

Angular Spectrum of the Spontaneous Emission from Dye Molecules Near a Boundary

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We studied experimentally the angular spectrum of the light emitted from dye molecules near a plane boundary. It is confirmed that the molecules near the boundary can emit light into the evanescent wave mode, and the light emission with the angle greater than the critical angle is detected with good accuracy. The angular spectrum of the spontaneous radiation is measured, and the spectrum shows contributions from the molecules both near and far away from the boundary. The polarization dependence and the pumping angle dependence are also measured. The experimental results are in good agreement with quantum theory.

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I. INTRODUCTION

Light refraction at a boundary between two dielectric media with different index of refraction is usually well described by geometrical optics. According to Snell's law of refraction, a light beam propagating nearly parallel to the plane boundary surface in the lower refraction index medium refracts and propagates into the higher index medium with the critical angle θ_C . Therefore, a light beam cannot propagate into the higher index medium with the angle θ greater than the critical angle θ_C . However, if an atom or a molecule is located very close to the boundary then the near field effect has to be taken into account, and the atom or molecule can emit light into the higher index medium with $\theta > \theta_C$ [1]. A molecule located within a wavelength of light from the boundary can excite the evanescent wave mode, which enables the emitted light to propagate into the medium with larger angle. Several authors have studied this phenomena theoretically [1-4] and a few experiments have been done also [5-7]. A full quantum theory on the spontaneous and stimulated emission of the evanescent photon was introduced only recently in which the spontaneous emission rate of the molecules near the boundary was calculated [8]. In this paper, we present detailed experi-

mental results with dye molecules pumped by a laser, and show that the angular spectra of the light emitted from the dye molecules are in good agreement with the theory. The contribution to the angular spectrum from the molecules near the boundary are quite different from the contributions from the molecules far away from the boundary, according to the theory, and it is confirmed in the experimental results.

II. TRIPLET MODE THEORY

The electromagnetic wave including the evanescent wave can be quantized using a triplet mode, which contains the incident, transmitted and reflected plane waves [1]. A full quantum theory for the atom-evanescent wave interaction using the similar triplet mode was developed recently [8]. An interested reader can find a rigorous treatment of the problem in the references. Here, we only use the result of the quantum theory.

The spontaneous emission rate from a molecule near the boundary is

$$\gamma_{21} = \frac{(2\pi)^2}{\hbar} \sum_{\alpha} \omega_{\alpha} |\mathbf{E}_{\alpha} \cdot \mathbf{d}_{12}|^2 \delta(\omega_{\alpha} - \omega_0) \quad (1)$$

in which we have written the molecular dipole moment matrix element as $\mathbf{d}_{12} = \langle 1|\mathbf{d}|2 \rangle$, and $\hbar\omega_0 = E_2 - E_1$. The \mathbf{E}_α is the electric field vector of the triplet mode with mode index α . The term $|\mathbf{E}_\alpha \cdot \mathbf{d}_{12}|^2$ is strongly dependent on the position of the molecule, the propagating direction of the triplet mode, and the polarization direction of the light. The triplet mode wave functions are summarized in the appendix.

One can split the decay rate according to the left and right triplet modes, or TE and TM polarizations, and we get

$$A_{21} = A_L + A_R \quad (2)$$

$$= A_{TE} + A_{TM} \quad (3)$$

For the light emission direction $\theta > \theta_C$, only the left triplet mode is needed to calculate the emission rate. When $\theta < \theta_C$, both the right and the left modes are needed to calculate the emission rate at a given angle θ [9]. This calculation contains the cavity QED effects which cause the transition lifetime of the molecule to oscillate as a function of the distance between the boundary surface and the molecule [10]. The classical theories have overlooked this feature, but the angular spectrum of the spontaneous emission can be changed by this effect. In our experiment, many molecules are excited by the pump laser beam, so that the emission rate has to be integrated over all molecules in the pumped region.

III. EXPERIMENT

We have constructed an experimental set-up as shown in Fig. 1 to study the spontaneous emission angular spectrum. An active medium is prepared with the laser dye DCM dissolved in methanol. The concentration of the dye in the solution is 0.25 g/l. To avoid the problem of the singlet to triplet transition in the dye molecules, the dye solution was circulated with a water pump, with the flow rate of 1.4 l/min. The dye cell has two windows, and one window is made with a hemisphere lens which enables us to measure the correct emission angle of the radiation from the pumped region of the dye solution. The index of refraction of the hemisphere lens is 1.515, and that of the dye solution is 1.330. The dye cell is attached to the rotation stage with a micrometer, and the detector is positioned on the rotating arm, in order to obtain a better angle resolution in the experiment. A HeNe probe laser was used to find the critical angle in the experiment, and was also used to check the accuracy of the angle rotation system. A second-harmonic beam from a diode-pumped solid state laser is used to pump the dye solution. The pump laser has 532nm output wavelength, and the laser was operated in single mode

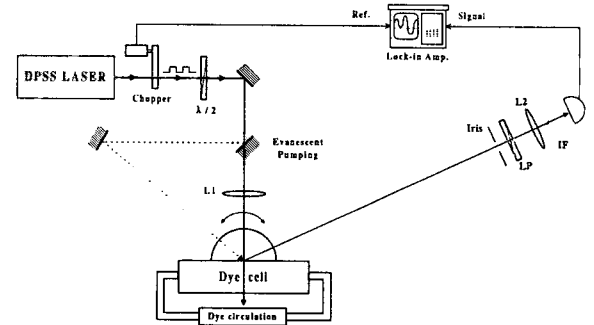


FIG. 1. Experimental set-up for the spontaneous emission angular spectrum measurement.

frequency. Two lenses including the hemisphere lens itself are used to focus the pump beam in order to reduce the pump spot size to about 100 μm , and a pin-hole is placed in front of the photo-detector so that the light from a very small volume in the pumped region of the dye solution can enter the photo-detector.

Because the radiation from the pumped dye region was very weak, we used a chopper to modulate the pump laser light intensity with 1.5 kHz modulation frequency, and the radiation signal is detected by the phase-sensitive detection method. An interference filter with center wavelength at 632.8 nm and bandwidth of 10 nm was placed in front of the photo-detector. The fluorescent light from the dye cell at 632.8 nm wavelength can pass through the filter with 50% transmission and the scattered pump light or any other stray light with different wavelength is blocked out by the filter. Finally, a half-wave plate is inserted in the pump beam path so that the polarization of the pump beam can be changed from TE-polarization to TM-polarization, and a linear polarizer is placed in front of the detector so that the polarization of the radiation signal can be selected.

We used two different pumping schemes in the experiment. First, the pump laser beam was sent in the direction normal to the boundary so that many molecules in the dye cell along the pump beam path are excited (normal pumping). Secondly, the pump beam was sent with the incidence angle slightly greater than θ_C , so that the pump beam is totally reflected from the boundary. In this case, only dye molecules in the evanescent wave region of the pump laser beam can absorb the pump photons and are excited (evanescent pumping). The result of the normal pumping experiment is shown in Fig. 2. The light emission above the critical angle θ_C was observed, even though the signal was very weak, and the emission rate decays very fast as the angle is increased.

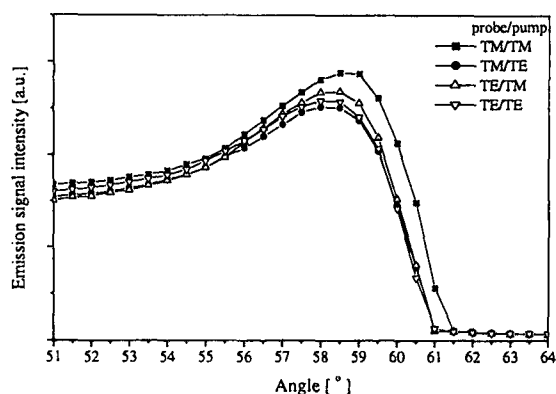


FIG. 2. Angular spectrum obtained with normal pumping.

The theoretical value of θ_C is 61.38° , and the critical angle determined in the experiment using the probe laser light scattering from the boundary surface as well as using the reflected probe laser light intensity measurement was 61.4° . The angular spectrum shown in Fig. 2 has its maximum at 58° . It is due to the fact that many molecules in the normally pumped region are far away from the boundary surface and those molecules cannot emit light above the critical angle. The signal drops to zero for these molecules as the angle approaches the critical angle. A very small portion of the pumped molecules are within a few wavelengths distance from the surface and it is those molecules that contribute to the emission above the critical angle.

Fig. 3 shows the effect of varying the pump angle. One can see that the emitted signal light intensity below the critical angle is dramatically reduced when the pumping angle goes over the critical angle for the pump laser beam. One can also find that the position of the peak in the spectrum curve moves towards the critical angle as the pump angle is increased. In the

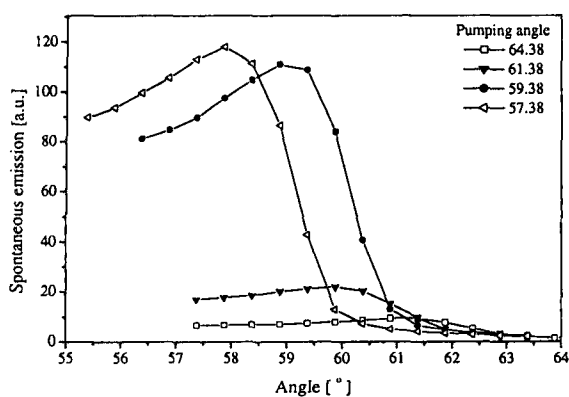


FIG. 3. Variation of the spectrum as the pump angle is changed.

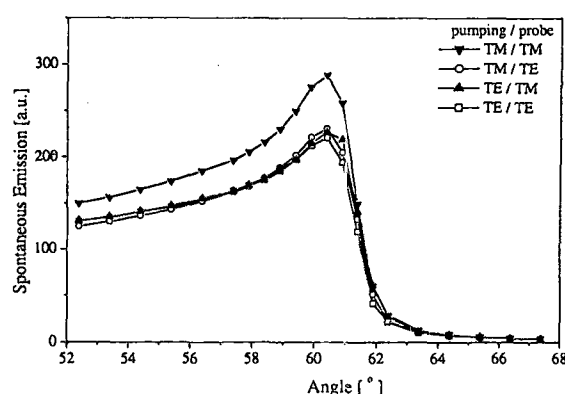


FIG. 4. Angular spectrum obtained with evanescent pumping.

case of the evanescent pumping, only molecules within a few wavelength distance from the boundary can be excited by the pump evanescent field. The amplitude of the pump evanescent field decreases exponentially in the dye solution. Therefore the molecules very close to the boundary surface make major contributions to the angular spectrum in this case. Figs. 2 and 3 show the role of the molecules near and far away from the boundary surface clearly.

It is interesting to look at the polarization dependence of the spectrum. Because the measurement was taken with flowing dye solution, we may consider the polarization of the dye molecules to be random, irrespective of the pump beam polarization. Let's look at the polarization dependence of the spectrum shown in Fig. 4, for the evanescent pumping case.

It is found that the TM-polarized signal obtained from the detector with the TM-polarized pump is about 20% stronger than the TE-polarized signal with the TE-polarized pump. It corresponds to the well known fact that the evanescent wave penetration depth of the TM-polarized light is about 20% larger than that of the TE-polarized light. The other two cases - the TE-polarized signal with TM-polarized pump and the TM-polarized signal with TE-polarized pump - are in between the two. It shows that the polarization of the dye molecules is randomized by the collisions in the flowing solution, and that the molecules run away from the boundary. The reason that all the spectrum curves become the same eventually when the emission angle is greater than the critical angle is due to the fact that the penetration depth for both polarizations decreases so fast when the angle is greater than θ_C that the radiation signal intensities go to zero.

In the case of normal pumping, the distinction between the two orthogonal polarizations of the pump is

obscure. When we look at the results in Fig. 2, the result seems to be a little bit different from that of the evanescent pumping case, at first glance. However, there is only a very small amount of emission signal when $\theta > \theta_C$ in the normal pumping case. Most contribution to the spectrum comes from the molecules far away from the boundary surface, and the molecules coupled to the TM-polarized signal evanescent wave, which has larger penetration depth, can make more contribution to the spectrum when $\theta > \theta_C$.

Both experimental results, shown in the Figs. 2 and 4, indicate that the emission spectrum is mostly determined by the coupling between the dye molecule and the signal evanescent wave. The role of the pump evanescent wave in the evanescent pumping case is only to confine the excitation of the molecules within a few wavelengths from the boundary, so as to change the portion of the molecules near the boundary in the total number of contributing molecules.

IV. CONCLUSION

We have presented experimental results of the angular spectrum measurement for the spontaneous emission from dye molecules near the plane boundary. It is shown that light emission below and above the critical angle is observed, and the contributions from the molecules near and far from the boundary surface are well distinguished. By comparing the normal pumping case and the evanescent pumping case, we reached the conclusion that the spontaneous emission above the critical angle is dictated by the coupling between the molecule and the evanescent wave, not by the pump wave. It is difficult to explain this result in terms of pure classical wave theory, because the evanescent wave is usually produced by the incident light undergoing a total internal reflection at the boundary, but there is no incident wave in our spontaneous emission experiment. However, it is easily explained by quantum theory, for there are always vacuum fields - vacuum evanescent field - around the molecules.

V. ACKNOWLEDGEMENT

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APPENDIX. TRIPLET MODE WAVE FUNCTIONS

The triplet mode functions in the right half space, where the molecules are ($z > 0$), are needed for the calculation of the spontaneous emission rate. They are given, in terms of the polarization (TE/TM), propagating direction(\mathbf{k}/k), and the position of the molecule(\mathbf{r}), as follows.

$$\mathbf{E}_{L,k,TE}(\mathbf{r}) = \hat{\varepsilon} \frac{1}{n} \frac{2k_3}{k_3 + K_3} \exp(i\mathbf{K} \cdot \mathbf{r}) \quad (4)$$

$$\mathbf{E}_{L,k,TM}(\mathbf{r}) = (\hat{\varepsilon} \times \hat{K}) \frac{2k_3}{k_3 + n^2 K_3} \exp(i\mathbf{K} \cdot \mathbf{r}) \quad (5)$$

$$\begin{aligned} \mathbf{E}_{R,k,TE}(\mathbf{r}) \\ = \hat{\varepsilon} \left[\exp(i\mathbf{K} \cdot \mathbf{r}) + \frac{K_3 - k_3}{K_3 + k_3} \exp(i\mathbf{K}^R \cdot \mathbf{r}) \right] \end{aligned} \quad (6)$$

$$\begin{aligned} \mathbf{E}_{R,k,TM}(\mathbf{r}) \\ = \hat{\varepsilon} \times \left[\hat{K} \exp(i\mathbf{K} \cdot \mathbf{r}) + \hat{K}^R \frac{n^2 K_3 - k_3}{n^2 K_3 + k_3} \exp(i\mathbf{K}^R \cdot \mathbf{r}) \right] \end{aligned} \quad (7)$$

where $\mathbf{K}^R = \mathbf{K}_{\parallel} - K_3 \hat{z}$ is the reflected wave vector of \mathbf{K} , and \hat{K}_{\parallel} is the parallel component of \mathbf{K} . When $\theta > \theta_C$, K becomes pure imaginary.

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