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Stimulated emission in high-gain organic media

S. V. Frolov
Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974
and Physics Department, University of Utah, Salt Lake City, Utah 84112

Z. V. Vardeny
Physics Department, University of Utah, Salt Lake City, Utah 84112

K. Yoshino
Electronic Engineering Department, Osaka University, Yamada-Oka 2-1 Suita, Japan

A. Zakhidov and R. H. Baughman
Allied Signal Inc., Morristown, New Jersey 07962
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Stimulated emission was studied in various scattering gain media, including thin π-conjugated polymer films, organic dyes-doped gel films, and opal crystals saturated with polymer and laser dye solutions. We found that at high excitation intensities a featureless amplified spontaneous emission band transforms into a finely structured spectrum having features as narrow as 0.1 nm. Stimulated emission in this regime is directional and characterized by a linear laserlike intensity dependence. We speculate that this phenomenon is due to optical feedback caused by light scattering inside the inhomogeneous gain media. [S0163-1829(99)50508-0]

Organic materials continue to attract researchers as promising semiconducting media for future electronics. After a recent demonstration of high optical gain and stimulated emission (SE) in films of several π-conjugated polymers,[1–5] these materials have been intensively studied worldwide as a possible gain medium for laser applications.[6–14] Considerable attention has been drawn to lasing in various optical cavities containing π-conjugated polymers,[9–14] as well as smaller organic molecules.[15,16] In our previous studies of the 2,5-dioctyloxy poly(*p*-phenylene-vinylene) [DOO-PPV] polymer we have reported the occurrence of regular SE regimes, such as amplified spontaneous emission[8] (ASE) and lasing.[9] In this work we demonstrate a regime of SE with characteristics that cannot be adequately explained within the simple pictures of neither ASE nor lasing models. We observe this SE regime not only in luminescent π-conjugated polymer films, but also in other media containing laser dyes (including liquid solutions). We argue that the newly found SE regime appears because of light scattering inside these materials, which provides the seed for optical feedback.

Thin (0.5-1 μm) DOO-PPV films were uniformly spin-coated on flat quartz substrates as described elsewhere.[8] Gel films were prepared using Rhodamine 6G (R6G) laser dye dissolved in ethylene glycol; this solution was then solidified by mixing it with clear household gelatin. In order to provide light scattering in the R6G solution, we mixed it with monodisperse silica balls of 300 nm in diameter. Both the polymer films and R6G samples were photoexcited by 100 ps pulses produced by a frequency-doubled (532 nm) Nd:YAG regenerative laser amplifier with a repetition rate of 100 Hz. The excitation beam was focused onto a sample with a cylindrical lens, forming a stripelike excitation area with variable length *L* and width *a*. Optical emission from the side of the sample was collected using a round lens positioned in the direction along the excitation stripe. Emission spectra were recorded using a 0.6 meter triple spectrometer and a charge-coupled-device (CCD) array with spectral resolution of about 1 Å.

Various π-conjugated polymers and oligomers produce SE when excited with short, high-energy laser pulses, as evidenced by dramatic spectral narrowing and substantial exciton lifetime shortening.[2–8] It has been demonstrated that these effects can be described using a simplified ASE model, where spontaneously emitted light is amplified by the same medium as it propagates along the path of the maximum optical gain.[6–8] Particularly, in the case of a thin stripe excitation, we found that SE occurred only in the direction along the stripe, whereas regular photoluminescence was isotropic.[8] Upon increasing the spectral resolution of our apparatus, however, we discovered new characteristics of SE, which do not agree with the ASE picture. Figure 1(a) shows the emission spectra measured in a DOO-PPV film at excitation intensities, *I*, greater than the SE threshold intensity, I_A. In this excitation intensity range the initial spectral narrowing results in a smooth SE band centered at 630 nm. At higher *I* ($I \geqslant I_B$, where I_B is a second threshold excitation intensity), however, this smooth peak transforms into a ‘‘spiky’’ band having features with a linewidth as narrow as 0.1 nm. As shown in Fig. 1(b), the emission spectra at $I > I_B$ are dominated by several narrow peaks. We found that the peaks wavelengths and heights changed whenever the excitation area was changed; this is illustrated in Fig. 1(b) showing the SE spectra measured under identical experimental conditions from two different illuminated areas of the same DOO-PPV film (lines 1 and 2). It is important to note, however, that the fine spectrum remained unaltered over an extended period of time, whenever the experimental conditions and *sample position* were kept constant [lines 2 and 3

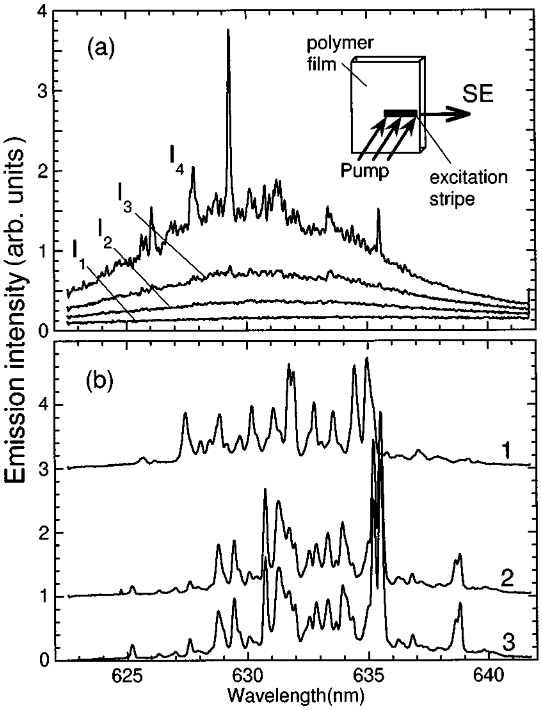

FIG. 1. Stimulated emission spectra of a DOO-PPV film obtained using a stripelike excitation area with length $L = 1$ mm and width $a = 30\,\mu$m: (a) SE at different excitation intensities I: $I_1 = I_A = 1$ MW/cm^2, $I_2 = 1.25 I_A$, $I_3 = 1.4 I_A$, $I_4 = 1.6 I_A$; the inset schematically shows the excitation geometry. (b) SE spectra (offset for clarity) measured sequentially at $I \approx 2 I_B$ from the same DOO-PPV film: line 2 was obtained from a different excited area vertically shifted by 0.3 mm from that of line 1, line 3 was obtained after 3 min delay from the same area as line 2.

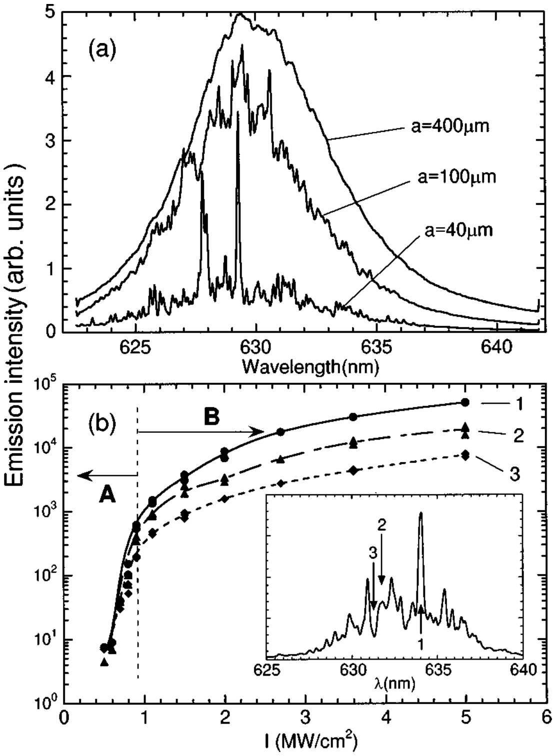

FIG. 2. (a) SE spectra at different values of a, where $L = 1$ mm and $I \sim 1.5 I_A$. (b) Emission intensity dependence on excitation intensity I in a DOO-PPV film ($L = 2$ mm, $a = 80\,\mu$m) for different wavelengths (1, 2, and 3), which are indicated by the arrows in the SE spectrum shown in the inset. The solid and dashed lines are guides to the eye.

in Fig. 1(b)]. This eliminates the possibility that the observed ‘‘super-narrowing’’ is due to noise or artifacts related to the experimental apparatus.

Although such spectrally narrow features have never been reported so far, their observation does not contradict previous reports of SE in various polymer films. We emphasize here the importance of the excitation geometry in SE measurements. First, the most commonly used experimental setup employs a round excitation area of 0.5–1 mm in diameter.[1–5] Using such an excitation geometry, we did not observe any pronounced super-narrowing. Therefore, we conclude that the effect requires a stripelike excitation. Second, the exact dimensions of the excitation stripe are also important, as illustrated in Fig. 2(a), which shows three spectra collected from the same DOO-PPV film at approximately equal I for different values of a. It is clear that the fine spectral structure observed at small a gradually washes out at larger a. This may be attributed to the spectral overlap of numerous narrow peaks originating from different parts of the film’s excited area. Then a smooth band appears due to area averaging at large a and in fact becomes similar to the SE bands in previous studies that employed round excitation areas.[2–8]

We may suggest a number of mechanisms, which can conceivably lead to the super-narrowing of the SE band into a finely structured spectrum. (I) First, the ‘‘spiky’’ SE spectra may be the result of spectral variations in the effective optical gain, $\gamma_{\mathrm{eff}} = \gamma - \alpha$, where γ and α are the optical gain and loss coefficients, respectively. Such variations can be due to either inhomogeneous broadening (Ia), e.g., caused by a chain length distribution in the π-conjugated polymer films, or homogeneous broadening (Ib) originating from strong electron-phonon coupling known to exist in polymers. Narrow bands in the subgap absorption spectrum associated with defects (Ic) can also lead to similar variations in γ_{eff} through variations in α. (II) Second, waveguide formation in the film[2,6] may directly modulate the optical gain spectrum, possibly leading to mode selection. (III) Third, structural cavitylike resonances in the gain medium may significantly affect the SE spectrum and produce laser-like lines. Such resonances could, for example, be due to reflections from the film’s facets (IIIa), which requires good quality film edges; these, however cannot be formed by spin coating and evaporation. Alternatively, for cases with no obvious optical cavities the laser-like modes may arise from multiple, loop-like scattering (IIIb), in accordance with the scenario originally proposed for photonic paints.[17–22] Even in pristine polymer films there might be substantial scattering due to impurities and fluctuations in the film’s density and thickness, which may produce weak backscattering resonances that consequently can lead to ‘‘random lasing.’’ In order to verify these different explanations of the spiky SE spectrum, we performed further measurements as follows.

Figure 2(b) shows the emission intensity, I_{se}, dependence on I for a second DOO-PPV film. Here I_{se} was measured at three wavelengths corresponding to the spectral positions of two different peaks and one dip, respectively, as indicated

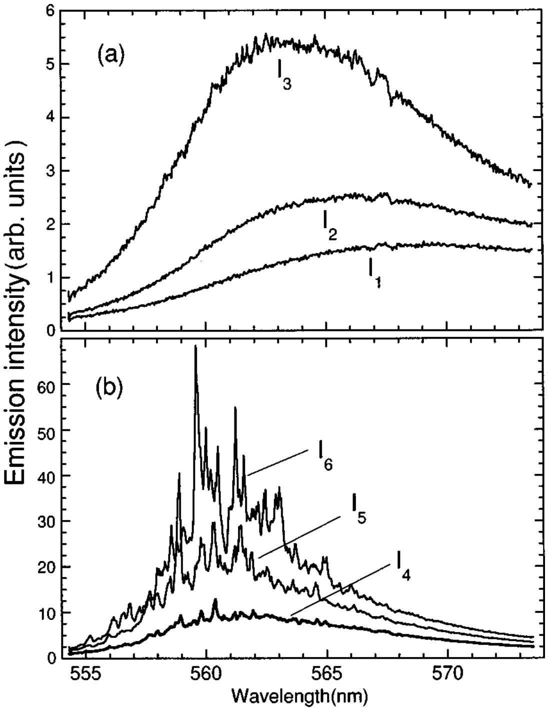

FIG. 3. Stimulated emission spectra of a Rhodamine 6G doped gel-film mixed with SiO_2 balls at different I ($L=3$ mm, $a=30$ μm): (a) ASE regime, where $I_1=1$ MW/cm^2, $I_2=1.5$ MW/cm^2, and $I_3=2$ MW/cm^2; (b) "lasing" regime, where $I_4=2.5$ MW/cm^2, $I_5=3.5$ MW/cm^2, and $I_6=4$ MW/cm^2.

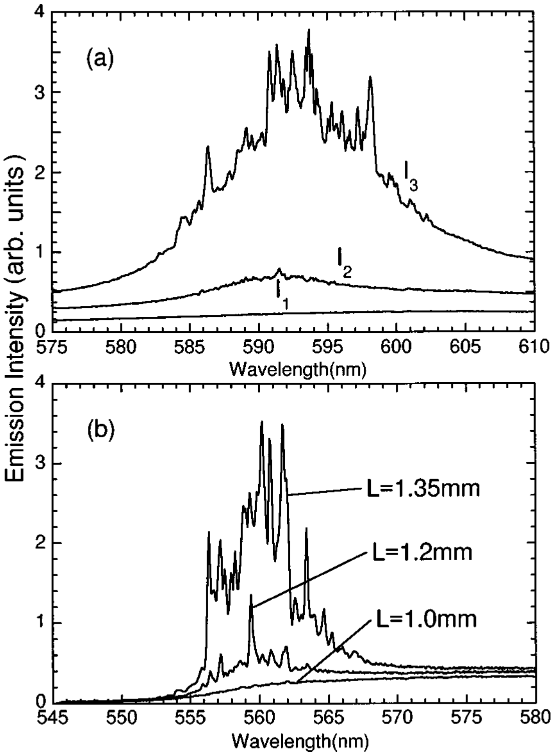

FIG. 4. (a) SE spectra of a microcrystalline opal slab saturated with DOO-PPV solution, where $L=3$ mm, $a=30$ μm, $I_1=0.6$ MW/cm^2, $I_2=1$ MW/cm^2, and $I_3=2$ MW/cm^2. (b) SE spectra of an opal saturated with R6G solution at various L and constant $a=40$ μm and $I=1.5$ MW/cm^2.

by the arrows in Fig. 2(b) inset. The intensity dependence $I_{se}(I)$ can be divided into two regions: region **A** with $I_{se} \propto \exp\{\sigma(I-I_A)\}$, where σ is a constant, and region **B** with $I_{se} \propto (I-I_B)$. Region **A** may be associated with the ASE regime; region **B** corresponds to the gain saturation regime,[8] where the ASE model fails to explain the finely structured emission spectra. We found that within the experimental uncertainty ($\leqslant$5%) the optical gain, which can be associated with the slope of the curves in Fig. 2(b) at small I, is the same for all three wavelengths. Also, the onset of gain saturation occurs at the same $I(\sim I_B)$ independent of the wavelength. This shows that the gain is homogeneously broadened, ruling out the previously proposed (Ia) and (Ic) scenarios. The "mesoscopic" behavior of the finely structured SE, where different excited areas produce different fine structures, counts out (Ib) scenario, since phonon sidebands should be the same everywhere in the sample. We note that the linear I_{se} intensity dependence on I in region **B** is typical for lasing.[9–16] Accordingly, we may associate the multiple spectral peaks in region **B** with laser-like emission lines.

Super-narrowing of SE was not only observed in polymers, but also in a number of other materials, which indicated that it may be a widespread phenomenon. We prepared gel films containing R6G as an active gain medium: 10^{-3} M R6G solution was thoroughly mixed with 2×10^{10} cm^{-3} SiO_2 balls and added to gelatin in a 1:1 volume proportion. After spilling the liquid onto a clean glass substrate and cooling, we obtained $\sim$30 μm thick semitransparent films saturated with R6G. Figure 3(a) shows the emission spectra measured at $I\sim I_B$ with the same experimental setup used before for the DOO-PPV films. The onset of SE ($I\approx I_A$) is now characterized by a smooth band peaking at $\sim$565 nm; at higher I this band was overridden by the narrow laser-like emission lines [Fig. 3(b)]. In addition, $I_{se}(I)$ of the R6G gel films was similar to those given in Fig. 2(b).

Super-narrowing was also observed in liquid solutions of both DOO-PPV and R6G infiltrated into opals. Similar effects were found using several other laser dyes, such as Rhodamine 560, Kiton Red, and Sulforhodamine 640, Porous polycrystalline opals were soaked in saturated chloroform solution of DOO-PPV and ethylene glycol solution (10^{-3} M) of R6G, respectively. Microcrystalline opals with crystallite sizes of 20–100 μm were prepared from crystallizing colloidal suspensions of nearly monodisperse SiO_2 spheres with diameters d varying between 190 nm and 300 nm, as described elsewhere.[23] A typical opal slab size was 1 mm$\times$1 cm$\times$1 cm. After the complete penetration of the solution, the opals became semitransparent due to close matching between the refractive indices of solvents and silica ($\Delta n\approx0.01$). As a result, light scattering from the silica nanoballs was relatively weak: from transmission measurements in the spectral range between 550 and 650 nm for opals infiltrated with ethylene glycol we estimated the mean photon diffusion length, $l^*\geqslant0.5$ mm. We found that Bragg scattering, which is known to exist in opals,[23] did not influence the SE spectra; in fact, the fine structures were not sensitive to the diameter of the opal's nanoballs.

The opal slabs soaked in solutions containing gain media (either R6G or DOO-PPV) were placed inside a 1 cm$\times$1 cm quartz cuvette and photoexcited using the previously described experimental setup. The stripelike excitation at intensities above the SE threshold resulted in the emission from the side of the slab of a ~5° divergent beam directed along the stripe axis. The corresponding emission spectra are shown in Fig. 4 for both DOO-PPV and R6G. Again, the onset of SE at $I_2 \approx I_A$, as shown in Fig. 4(a) for DOO-PPV solution, was followed by the development of a series of narrow spectral lines at higher $I (I_3 \approx I_B)$. The R6G solution infiltrated into the opal crystals exhibited a similar effect, but in a slightly different spectral range corresponding to the maximum optical gain of R6G, as shown in Fig. 4(b). In this case, however, instead of increasing I at constant L, we achieve super-narrowing by increasing L while keeping I constant. Analogous measurements were done with DOO-PPV films and solutions; these experiments showed that the magnitudes of both I_A and I_B decrease as L increases. Such a behavior has been observed before in ASE processes[8] and distributed feedback (DFB) lasers.[24] We note that in these latter experiments we used bulky opal slabs, where there was no waveguide formation; we therefore can eliminate scenario (II) from the list of possible origins for the super-narrowing phenomenon. We also note that in identical experimental conditions, SE from free-standing pure solutions of either DOO-PPV or R6G *did not* produce similar super-narrowing; this demonstrates the super-narrowing is indeed due to light scattering inside the opals.

According to scenario (III), laser action should require a resonant optical feedback mechanism, e.g., reflections from the sample edges. However, such reflections do not exist in neither the polymer films nor the opal slabs. Furthermore, the extreme sensitivity of the finely structured spectra to the exact position of the excitation area on the sample [Fig. 1(b)] indicates that the structural resonances must come from inside of the excited region. In this case the spectral super-narrowing is due to random feedback produced by light scattering in the bulk. However, whereas scattering centers can be easily identified in opals and gel-films as silica nanoballs, it is not clear at present what could play such a role in pristine DOO-PPV films. Also, scenario (IIIb) contradicts the theoretical predictions that random lasing can occur only in strongly scattering media where $l^* \sim \lambda$,[25,26] whereas in our case we estimated that for the opals $l^* > 0.5$ mm.

In conclusion, we found an unusual regime of stimulated emission in various scattering media containing π-conjugated polymers and organic laser dyes characterized by high optical gain. We could clearly identify and separate the regime from the more regular ASE. The emission spectrum in this regime contains a fine spectral structure having features as narrow as 1 Å, the intensity of which grows linearly with the excitation intensity. We investigated various possible causes of this phenomenon and tentatively attributed it to random optical feedback caused by light scattering inside the gain region. However, new experimental and theoretical studies are needed to fully explain such an unusual behavior of stimulated emission.

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