Cavity-mode selection in spontaneous emission from oriented molecules in a microparticle

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We observe preferential cavity-mode selection in spontaneous emission by oriented molecules at the surface of a microparticle. Polarization-analyzed images of a levitated microdroplet containing surface active molecules reveal a well-defined system in terms of molecular position and orientation. The measured fluorescence spectrum is compared with that of a semiclassical emission-rate-enhancement model that treats the coupling between an excited state and Mie resonances as an oscillating dipole interacting with its self-scattered field. By comparing results obtained with this theory with the relative strengths of TE to TM modes measured in the emission spectrum, we show that one can elucidate the heterogeneity of a particle from this resonant structure and determine the orientation of the emission moments relative to the phase boundary.

In this Letter we report what we believe to be the first observation of preferential mode selection in spontaneous emission by oriented molecules at the surface of a microparticle. Aside from its basic importance, preferential mode selection in emission spectroscopy is expected to provide a means for discriminating between structured and homogeneous particles, for following phase transitions within monolayer, and for designing particles with particular gain characteristics for lasing experiments.

The imprinting of orientational information onto the emission spectrum is the result of cavity-enhanced mode selection in the spontaneous-emission process. In particular, a molecule with an emission moment that is oriented perpendicular to the surface of a spherical particle can stimulate only TM modes. On the other hand, an emission moment that is oriented parallel to the surface will preferentially stimulate TE modes, although it can also excite TM modes. In the parlance of cavity QED for which the emission rate at a given frequency is controlled by the photon density of states, oriented molecules have access to states that is limited by the projection of their emission moments onto the photon-state functions.1

Our study contrasts with measurements of soluble fluorors in liquid droplets, for which it has been found that, in the absence of significant absorption, the integrated intensities beneath resonant peaks in the emission spectrum are relatively constant.2 Based on the discussion in the previous paragraph, the lack of pronounced mode selectivity in such particles can be expected to be the result of randomness in molecular orientation and position.

Our studies are currently performed in the aerosol particle microscope—spectrometer shown in Fig. 1. Charged particles are injected into a Paul trap after the microscope barrel is withdrawn vertically and a picopipette4 is positioned just above the top electrode of the trap. We prepare the charged μ drop by (1) drawing a glycerol—methanol—dye solution through a micrometer-sized orifice of the picopipette, (2) squeezing a few picoliters from the orifice by momentarily electifying piezoelectric strips attached to the pipette body, and (3) charging the droplet inductively as it is emitted. Once trapped in dry air, most of the methanol evaporates, leaving a single dyed glycerol droplet. The microscope barrel is then lowered to focus an image of the particle upon the CCD and upon the entrance slit of our spectrometer (resolution, 0.1 nm).

The particle is irradiated with the beam from an Ar laser (488 nm). The laser can be directed either from the side (plane-polarized illumination, sidelit) or the back (circularly polarized illumination, backlit).

We performed preliminary sizing of the levitated particle by using both the parametric instability of the trap and the separation between glare spots in the image of elastic scattering.3 Precision sizing was done.
by correlation of the position of the narrow peaks in the fluorescence spectrum with resonances in Mie theory. The particular dye chosen is known as 1,1'-dioctadecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate (DiI(3)). This molecule has a hydrophilic chromophore (carbocyanine head group) and hydrophobic aliphatic chains on either side (two C₁₈ tails). DiI(3) has successfully been used to prepare Langmuir–Blodgett films on water, and its homolog DiI(5) has been shown to orient on glycerol.

In Fig. 2(A), (i) is a typical image of a DiI-doped particle (10⁻⁶ M) that is ~10 μm in radius and backlit with a circularly polarized beam from an Ar⁺ laser at 488 nm (Fig. 1). A pronounced rim is seen in addition to a central spot. These features indicate surface-layer formation. The orientation of the transition moments in the layer can be inferred by polarization-selective imaging, as seen in image (ii) of Fig. 2(A). Fluorescence from the rim is nulled at positions for which the axis of the polarizer is perpendicular to the surface tangent. We infer from this image that the transition moment is aligned parallel to the particle surface.

Figure 2(B) shows a portion of a typical emission spectrum of a sidelit glycerol particle doped with DiI(3). The resonances that are responsible for each of the peaks in this spectrum were identified from their correlation to Mie resonances. The resulting size determination (radius \( a = 7.3656 \, \mu m \)) is consistent with all of the aforementioned sizing techniques. This spectrum is quite different from the spectra taken on droplets in which the dye is soluble. For soluble dyes the integral under each peak is relatively constant. In Fig. 2(B) we see a clear preference for TE modes. Although optical absorption can profoundly affect the sizes of low-order resonances such as the fourth-order resonances in the figure, our calculations show that higher-order resonances such as the fifth-order modes should not be sensitive to bulk absorption by glycerol, or reabsorption that is due to DiI. The ratio of integrated intensity under the TE₈₈,₅ peak to that under the TM₈₉,₅ (\( R_{89,5,} \)) peak is 4.5 ± 5%. A similar ratio was found for the (TE₈₈,₅, TM₈₈,₅) pair, (\( R_{88,5} \)) = 4.5 ± 5%.

Unlike the fifth order TE modes, the fourth-order TE modes are sensitive to optical reabsorption. Their heights are seen to decrease systematically at shorter wavelengths as the molar extinction of the surfactant increases [Fig. 2(B)]. On the other hand, the heights of the fourth-order TM mode remain relatively constant. This is dissimilar to the effect of optical absorption in bulk. The attenuation owing to bulk absorption for modes that differ by only polarization is much more democratic. However, such polarization-dependent reabsorption might be expected from oriented surfactant species. If modes of a particular polarization can be preferentially excited by oriented molecules, then the energy in these modes can be preferentially reabsorbed by the same molecules, given similar directions for absorption and emission moments.

There is currently no cavity QED model for calculating the interaction of an oriented molecule with a spherical particle. However, the ratios of the peak areas may be accounted for by a semiclassical model in which the enhancement in emission at a particular frequency is treated as proportional to the enhancement in the semiclassical rate of decay. Chew calculated the radiative rate enhancement relative to bulk \( \gamma(\omega)/\gamma_0 \) from an oscillating dipole within a dielectric sphere. By evaluating his results on resonance (polarization \( p = E \) or \( M \), for TE or TM) and at the surface for two distinct orientations (orientation \( q = t \) or \( p \), for tangential or perpendicular) we can form a simple matrix (i.e., \( \gamma_{pq}/\gamma_0 \)) with which peak heights and shapes in the emission spectrum can be described. It is even possible to obtain analytical expressions for the key ratio \( \langle R \rangle \) by incorporating the more recent asymptotic research of Lam et al. Although the complete model will be described elsewhere, we review the key result here for completeness.

Suppose that a molecule at the surface has an emission moment that is oriented at an angle \( \theta \) to the normal. For a TE mode, only the component of the emission moment tangent to the surface can couple to the mode. Since the rate of coupling is proportional to the square of the transition moment, the energy coupled into a TE mode is proportional to \( \langle \gamma_{E,t}/\gamma_0 \rangle \sin^2(\theta) \), where \( \langle ... \rangle \) indicates that we have integrated over the peak width. On the other hand, for a TM mode both tangential and normal components can couple energy into the mode, and the rate of coupling is proportional to \( \langle \gamma_{M,t}/\gamma_0 \rangle \sin^2(\theta) + \langle \gamma_{M,n}/\gamma_0 \rangle \cos^2(\theta) \). Together the

Fig. 2. (A) Fluorescent images of a backlit DiI doped glycerol particle (10⁻⁶ M) ~10 μm in radius. Image (i) was taken with a colored filter to block the laser beam. Image (ii) was taken through an additional polarizer. (B) Fluorescence spectrum of a sidelit particle. The assignment of resonant modes is based on a particle radius of 7.3656 μm. The dashed curve is a plot of the molar extinction of DiI measured in a methanol–glycerol (2:1) solution.
ratio of emission into a TE mode to that into a TM mode is
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\langle R \rangle = \frac{\langle y_{E,l} \rangle}{\langle y_{M,l} \rangle} = r_{lt} = \frac{1}{1 + \left(\frac{r_{pt}}{r_{lt}}\right)\cot^2(\theta)},
\]
where we divided out the bulk rate and condensed our notation as indicated. The mode-selection sensitivity is clearly spelled out by Eq. (1). As the emission moment is turned from the normal, the ratio of peak area grows from zero to its full tangential ratio, moment inclination from the surface normal.

Fig. 3. Comparison between Eq. (1) and experimental polarization area ratios \(\langle R \rangle\) as a function of the emission-moment inclination from the surface normal.

where the effect of reabsorption by the oriented surfactants is minimized, the measured \(\langle R \rangle\) value is 3.1 ± 5%, whereas the predicted ratio from Eq. (1) for a tangentially oriented emission moment is 3.2.

In summary, we have shown that oriented molecules can preferentially select particular mode polarizations in both emission and reabsorption processes. This selectivity in the emission spectrum within a droplet provides a signature for heterogeneity and permits the determination of the emission-moment orientation. This phenomenon leads to a new method for determining the conformation of molecules at a liquid surface with optical spectroscopy. Although the reported measurements in this Letter are for a dilute layer (<1/10 of a monolayer), preliminary measurements at our laboratory with supporting structures (e.g., stearic acid) at much higher concentrations, along with other surfactant fluorophors, have enabled us to witness the re-orientation that accompanies phase transitions from a two-dimensional gas to a two-dimensional liquid to a two-dimensional solid.

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