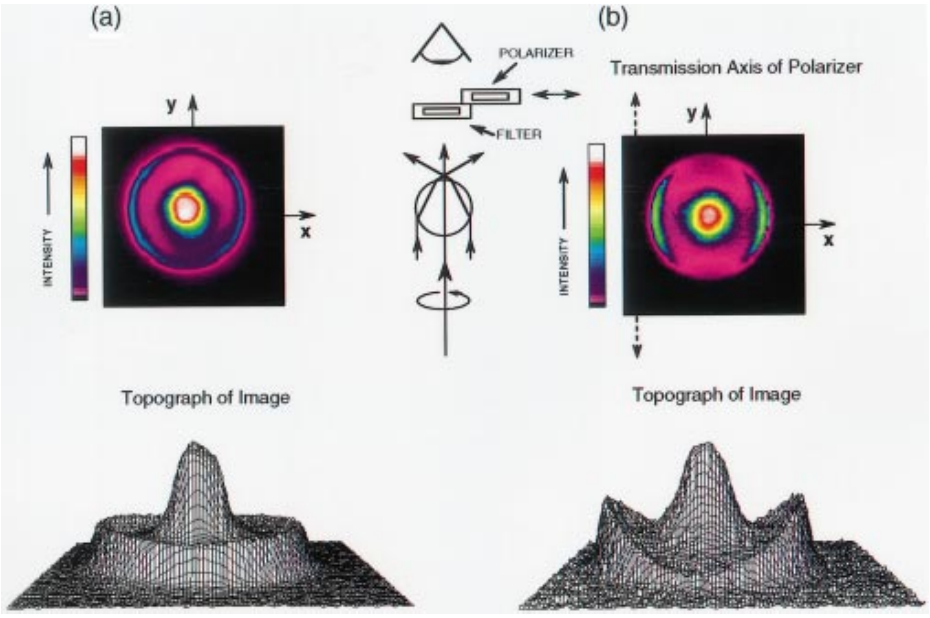

FIG. 1(color). Fluorescence images of octadecyl rhodamine B (ODRB) in a levitated glycerol microdroplet using an aerosol particle microscope (Ref. [14]). The inset shows a schematic of the imaging geometry. Light passing through the droplet is focused to a spot near the surface giving rise to a peak in the center of the image. Image (a) is taken without a polarization analyzer while (b) shows the fluorescence imaged through a polarizer with transmission axis along the "**y**" direction. The peak in the center is unpolarized since all azimuthal orientations are present for the molecules on the surface.

to the surface normal. Similar fluorescence images recorded using rhodamine B (rhB) show an unpolarized fluorescence intensity profile across the particle consistent with a homogeneous distribution of molecules having a random transition moment distribution.

Glycerol microdroplets were produced using an on-demand piezoelectric pipet and levitated in an electrodynamic trap [15]. The ODRB concentration in glycerol was $10^{-6}M$ corresponding to an average distance between molecules on the surface of about 50 nm. The droplet size was determined by measuring the elastic scattering intensity as a function of laboratory angle. Elastic scattering from the droplet was collected at an angle of 45° with respect to the direction of propagation of a vertically polarized HeNe laser and dispersed across a plane angle of 30° onto a charge coupled device camera. The resulting "fringe" pattern (corresponding to 0° azimuth with respect to the scattering plane) was compared to calculated patterns from Mie theory allowing the droplet size to be determined to within about 10 nm. The decrease in droplet diameter with time due to evaporation was measured to be ≈ 1 nm/s, therefore fluorescence data collection times were limited to 1–3 min so that the change in droplet diameter during data acquisition was less than 0.2 μm.

Fluorescence decay rates of ODRB in glycerol microdroplets were measured using time-correlated single photon counting with a time resolution (channel width) of about 10 ps. A mode-locked Ar^+ ion laser was used in combination with an acousto-optic switch to produce 100 ps FWHM excitation pulses (514.5 nm) at a repetition rate of 4 MHz. In these experiments, fluorescence from the droplet was measured at an angle of 135° with respect to the direction of propagation of the laser and filtered through a 577 nm center wavelength bandpass filter with 25 nm bandwidth. Excitation pulse energies ($\leq$100 pJ) were adjusted so that on average less than one excited state is prepared per pulse. Typical detector count rates were held to $\leq$5 kHz, and the overall photon detection efficiency was known from previous experiments to be 0.002. Thus, the average number of excited states generated per pulse is <1 which ensures that the contribution of *stimulated* emission to the measured fluorescence decay signals is negligible.

As a benchmark, fluorescence lifetimes of rhB were measured in droplets ranging from 4 to 15 μm in diameter. The observed fluorescence decay kinetics were similar to those previously measured for rhodamine 6G [5]. For large sizes (10–15 μm), single exponential decays were observed with the same time constant as rhB in bulk glycerol ($\tau_B = 3.12$ ns). The same decay constant was measured for ODRB as for rhB in bulk glycerol. For small droplet sizes (4–8 μm), biexponential decay was observed for rhB where the decay constant associated with the fast component increases with decreasing droplet size. The biexponential decay can be qualitatively explained by noting that only molecules near the surface of the droplet may couple emission into high Q modes; molecules near the center couple into low Q "radial" modes which do not significantly alter the fluorescence decay rate. Unlike rhB, the fluorescence decay for ODRB was well described by a single exponential for all droplet sizes examined. The average decay rate enhancement for 4 μm droplets was about 1.6 which is in excellent agreement with our calculated value of 1.5 for a perpendicularly oriented transition moment and a homogeneous linewidth of 100 cm^{-1} (see Ref. [5]). In contrast, the calculated enhancement factor for the parallel orientation with the same homogeneous width is 4.5.

Observation of single exponential decay for ODRB in the small diameter regime lends further support to our original interpretation of the biexponential decay kinetics for rhB; there is no "bulk" decay component for ODRB since the molecules are spatially localized on the particle surface. However, biexponential decay might also be expected for ODRB since emission may be coupled into both MDR and free-space modes. The fact that no bulk (or inhibited) component was observed for the smaller sizes can be explained on the basis of spectral diffusion [16]. Such an argument cannot, however, explain the anomalous decay times observed for ODRB in larger droplets. Figure 2 shows the fluorescence decay rate for ODRB normalized to the bulk decay rate as a function of droplet size. For small droplets ($\leq$6 μm), the fluorescence decay rate has a similar size dependence as observed for rhB and rhodamine 6G. In this size regime, the resonance Q's are of the order of 10^3–10^4 and weak coupling is expected. Thus, the decay rate should scale approximately as the ratio of the mode spacing (proportional to $1/r$) to the homogeneous width. However, in sharp contrast with previous observations

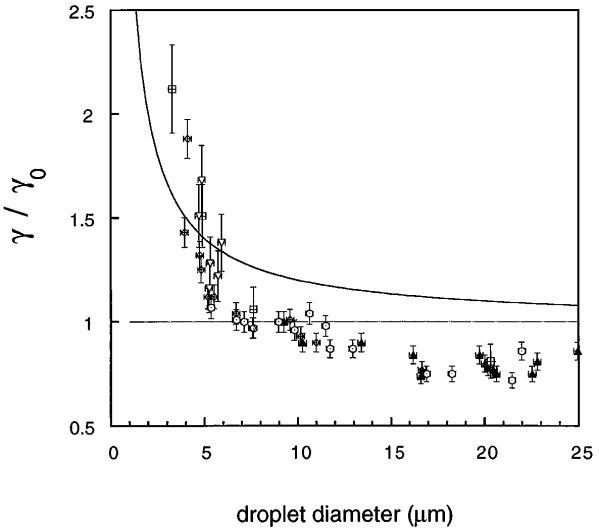

FIG. 2. Fluorescence decay rates of ODRB (normalized to the bulk decay rate of rhodamine B) in levitated glycerol droplets as a function of droplet size. Different symbols denote data from separate runs. The solid curve shows the size dependence on the decay rate expected from the Yokoyama-Brorson (Ref. [12]) model constrained to fit the semiclassical calculation of the decay rate at 4 μm diameter.

for rhB and rhodamine 6G which show bulk behavior for droplet diameters larger than 10 μm, the apparent fluorescence decay times for ODRB are significantly longer ($\approx$30%) than the bulk. This effect was presumably masked by the significant contribution to the signal from molecules near the center of the sphere which do not couple to droplet MDRs.

Figure 2 also shows, as a comparison, the size dependence of the fluorescence decay predicted from the Yokoyama-Brorson model [12] which assumes weak coupling. The significant deviation of the experimental results presented here from the predictions of the Yokoyama-Brorson model clearly indicates a different physical mechanism. We believe this result is a manifestation of intermediate coupling in microdroplets first predicted by Young and co-workers [7]. The Q's for MDRs for glycerol droplets in this size range are known to be $\geq 5 \times 10^6$ [17] which means that the cavity damping time, $\tau_{\text{cav}} = Q/\omega$, is approximately equal to the (bulk) fluorescence decay time. It has been predicted [7], for two-level atomic systems, that the excited state decay rate should be fastest in an intermediate coupling regime; however, the present experiments do not provide a measure of excited state population lifetime in this size (coupling) regime. The anomalous decay times observed in this size regime result from the fact that, in these experiments, we measure the time dependence of fluorescence arriving at the *detector*. In a weak coupling case, where the energy storage time in the cavity mode is small compared to the excited state lifetime, the experiments provide a direct measure of the excited state population decay rate. However, in a regime where the energy storage time in the cavity mode is not negligible with respect to the excited state lifetime, our experiments measure the characteristic energy damping time from the molecule-cavity *system.*

The observation of single exponential decay for the larger sizes suggests that only a small fraction of the emission is coupled into free-space modes even though weak-coupling models predict no change in the spontaneous emission rate at these sizes. At present, there is no comprehensive theory which describes spontaneous radiative decay from molecular systems in a microsphere also coupled to a thermal bath. This situation therefore precludes definitive statements on the physical origin of the anomalous decay times observed at the larger sizes. It is hoped that these results will stimulate more theoretical work in this area.

It is clear from the combined evidence of polarized fluorescence imaging and fluorescence lifetime data that we have achieved a unique system in which the molecular position and orientation is well defined in the cavity. In addition, the size range of droplets studied spans resonance Q's corresponding to cavity damping times both small and roughly equal to the (bulk) fluorescence lifetime. For small droplets ($\leq$6 μm) where weak coupling is expected, our experimental results agree quantitatively with semiclassical calculations (at 4 μm diameter) and the spontaneous emission rate is observed to scale roughly as the ratio of the mode spacing to the homogeneous width. At larger sizes (10–25 μm), these experiments have revealed an anomalous decay time related to the energy storage time in the cavity masked in previous studies where fluorescence from the "bulk" portion of the droplet dominated the signal. Furthermore, the observation of single exponential decay indicates a clear molecular "preference" for MDRs over free-space modes. In summary, these results have provided a quantitative test of cavity QED models in liquid microspheres and serve as a test case of a more general class of atom-cavity systems in which nonradiative coupling to a thermal bath is important.

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