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Homogeneous linewidths of Rhodamine 6G at room temperature from cavity-enhanced spontaneous emission rates

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The ability to modify emission rates from atoms or molecules in an excited state is of great importance since experimental control over the pathway for excited state deactivation can be obtained. For example, inhibition of spontaneous emission can be used to direct excited state chemical reactions and multiphoton processes. Alternatively, the possibility of enhanced spontaneous emission rates in micron-sized liquid droplets could provide increased sensitivity in low-level fluorescence applications, such as DNA sequencing or effluent tracing, requiring single-molecule detection limits.[1,2] Recently, both enhancement and inhibition of spontaneous emission have been demonstrated for chelated ions.[3] However, whether such effects could be observed for polyatomic dye molecules was uncertain principally because it was assumed[4,5] that large homogeneous linewidths (taken to be approximately equal to the fluorescence spectral width) would result in, at best, only a small emission rate enhancement. In this Communication, we show that a dramatic increase in the fluorescence emission rate of Rhodamine 6G occurs in glycerol microdroplets, implying that the homogeneous linewidth is actually only a fraction of the fluorescence spectral width.

Fermi's "Golden Rule," given in Eq. (1), provides a basic understanding of how emission rates can be modified by the geometrical structure of the matrix in which the atom or molecule is solvated. The transition rate from state i to state j may be expressed as,[6]

$$A_{i\to j}=\frac{1}{\hbar^2}\langle i|H_{ij}|j\rangle^2\rho(\nu), \tag{1}$$

where $\langle i|$ represents the excited state with no photon present, $|j\rangle$ is the ground state with one photon, h is Planck's constant, $\langle i|H_{ij}|j\rangle$ is the volume-normalized Hamiltonian matrix element representing the atom-field interaction, and $\rho(\nu)$ is the density of final photon states. Placing the emitter inside an optical cavity whose dimension is on the same order as the transition wavelength causes the emitted light to be coupled into discrete cavity modes rather than into the continuum of vacuum states in free space. Since the density of states is large when ν corresponds to a cavity mode, and small when ν is nonresonant, the emission rate will be modified (enhanced or inhibited) depending upon whether the emission frequency corresponds to a particular cavity mode.[7]

Modification of spontaneous emission rates was first observed by Drexhage and co-workers[8] by measuring emission rates from europium ions layered in Langmuir–Blodgett films above a reflective surface. Using a waveguide structure as a linear microcavity, Kleppner and coworkers[9] were able to demonstrate inhibited spontaneous emission of Rydberg atoms at microwave frequencies. De Martini and co-workers[10] demonstrated both enhancement and inhibition of spontaneous emission at optical frequencies using a linear tunable Fabry–Perot cavity. However, with the exception of the work of Drexhage and coworkers, these investigations all involved linear microcavities where, despite the simple geometry, exact calculations of internal fields are not possible. The spherical cavity is an alternative which offers a geometry which is much more amenable to theoretical modeling since all fields and modes are exactly calculable from Lorenz–Mie theory.[11]

It has been known for some time that micrometer sized dielectric spheres act as high Q resonators, where photons propagate around the sphere near its edge. Spherical cavity modes in these microspheres arise from so-called "morphology dependent resonances," or MDRs, which occur at specific values of the size parameter, X, where $X=2\pi a/\lambda$, a is the radius of the sphere, and λ is the wavelength of light. Cavity effects such as stimulated emission[12] and lasing[13,14] as well as enhanced energy transfer[15,16] from liquid microdroplets have been reported. Recently, Campillo and co-workers[3] have demonstrated cavity enhanced spontaneous emission of chelated europium ions in a stream of falling ethanol droplets and observed an increase in the spontaneous emission rate of a factor of 2.5 above the bulk value. These authors point out that, if the homogeneous linewidth (Γ_{hb}) is much less than the cavity mode bandwidth (δ_c), large enhancements should be observed as predicted by Purcell.[7] Conversely, if Γ_{hb} is larger than the cavity mode spacing (Δ_c), no enhancement should be observed. However, in the regime, where $\Delta_c>\Gamma_{hb}>\delta_c$, the enhancement, ξ, is independent of the cavity Q and can be approximated by the expression[17,3]

$$\xi=\Delta_c/\Gamma_{hb}. \tag{2}$$

Because the cavity mode spacing, Δ_c, can be calculated from the droplet diameter and refractive index, it is possible to estimate the homogeneous linewidth of a fluorescing molecule by measuring the fluorescence emission rate enhancement. We report here the results of fluorescence lifetime measurements of Rhodamine 6G (R6G) in glycerol droplets with diameters ranging from 4–20 μm. The observed enhancement is large ($\approx 10\times$) for the smallest droplets and decreases rapidly with increasing droplet diameter, with no enhancement observed for droplets larger than 10 μm in diameter. Estimating the enhancement using Eq. (2) with different values of Γ_{hb} suggests a value of

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about 100 cm^{-1} for the homogeneous linewidth of R6G in glycerol at room temperature.

Spontaneous emission rate enhancements of R6G in levitated microdroplets were determined by fluorescence lifetime measurements using a time-correlated single photon counting technique.[18] Briefly, glycerol droplets with R6G concentrations ranging from 10^{-7}–10^{-5} M were levitated in an electrodynamic trap.[19] Short (150 ps FWHM) excitation pulses at 514 nm were generated by a mode-locked Ar^+ laser (Spectra Physics 171), with pulse energies of about 150 picojoules. The laser beam was focused to a 50 μm diameter giving a peak intensity at the droplet of about 70 kW/cm^2. Fluorescence from the droplet was filtered with an interference filter centered at 575 nm with 26 nm FWHM bandwidth and focused onto a cooled photomultiplier (Hammamatsu R943-02). The droplet diameter was determined by measuring the distance between reflected and refracted glare-spots[20] from He–Ne laser illumination using an eyepiece reticle with rulings that correspond to 1 μm. The uncertainty in the diameter measurement was estimated to be about 10%–20%. In these experiments, the time elapsed between detection of fluorescence photon and the arrival of an excitation pulse was measured using a 16 ns time window divided into 512 channels; each channel having a width of about 33 ps. For lifetime measurements made on bulk glycerol solutions, the upper end cap electrode of the trap was removed and a 1 cm square cuvette was placed inside. All other experimental parameters were identical for droplet and bulk measurements.

Figure 1 shows the instrument response function and normalized fluorescence decay data for 4, 7, and 9 μm droplets (10^{-6} M/glycerol), as well as for 10^{-6} M glycerol solution in a cuvette. Fluorescence decay from R6G in bulk glycerol is described well by a single exponential decay with $\tau = 3.65 \pm 0.05$ ns, and all measurements made on droplets with diameters larger than 10 μm gave fluorescence decay curves which were essentially the same as observed for the bulk solution. As the droplet diameter was decreased, increasingly nonexponential decay was observed, with the 4 μm droplet data clearly showing more than one decay component. Because the density of states (and therefore the enhancement) should vary according to the radial position of the molecule within the droplet,[21] a distribution of decay rates was expected to provide a more accurate representation of the system than a simple biexponential decay function. Using a Laplace inversion technique,[22,23] decay rate probability distributions were extracted from the fluorescence lifetime data to determine the emission rate enhancement.

Figure 2 shows decay rate probability distributions obtained for 4, 6, and 11 μm droplets. Each distribution shows a strong peak centered around the bulk decay rate (0.27 ns^{-1}). However, distributions for the 6 and 4 μm droplets show a fast decay component whose most-probable decay rate and probability amplitude increases as the droplet diameter becomes smaller. In the decay rate probability distributions obtained from our experimental data, the width of the peaks arise primarily from the limited sampling (512 points) and the noise in the data. Thus, the non-zero probability for photon emission at extremely large rates near the edge of the solution grid is probably not physically significant. Although it was expected that an inhibited component with approximately the same relative probability amplitude as the enhanced component should be present, no significant inhibited emission was observed in our work. Because the time window for photon counting was only 16 ns, any inhibited decay rate component would tend to be hidden in tail of the fluorescence decay curve.

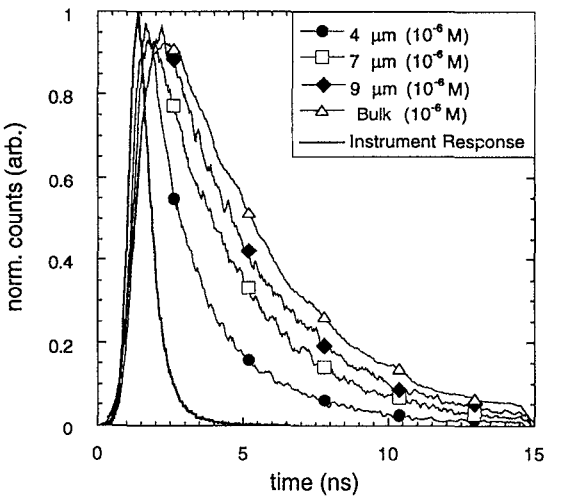

FIG. 1. Instrument response function and R6G fluorescence decay curves for 4, 7, and 9 micron diameter glycerol droplets, as well as for bulk glycerol solution. All concentrations are 10^{-6} M. Each curve is made up of 512 points and have been smoothed using a 5-point running average. Symbols are for illustration only.

The decay rate enhancement for the 4 μm droplet shown here is about a factor of 10 larger than the bulk

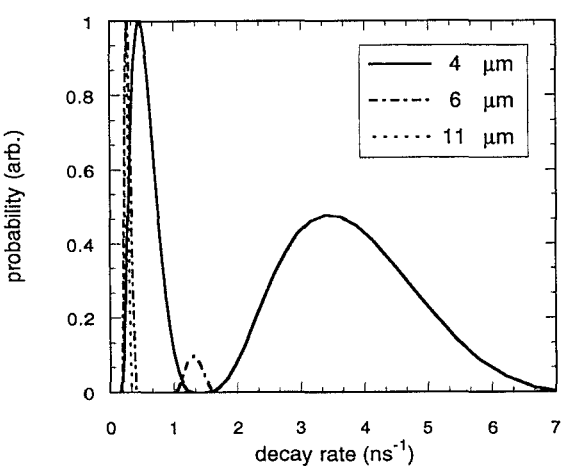

FIG. 2. Decay rate probability distributions obtained by Laplace inversion of measured fluorescence decay data for 4, 6, and 11 μm diameter droplets. Curves have been scaled so that the peak of the slow component is unity. The ordinate represents the probability that a photon will be emitted at rate λ, therefore the number of molecules with a given decay rate is proportional to the decay rate probability divided by the decay rate, λ.

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decay rate corresponding to a fluorescence lifetime of about 300 ps. Observation of decreased fluorescence lifetimes in the smaller droplets, however, does not prove that the effect is due to cavity enhancement. For example, dye fluorescence is known to be self-quenched at high ($\geqslant 10^{-3}$ M) concentrations.[24] However, this effect should not be significant at the concentrations used for the experiments reported here, and no dependence of decay rate or probability amplitude on R6G concentration was observed. Other (unknown) quenching processes can also be effectively ruled out since our observed fluorescence yield per molecule is at least as large for the smaller droplets as it is for the larger ones. On this basis, it appears that the increased spontaneous emission rate is not attributable to any quenching process.

Since it is well known that stimulated emission[9] and lasing[10,11] can occur in microdroplets, the question arises as to whether the enhanced decay rate can be attributed to stimulated emission. The possibility of lasing was estimated using an expression given by Lin *et al.*[11] Substituting values appropriate for our experimental conditions, it was concluded that, even at the highest dye concentration and excitation pulse power, the threshold for lasing would not be exceeded. Although it is almost certain that the enhanced decay rate component is not due to droplet lasing, the possibility still exists that we are observing stimulated emission. The probability of stimulated emission was estimated to be on the order of 10^{-4}, suggesting that the fast decay component is indeed due to cavity enhanced *spontaneous* emission.

A qualitative explanation for the observed differences in fluorescence decay behavior as a function of droplet size can be given by considering how the "mode volume" and degree of enhancement change as the droplet size is varied. Light waves which propagate near the surface of the sphere in the high-Q cavity modes occupy a certain volume which is defined as the mode volume. Most of the molecules will be unaffected by the presence of cavity modes near the surface and emit at a rate similar to that of the bulk medium. However, molecules located in the mode volume will have their emission coupled into cavity modes and their decay rate will be enhanced or inhibited depending on whether the emission is resonant with a cavity mode. For a 4 μm diameter glycerol droplet, V_m/V is about 0.1 and falls off approximately as $X^{-1/2}$, where X is the size parameter. Thus, for smaller droplets, a greater percentage of molecules interact with a cavity mode which will be reflected in the lifetime spectrum as an increase in the relative probability amplitude of the enhanced rate component.

The observed increase in decay rate enhancement with decreasing droplet diameter can be qualitatively explained using Eq. (2). The mode spacing, Δ_c, increases with decreasing droplet diameter as $f(n)/2\pi r$ [where $f(n)$ is a function of the index of refraction, and r is the radius of the sphere].[25] Thus, within the approximations contained in the model used to derive Eq. (2), the rate enhancement should also increase with decreasing droplet diameter with a magnitude inversely proportional to the homogeneous linewidth. Figure 3 shows the average decay rate enhancement for droplet diameters ranging from 4 to 10 μm along with the variation of enhancement expected from Eq. (2) for three different homogeneous linewidths. There is qualitative agreement between the experimental rate enhancements and those predicted from Eq. (2), however, the fit to the experimental rate enhancements using this simple model is rather poor. This is not surprising considering the fact that the real physical situation is much more complicated than implied from Eq. (2) due to the complex fluorescence spectrum (i.e., emission from several different vibronic levels is likely). We are currently developing a more detailed theoretical model for decay rate enhancement in these small droplets which should provide a clearer physical picture of the interaction of fluorescent molecules with cavity modes in these microdroplets. However, within the context of this simple model, the experimental data suggest a value of about 100 cm^{-1} for the homogenous linewidth of R6G in glycerol at room temperature.

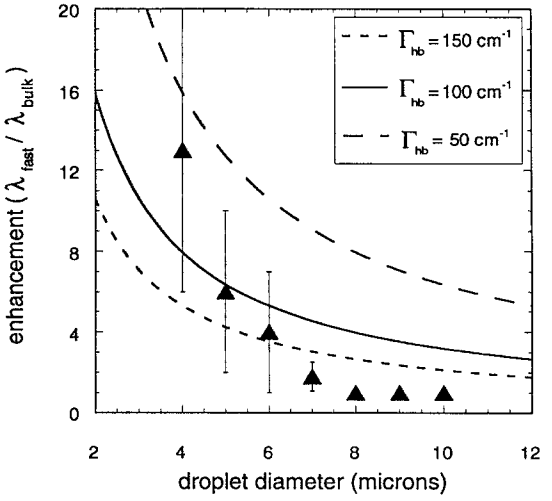

FIG. 3. Average decay rate enhancement vs droplet diameter. Symbols represent mean enhancement ($\lambda_{fast}/\lambda_{bulk}$) using the most probably emission rates for 5 different droplets of a given size and error bars are $\pm 1\ \sigma$. Curves represent decay rate enhancement approximated by Δ_c/Γ_{hb} for three different homogeneous linewidths.

This value for the homogeneous linewidth suggested by our experiments is supported by spectral hole burning data. Brito Cruz *et al.*[26] measured dephasing times for different dyes in an ethylene glycol dye jet using a femtosecond pump-probe technique. similar dephasing times ($T_2 \approx 80$ fs) were measured for the dyes cresyl violet, nile red, and HITC, corresponding to a homogeneous linewidth of 140 cm^{-1}. Extrapolation from hole burning data on porphyrin molecules in cold (80° K) polymer matrices[27] suggests homogeneous linewidths at 300° K on the order of 50 cm^{-1}. It is therefore reasonable to expect that the homogeneous linewidth for R6G is narrower than the cavity mode spacing for droplet diameters less than 10 μm and that such a narrow linewidth could produce the large emission rate enhancements which have been observed experimentally.

Measurements of R6G fluorescence lifetimes in levitated glycerol microdroplets have shown a striking spon-

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taneous emission rate enhancement which is attributed to the coupling of emission into spherical cavity modes of the droplet. The magnitude and relative probability amplitude of this enhanced rate component increase dramatically as the droplet diameter is decreased. Within the simple model implied by Eq. (2), homogeneous linewidths at room temperature can be estimated from these fluorescence lifetime measurements which could previously be determined only with spectral hole-burning techniques involving femtosecond time resolved measurements or in cryogenic samples. Although the agreement between experimental rate enhancements and this simple model is not quantitative, these data suggest a value for the homogeneous linewidth of R6G in glycerol at room temperature much smaller than previously assumed. The observation of large emission rate enhancements also suggests that small microdroplets offer an additional advantage in low level fluorescence detection applications. With the development of a more detailed theoretical model, we hope to gain more insight into the interaction of fluorescent molecules with microoptical cavities.

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