Spontaneous emission spectra from microdroplets

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The emission spectrum from a fluorescent microdroplet is compared with theory for the first time. The spectrum of oriented surfactant molecules on a levitated microdroplet is found to be in good agreement with semiclasical theory of the interaction of whispering gallery modes with excited molecules. The orientation of these surface entities is estimated through this comparison. © 1998 American Institute of Physics. [S0021-9606(98)02716-0]

Recently, a plethora of papers have appeared reporting the enhanced emission (e.g., spontaneous fluorescence and Raman) associated with the coupling of a molecular emission moment to geometric resonances of a spherical micro-particle. Although heuristic descriptions using cavity QED concepts (CQED) have been discussed, 3 no quantitative comparison with theory has emerged. In part, this disparity is due to a lack of well defined experiments. Advances in experimental technique using surfactant fluors on levitated microparticles b) have been discussed, 3 no quantitative agreement with semiclassical theory of the interaction of whispering gallery modes with excited molecules. The orientation of these surface entities is found to be in good agreement with semiclassical theory of the interaction of whispering gallery modes with excited molecules. The orientation of these surface entities is estimated through this comparison. © 1998 American Institute of Physics.

Theory suggests that by placing an excited atom/molecule near the surface of a spherical dielectric, the interaction of the radiating atom/molecule with its self-scattered field can produce enormous enhancements in its emission rate at frequencies associated with whispering gallery modes. 7–9 The model in its semiclassical form depicts the field which is the Poynting vector. ~

\[ \mathbf{E}_\nu(x) = \mathbf{G}(r, \mathbf{r}, \omega \cdot \mathbf{x}) \cdot \mathbf{x}, \] where \( \mathbf{G}(r, \mathbf{r}, \omega \cdot \mathbf{x}) \) is the Green’s function dyadic. 7,9 Radiation is emitted into the far field at an arbitrary far field position \( \mathbf{r} \),

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\[ \gamma_\nu = \frac{\mathbf{E}_\nu \cdot \mathbf{n} \cdot dA}{\hbar \omega} = \frac{c \epsilon_0}{2\hbar \omega} \mathbf{r}^2 \int |\mathbf{E}_\nu|^2 d\Omega, \] (1)

where \( \mathbf{S} \) is the Poynting vector.

Our interest is in calculating the emission from ionic chromophores tied to the surface of a polar microdroplet using aliphatic chains. This positions the chromophore just beneath the droplet surface, and restricts its orientation. Although the excitation and emission moments will in general be in different directions, the rapid vibrational relaxation (\( \sim 10^{-11} \) s) of the excited state at room temperature leaves

\[ \gamma_\nu(\theta, \omega) \gamma_\nu \sim \frac{3n}{2X^2} \sum_{l=1}^{\infty} (2l + 1) \left| \mathbf{T} \right| \left| I(l + 1) \right| \]

\[ \times \left( \frac{j(nX)}{(nX)} \right)^2 \cos^2 (\theta) \]

\[ + \frac{1}{2} \left[ \frac{(nX)j(nX)}{(nX)} \right] ^2 \sin^2 (\theta) \]

\[ + \frac{1}{2 n^2} \left| j_l(nX) \right| ^2 \sin^2 (\theta), \] (2)

where \( \theta \) is the angle between the emission moment and the normal to the droplet surface, \( n \) is the refractive index of the particle, and \( X \) is the free space angular wave number times the particle radius, i.e., \( X = k \). \( \mathbf{TE}_l \) and \( \mathbf{TM}_l \), the resonant coefficients associated with the coupling to transverse magnetic and transverse electric modes, are

\[ \mathbf{TM}_l = \frac{1}{n^2 j_l(nX) \left| X h_{11}^l(X) \right| - h_{11}^l(nX) \left| n X j_l(nX) \right|^2} \]

and

\[ \mathbf{TE}_l = \frac{1}{j_l(nX) \left| X h_{11}^l(X) \right| - h_{11}^l(nX) \left| n X j_l(nX) \right|^2}, \]

where \( j_l \) and \( h_{11}^l \) are spherical Bessel and spherical Hankel functions with mode number \( l \). Each of these coefficients is a spectrum in \( X \) of Lorentzian peaks characterized by mode orders \( \nu \) (i.e., modes are designated by \( \nu P^2 \), where \( P \) is the mode polarization, \( \mathbf{TE} \) or \( \mathbf{TM} \)). With \( \theta \) set equal to 0 or 90°
imaging, 4, 5, 6, 14, 15 and collecting light through various filters.

erol droplet. A microscope barrel is lowered for viewing, of the methanol evaporates leaving a single dye doped glyc-

ing the droplet as it is emitted. Once trapped, in dry air, most strips attached to the pipette body, and

from the orifice by momentarily electrifying piezoelectric

amounts of dissipation experienced in the current work (i.e., imaginary part of the complex refractive index, \(\text{Im}[m] \sim 10^{-7}\)) the major effect of dissipation is in the broadening and attenuation of resonant peaks. This effect is adequately described by using the complex refractive index in the place of \(n\) in the resonant coefficients.

Equation (2) reveals an important distinction associated with coupling to different polarization modes. Although a dipole oriented tangential to the surface can couple to both TE and TM modes, a perpendicular dipole will stimulate only TM modes.

All experiments were carried out using an Aerosol Particle Microscope-Spectrometer (APMS) (Ref. 6) shown in Fig. 1. The core of the apparatus is a levitator capable of trapping a particle using alternating gradient forces (Paul trap), 12 This enables isolated droplet samples to be studied free of contaminating elements such as glass surfaces of cuvettes, etc. The charged microdroplet is prepared by (1) drawing glycerol/methanol/dye solution through a micron sized orifice of a picopipette, 13 (2) ejecting a few picoliters from the orifice by momentarily electrifying piezoelectric strips attached to the pipette body, and (3) inductively charging the droplet as it is emitted. Once trapped, in dry air, most of the methanol evaporates leaving a single dye doped glycerol droplet. A microscope barrel is lowered for viewing, imaging, 4, 5, 6, 14, 15 and collecting light through various filters for analysis with a spectrometer.

An Ar\(^+\) laser at 488 nm illuminates the droplet from the side, and the fluorescent light is collected at 90° using a high numerical aperture (NA=0.4) objective. This light is directed out of the microscope barrel using a beamsplitter and imaged onto the slit of the spectrometer (resolution, 0.1 nm).

DiI(3) from Molecular Probes (1,1′-dioctadecyl-3,3′, 3′-tetramethylindocarbocyanine perchlorate) was chosen for testing theory [Eq. (2)]. This molecule has a hydrophilic chromophore (carbocyanine head group) and hydrophobic aliphatic chains on either side (two C\(_{18}\) tails). DiI(3) has successfully been used to prepare Langmuir–Blodgett films on water, 16 its homolog DiI(5) has been shown to orient on glycerol. 17 Furthermore, recent fluorescence imaging experiments in the APMS indicate that DiI(3) acts as a surfactant on glycerol and is likely to be oriented with its emission moment nearly tangent to the spherical particle surface. 6

Figure 2 shows the experimental emission spectrum (2A) of a particle containing DiI(3) \([10^{-5} \text{ M}]\), and theoretical emission rate spectra, \(\gamma(\omega)/\gamma_0\), for the two extreme orientations [i.e. tangential (b) and perpendicular (c) to the interface] for a dilute layer of DiI(3) surfactant on the glycerol particle of radius \(a = 7.3656 \mu\text{m}\).

FIG. 1. Aerosol Particle Microscope-Spectrometer.

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FIG. 2. Comparison between the experimental emission spectrum (a) and theoretical emission rate spectra \(\gamma(\omega)/\gamma_0\) for the two extreme orientations [i.e. tangential (b) and perpendicular (c) to the interface] for a dilute layer of DiI(3) surfactant on the glycerol particle of radius \(a = 7.3656 \mu\text{m}\).

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(FIG. 2. Comparison between the experimental emission spectrum (a) and theoretical emission rate spectra \(\gamma(\omega)/\gamma_0\) for the two extreme orientations [i.e. tangential (b) and perpendicular (c) to the interface] for a dilute layer of DiI(3) surfactant on the glycerol particle of radius \(a = 7.3656 \mu\text{m}\).)
ance of both mode polarizations, the relative shapes of the spectra (i.e., peak heights and linewidths) between Figs. 2(a) and 2(b) compare favorably. The only disparity is associated with the TE(4,1) series for which the heights of the resonances decrease below theoretical expectations as the wavelength decreases. This can be explained from wavelength dependent reabsorption, which increases at shorter wavelength, and which can be expected to be polarization sensitive (i.e., TE modes more readily couple to tangentially oriented molecules). This reabsorption effect is almost negligible at the longest wavelengths where the comparison between experiment and theory [Fig. 2(b)] clearly indicates that the transition moment is tangential to the glycerol surface.

Although we have not measured the fluorescence lifetime from a droplet, our calculations may be used to shed light on recent fluorescence lifetime measurements for octadecylrhodamine B (ODRB) on glycerol. In Ref. 5 the authors inferred, through fluorescence imaging, that the emission moment of ODRB is tangent to the glycerol surface. In addition, they found that the fluorescence decay rate is only \( \sim 75\% \) of the rate in bulk glycerol for particle diameters in the \( 15-25 \, \mu m \) range. A decrease in the fluorescence decay rate below the bulk value could not be understood using 1D CQED ideas, however we clearly see that a substantial decrease in the rate of emission is predicted in the off resonance region for our tangential semiclassical calculations [e.g., see Fig. 2(b)]. To be more quantitative, the measured rate of decay is expected to correspond to the average of \( \gamma_0 \) over a homogeneous linewidth. For a droplet 15.5 \( \mu m \) in diameter the free spectral range between resonances is less than the homogeneous linewidth, and the measured rate of decay should correspond to a simple average over the spectrum. The computed average for the tangential and perpendicular cases in Fig. 2 are 0.70 and 0.30, respectively. Our calculations show a distinct sensitivity to orientation and strongly suggest, by comparison to experiment, a tangential orientation for ODRB on glycerol. Recent work on CQED shows that the disparity between 1D CQED and semiclassical calculations can be narrowed considerably by expanding mode counting to three-dimensions and by considering leakage of modes at the phase boundary.

It is apparent from recent fluorescence lifetime measurements vs particle size that molecular dynamics plays an important role as evidenced by the distinct effect which the ratio of homogeneous linewidth to free spectral range has on the fluorescence lifetime. However, our preliminary measurements indicate that the shape of emission spectra agree with theory [i.e., Eq. (2)] even for smaller particles (\( \alpha \geq 4 \, \mu m \)) for which the homogeneous linewidth is comparable to the free spectral range between resonances. Notably, the relative level of background fluorescence (i.e., off resonance fluorescence) agrees better with theory [i.e., Eq. (2)] at smaller particle sizes, and we believe that molecular dynamics may play a role in these regions.

We have shown that semiclassical theory can be used to describe the emission spectrum of a tangentially oriented fluor on glycerol. Our theory suggests that the spectrum should change dramatically as the emission moment is rotated into a perpendicular orientation. We have carried out preliminary measurements in which a molecular scaffold (e.g., stearic acid) is used to turn emission moments of other surfactant fluoros toward the droplet normal. Indeed, the spectrum changes by reducing the relative amplitude of TE peaks substantially. Although a complete theoretical understanding of emission spectra is still not at hand (e.g., the background level), the semiclassical formalism appears to describe other aspects of the phenomenon.

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