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## LOCALIZATION OF SPONTANEOUS EMISSION IN FRONT OF A MIRROR

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We show that the fluorescence emitted in front of a mirror exhibits angular and spectral localization effects that are caused by self-interference in the spontaneous emission from a Wiener-fringe pattern. A semi-classical description is given and found to be in good agreement with the observations.

### 1. Introduction

About two decades ago it has been shown that the lifetime of the spontaneous emission of a molecule or atom in front of a mirror can be influenced by the presence of a mirror at distance comparable to the wavelength of the emitted light [1]. The influence of boundary conditions on radiation was pointed out long ago by Purcell [2] and first observed by Drexhage [1] in a pioneering study of the fluorescence of organic dyes close to a mirror. Drexhage et al. [1] showed that the fluorescence lifetime of a dye molecule close to a mirror exhibits an oscillatory behaviour as a function of distance between the molecule and the mirror. This effect has been explained classically [3,4] as arising from coupling between the molecule's radiating dipole and its fictitious mirror image. At some distances the two dipoles oscillate in phase, leading to a shorter fluorescence lifetime; at other distances they oscillate out of phase and the lifetime is lengthened. One can also consider the effect to arise from self-interference between the wave packet emitted into the solid angle of observation with its reflection from the mirror in the same direction [5]. Quantum electro-dynamically, spontaneous emission results from the coupling of the excited molecule to the vacuum states of the electromagnetic field. The effect of a mirror near a radiating molecule is explained as a change of the mode density of the vacuum field to which the excited molecule is coupled by the molecule-radiation

field hamiltonian. If the density of resonant "vacuum" states is reduced lifetime lengthening occurs, if the density is increased the spontaneous emission lifetime decreases.

Recently it has been suggested by de Martini [6] and Innocenti [7] that the observed angular dependence of the spontaneous emission of a thin ruby slab in front of a mirror provides clear evidence for "the physical reality of the zero-point electromagnetic field". In other words, they claimed that this angular dependence of the spontaneous emission could only be explained quantum electro-dynamically. This remarkable statement inspired us to reinvestigate this phenomenon, using a thin polymer film doped with the strongly fluorescing molecule Rhodamine 6G as a probe. We show in this letter that the angular and spectral localization effects observed in the luminescence of atoms and molecules near a mirror can be explained also classically as resulting from self-interference in spontaneous emission from a Wiener-fringe pattern [8,9]. We further show that the observed enhancements in the spontaneous emission at long wavelengths rule out the importance of Lippmann fringes [9] in the observed effects.

### 2. Experimental

Fig. 1 shows schematically the outline of the experiment. A low-divergence ( $< 0.5$  mr), expanded laser beam ( $\approx 20$  mm diameter, power density 17

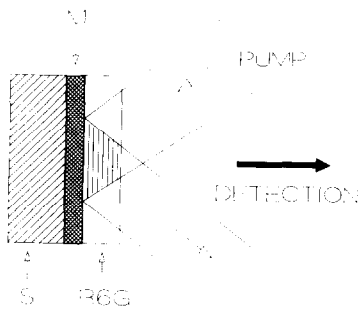


Fig. 1. Schematic outline of the geometry of the experiment. S, M and R6G denote substrate, mirror and the polymer film doped with R6G, respectively.

mW/cm<sup>2</sup>) is used to excite the fluorescence of a thin polymer film doped with Rhodamine 6G. As exciting laser source we used the frequency-doubled output of a modelocked Nd-YAG or a cw Ar<sup>+</sup> laser. The exciting light beam was polarized perpendicular to the plane of incidence with an angle  $\nu_p$  with respect to the mirror normal.

The polymer (poly-4-vinylpyridine) film doped with Rhodamine 6G (R6G) was oriented parallel to the mirror. The polymer films were prepared by spin-coating a solution of 14 weight% polymer, 0.8 weight% R6G in 2-chloro ethanol either directly onto an aluminum mirror or on a pre-existing polystyrene layer on the mirror. The thickness of the films and intermediate polystyrene layers used in these experiments varied between 1 to 10  $\mu\text{m}$ ; the concentration of R6G was adjusted to an optical density of about 0.2 in a single pass for all films.

The emission of the R6G film was angularly resolved with a resolution better than 0.5 mrad using a 155 mm focal length lens and a 0.05 mm diameter pinhole. A polarizer was placed behind the pinhole, and oriented such that s-polarization of the emission was selected. The emission was also wavelength resolved using a 1 m grating spectrometer (Spex 1704). Special care was taken to insure that the emission properly filled the mirrors and grating of the spectrometer, as misalignment affected the results.

### 3. Results and discussion

Fig. 2 shows a typical R6G fluorescence spectrum

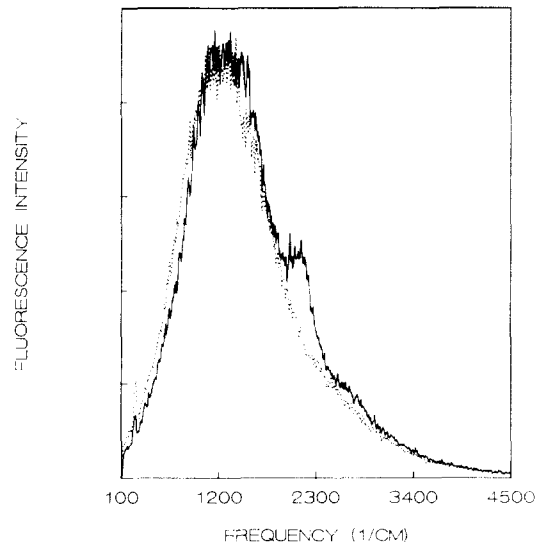


Fig. 2. Fluorescence spectra of R6G in a polymer film: on top of a mirror (solid line), and without mirror (dashed line). The horizontal scale denotes the red shift in  $\text{cm}^{-1}$  with respect to the 532 nm Nd-YAG laser line.

observed in a direction perpendicular to the mirror. The 7  $\mu\text{m}$  thick R6G film was directly spin-coated onto the Al mirror and excited by a Nd-YAG laser beam at an angle of 40 degrees with the mirror normal in air. On comparing this spectrum with that of a film spin-coated on an optical flat, one notes an enhancement of the emission intensity about 2050  $\text{cm}^{-1}$  to the red of the exciting laser line. This enhancement of the emission intensity is certainly not due to stimulated emission, as all spectra at any detection angle  $\nu$  could be reproduced with a tenfold decrease in pump intensity (i.e. 1.5 mW/cm<sup>2</sup>). We note that De Martini et al. [6,7] observed a similar localization effect in the case of a ruby crystal when the total emission in the perpendicular direction was monitored as a function of pump angle  $\nu_p$ .

In order to explain these angular and spectral localization effects, consider an emitter at distance  $z$  from the mirror. The total field  $E_t(t)$  is detected at distances much larger than  $z$ , in which case the direct ( $E_d(t)$ ) and reflected field ( $E_r(t)$ ) have nearly the same weight, i.e.

$$E_t(t) = E_d(t) + E_r(t) \quad (1)$$

(in the above equation  $E_t$  is the projection onto the s-polarized polarizer).

When the emission is detected at angle  $\nu$  with respect to the mirror normal, a simple geometrical consideration gives for the path difference between the direct and reflected light  $2z\cos\nu$ . We then may write for the reflected field

$$E_r(t) = R \exp(i\Delta) E_d(t - \tau_m), \quad (2)$$

where  $R$  is the reflectivity,  $\Delta \equiv \Delta(\nu)$  the phase jump due to the mirror in the direction  $\nu$ ,  $\nu$  the angle with the mirror normal ( $\nu=0$  is perpendicular to the mirror), and  $\tau_m = 2z\cos(\nu)/c$ , with  $c$  the speed of light in the R6G film. In the present experiments the spectral content  $I_t(\omega)$  of the total field (consisting of both the direct and reflected light) is determined. The spectral intensity is proportional to the Fourier transform of the auto-correlation function of  $E_t(t)$  [10], i.e.

$$I(z, \omega) \propto |E_t(\omega)|^2 = (1/4\pi)^2 \times \int_{-\infty}^{+\infty} dT \exp(i\omega T) \langle E_t^*(t) E_t(t+T) \rangle. \quad (3)$$

In the above equation, the coherence time of the auto-correlation function of the spontaneous emission is determined by the decay time of the homogeneously broadened transition, averaged over the static inhomogeneous distribution of the center-frequencies of the emitters, and summed over the vibronic transitions. In working out the above equation one easily obtains for the spectral content of an emitter located at  $z$

$$I_t(z, \omega) = I_d(\omega) + R^2 I_d(\omega) + 2R I_d(\omega) \cos(\omega\tau_m - \Delta), \quad (4)$$

where  $I_d(\omega)$  corresponds with the spectral intensity of the field  $E_d(t)$  only.

Interestingly enough, the interference term given by the last term in eq. (4) is independent of any the factors which determine the coherence length of the emission of R6G. This despite the fact that the emission is allowed to interfere before its spectral content is determined. The above result is identical to the results of Drexhage [1] and Fleck [11] derived under the limiting condition of a monochromatic emitter. The result of eq. (4) is also very similar to the

case where wide angle interference is studied [12,13]. In order to obtain the emission of the R6G film, the Wiener fringes [8,9] formed by the incident and reflected pump beam should be taken into account. The resulting density of excited molecules as a function of  $z$  is given by

$$\rho(z) = 1 + R^2 - 2R \cos(2k_{pz}z), \quad (5)$$

where  $k_{pz} = k_p \cos\nu_p$ . It is assumed that the index of refraction of the R6G film is about the same as the transparent film, and that the phase jump is  $\pi$  upon reflection.

The total emission of the sample then follows simply by adding the intensities of eq. (4) with a weight given by eq. (5), i.e.

$$I_1(\omega) = \frac{1}{L_2 - L_1} \int_{L_1}^{L_2} dz \rho(z) I(z, \omega), \quad (6)$$

where  $L_1=0$  if the R6G film is on top of the mirror and  $(L_2 - L_1)$  the thickness of the sample. In writing out eq. (6) many terms arise; the dominant terms are

$$I_1(\omega)/I_d(\omega) = (1 + R^2)^2 + 2R^2 \cos[(k_{pz} - k_z)(L_2 + L_1)], \times \text{sinc}[(k_{pz} - k_z)(L_2 - L_1)], \quad (7)$$

where  $\text{sinc}x = (\sin x)/x$ ,  $k_z = k \cos\nu$ , and  $k$  the wave-vector of the emission. Eq. (7) is the central result of this paper.

We first note that when  $L_1=0$  and  $R=1$ , eq. (7) reduces to the expression obtained by De Martini et al. [6,7] (vide infra). These authors, however, derived this result quantum electrodynamically whereby explicitly a zero-point standing-wave field perpendicular to the mirror was introduced. The observed angular dependence of the ruby luminescence, as described by the second term of eq. (7), was interpreted by them as a clear indication of the physical reality of a zero-point vacuum field in front of a boundary. This interpretation is certainly not unique as eq. (7) was derived entirely classical without explicit reference to the existence of a zero-point field.

Eq. (7) predicts that for R6G films spin-coated directly on top of the mirror the fluorescence spectrum consists of two components: (a) the normal fluorescence spectrum with weight  $(1 + R^2)^2$ , and (b)

an interference term given by  $2R^2 \text{sinc}[2(k_{pz} - k_z)L_2]$ . The maximum of the sinc function is located at  $k_z = k_{zp}$ . Thus by varying the pump angle  $\nu_p$ , one changes  $k_{zp} = 2k_p \cos \nu_p$  which causes a shift of the top of the sinc function to a different region of the emission spectrum. Similarly, if  $\nu_p$  is held constant, changing the angle  $\nu$  at which the emission is viewed also moves the top of the sinc function to another wavelength (recall that  $k_z = 2k \cos \nu$ ).

The above mentioned features were found to be in agreement with the experimental results. In general, eq. (7) was found to be in quantitative agreement, provided that for large angles  $\nu$  or  $\nu_p$  the appropriate phase jump upon reflection is used. Notable exceptions were found only for films directly spin-coated on the mirror and having a thickness less than about  $1.5 \mu\text{m}$ . The explanation of this anomaly is outside the scope of the present paper.

It is of interest to note that by integrating eq. (7) over  $\omega$  space, the total emission intensity as a function of pump angle  $\nu_p$  is obtained. In the special case of  $L_1 = 0$  and a sample thickness much less than the coherence length of the emission, one can easily see that eq. (7) remains valid with  $I_1(\omega)$  replaced by  $I_1 \equiv \int I_1(\omega) d\omega$ . These conditions were actually met in De Martini's experiments on ruby [6,7].

Eq. (7) further predicts that for films separated from the mirror an additional cosine modulation should be present. The emission spectra obtained were found to be in quantitative agreement with eq. (7). An example is shown in fig. 3 where the R6G film was separated from the Al mirror by a transparent polystyrene film. Larger separations between the R6G film and the mirror (up to about  $0.5 \text{ mm}$ ) have been realized by spin-coating the R6G film on a separate optical flat (flatness better than  $\lambda/10$ ). The film faced the reflective surface of an Al or dielectric mirror. The interference patterns were also found to be remarkably insensitive to mechanical vibrations, despite the fact the total length of optical path was in excess of  $5 \text{ m}$ . This stability basically results from the presence of the Wiener fringes, which keep the excited molecules at a fixed distance from the mirror.

Finally, we have also used the interference effect to assess the importance of Lippmann fringes [9,14,15] in these type of experiments. A Lippmann fringe arises from energy-transfer among near-reso-

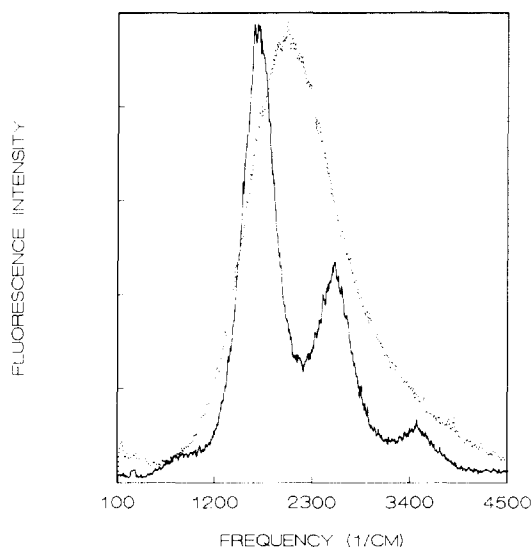


Fig. 3. Fluorescence spectra of R6G in a  $2 \mu\text{m}$  thick polymer film:  $2.2 \mu\text{m}$  separated from the mirror by a transparent film (solid line), and without mirror (dashed line). From the periodic modulation, described by the cosine term in eq. (7), one obtains the distance of the film to the mirror. The horizontal scale denotes the red shift in  $\text{cm}^{-1}$  with respect to the  $514 \text{ nm}$   $\text{Ar}^+$  ion laser line.

nant molecules in front of a mirror. The spatial fringe pattern is similar to the Wiener one of eq. (5) except for an additional factor  $z^{-2}$  [14,15]. Two conclusions can be immediately drawn: (a) Lippmann fringes will only be formed in spectral regions where the absorption and emission overlap, (b) the effect of Lippmann fringes will rapidly diminish for thicker layers. Our experiments clearly show that for sample thickness between  $1.5$  and  $20 \mu\text{m}$  the observed emission enhancements are in accord with eq. (7). Using thick samples ( $> 10 \mu\text{m}$ ) the fluorescence interference effect can be shifted to spectral regions where absorption and emission do not overlap. In this case we also found the predicted enhancement.

We therefore conclude that Lippmann fringes are of no importance to the description of the interference effects discussed in this paper.

Whether Lippmann fringes play a role in the observed anomalous emission spectra from thin samples ( $< 1.5 \mu\text{m}$ ) deposited on mirrors, remains to be studied.

In conclusion: we have shown that the angular and

spectral localization effects observed in the spontaneous emission of molecules in front of a mirror can be explained satisfactorily using classical theory. It was further shown that Wiener and *not* Lippmann fringes determine the observed enhancement of the spontaneous emission.

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