

## Amplified resonant Raman scattering in conducting polymer thin films

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Using picosecond pulsed laser excitation, we investigate the optical emission characteristics of poly(2,5-dioctyloxy-*p*-phenylenevinylene), (DOO-PPV), thin films at high excitation intensities ( $\sim 1\text{--}90\text{ MW/cm}^2$ ). We observe the presence of amplified resonance Raman scattering in the emission spectra of conducting polymer films. The effect results in sharp Raman lines (widths smaller than  $3\text{ \AA}$ ) superimposed on a significantly broader, well known, spectrally narrowed emission band (width  $\sim 10\text{ nm}$ ) caused by the amplified spontaneous emission in the waveguided polymer film. At the highest used excitation intensities, Raman scattering dominates the DOO-PPV emission spectrum resulting in a highly monochromatic, single-line emission spectrum. © 1998 American Institute of Physics. [S0003-6951(98)02646-1]

There is currently wide interest in the optical emission behavior of electroluminescent  $\pi$ -conjugated polymer thin films. The recent achievement of spectrally narrowed emission (SNE) under high intensity pulsed laser excitation<sup>1–12</sup> demonstrated that high optical gain can occur in thin films of these materials. This raises the prospects of eventually using polymers as novel active media in organic injection laser structures. Fast progress has been made in this direction by several groups, engineering low-threshold, optically pumped microcavity lasers<sup>1,13–16</sup> and generating increasingly high excitation densities via current injection.<sup>17,18</sup> In order to further explore the basic physics phenomena occurring in luminescent  $\pi$ -conjugated polymers, we investigated in this work their nonlinear emission behavior under high intensity picosecond pulsed laser excitation. In addition to the “normal” SNE, we find at higher intensities novel spectral features which we attribute to Raman scattering amplification. This effect correlates with previous observations by several groups, who detected transient Raman gain in femtosecond pump-probe experiments in various  $\pi$ -conjugated polymer films (see, e.g., Ref. 19).

For our measurements we used thin films of poly(2,5-dioctyloxy-*p*-phenylenevinylene) (DOO-PPV) [chemical structure given in the inset of Fig. 1(a)], produced by spin-coating 5 mg/ml polymer solutions onto glass substrates. The typically 200–600 nm thick films were excited with  $\sim 100\text{ ps}$  laser pulses at three different wavelengths, 532, 559, and 563.5 nm, respectively, in the long-wavelength tail of the fundamental  $\pi$ - $\pi^*$  absorption band. The pulse excitation energies were varied from 0.1 to  $90\text{ }\mu\text{J}$ , and the illuminated sample spot area was about  $1\text{ mm}^2$ . The emission spectra were measured with a 0.6 m spectrometer (SPEX Triplemate), employing 300, 600, and 1200 grooves/mm gratings and a cooled charge coupled device (CCD) array. To avoid photooxidation, the films were mounted into a cryostat and kept under vacuum; the temperature could be varied between 80 and 300 K.

At low excitation levels, DOO-PPV films exhibit the well known partly inhomogeneous, partly phonon-

broadened, excitonic spontaneous emission in the form of a photoluminescence (PL) band, shown in Fig. 1(a). The PL band peaks at 585 nm, with a 1 phonon resolved side band at  $\sim 625\text{ nm}$  (having only slightly reduced intensity compared

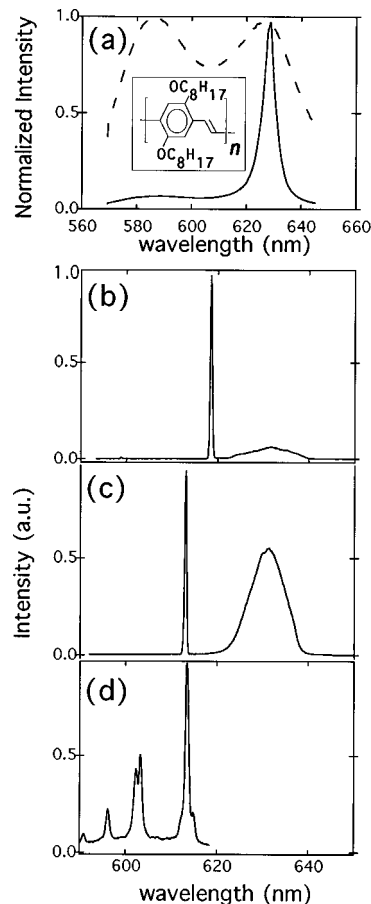


FIG. 1. (a) Emission spectra of DOO-PPV films at 300 K, obtained with 532 nm, 100 ps pulsed excitation at pulse energies below (dashed curve) and above (solid curve) the excitation intensity onset of spectral narrowing (occurring at  $\sim 0.15\text{ }\mu\text{J/pulse}$ ). The chemical structure of DOO-PPV is shown in the inset; (b) and (c) DOO-PPV emission spectra at high excitation pulse energies (90 and  $12\text{ }\mu\text{J}$  for excitation at 563.5 and 559 nm, respectively); (d) first-order, off-resonance, spontaneous Raman spectrum, measured with continuous-wave, low-power 752 nm laser excitation and plotted vs wavelength for a hypothetical 559 nm excitation. Spectral overlap exists between the longest-wavelength Raman mode and sharp spectral feature in (c).

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to the peak) and total width of  $\sim 70$  nm. At excitation energies higher than about  $0.3 \mu\text{J}$ , the total spectral width of the PL band collapses by about an order of magnitude to about 10 nm. As reported earlier, this spectral narrowing is accompanied by drastic shortening of the radiative lifetime.<sup>5</sup> The physical origin of the SNE is still under contest, being attributed to amplified spontaneous emission,<sup>2,10,13</sup> cooperative emission or superfluorescence,<sup>4,5,7</sup> and mirrorless lasing.<sup>3</sup> In the following we will refer to this emission simply as SNE.

At excitation pulse energies above the threshold for SNE, we observe in addition to SNE new, sharp, spectral features in the vicinity of the SNE band, as shown in Figs. 1(b) and 1(c), for the film emission at 300 K and at two different excitation wavelengths, 563.5 and 559 nm, respectively, which both excite the long-wavelength tail of the polymer absorption band. In both cases, the SNE band is centered at  $\sim 630$  nm and remains unshifted. However, a very intense, single, sharp emission line appears in both cases on the high energy side of the SNE band. We determined the width of this sharp line to be less than  $3 \text{ \AA}$ . The position of the line shifts by  $4.5 \text{ nm}$  ( $143 \text{ cm}^{-1}$ ) when changing the excitation wavelength from 559 to 563.5 nm, thus corresponding exactly to the frequency difference of the excitation light. This fact clearly supports the presence of a Raman scattering gain in our DOO-PPV films.

To identify the active Raman modes in the optical gain of the film, we measured the off-resonance, spontaneous Raman scattering response at low intensities, using  $90^\circ$  scattering geometry, and unpolarized detection. To avoid background luminescence, we used long-wavelength excitation at 752 nm. The resulting Raman scattering spectrum revealed strong Raman scattering lines at 968, 1117, 1285, 1313, and  $1584 \text{ cm}^{-1}$ , respectively. The strongest Raman line occurs at  $1584 \text{ cm}^{-1}$ , and therefore is the most likely candidate to participate in Raman scattering gain processes at high excitation intensities. According to Sakamoto *et al.*,<sup>20</sup> who measured the Raman spectra of unsubstituted PPV, this line can be assigned to a polymer ring mode; in particular the  $\nu_{8a}$  mode of benzene in the Wilson notation. To compare the spectral positions of the Raman scattering lines with the sharp emission feature in Fig. 1(c), we plotted in Fig. 1(d) the low-intensity Raman response versus wavelength for a hypothetical excitation at 559 nm. Apparently, we obtain excellent spectral overlap for the  $1584 \text{ cm}^{-1}$  benzene ring mode.

Furthermore, exciting the polymer films with high pulse energies at 532 nm, we obtain at 80 K the emission spectrum shown in Fig. 2(a). In this case two sharp spectral features appear simultaneously on the low- and high-wavelength shoulders of the SNE band, at 629 and 640 nm, respectively. The frequency shift between the pump laser and sharp spectral features is on the order of about  $3000 \text{ cm}^{-1}$ . This frequency shift is too large for any known first-order spontaneous Raman scattering mode in DOO-PPV. However, we obtain again good spectral overlap of the observed sharp spectral features and the Raman scattering modes if we consider higher-order Raman scattering. Apparently, the sharp emission feature at 640 nm overlaps with the second order of the  $1584 \text{ cm}^{-1}$  Raman mode, and the 629 nm peak overlaps

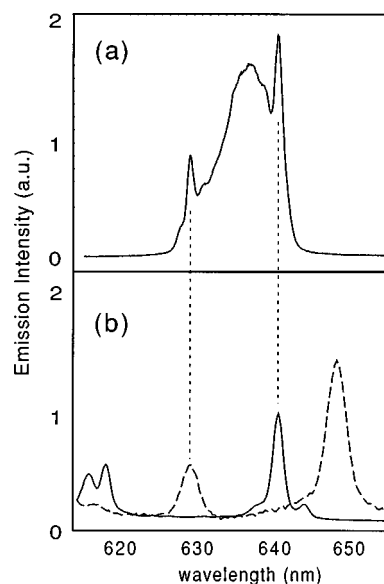


FIG. 2. (a) DOO-PPV emission spectrum obtained at 80 K with 532 nm laser at high excitation energy ( $7 \mu\text{J}$  pulse); (b) Raman spectra in the region of 1285, 1313, and  $1584 \text{ cm}^{-1}$  modes, shown in second order (solid curve), and Raman spectra in the region of 968 and  $1117 \text{ cm}^{-1}$  modes, shown in third order (dashed curve).

with the third order of the  $968 \text{ cm}^{-1}$  mode. This indicates that strong Raman scattering is observed whenever the following two conditions are simultaneously fulfilled: (i) the excitation wavelength overlaps the low-energy tail of the polymer fundamental absorption band, and (ii) a spectral coincidence is realized between the Raman scattering mode, either in fundamental or higher order, and the spectral emission region of maximum optical gain, i.e., the spectral vicinity of the SNE band. The first condition leads to resonance Raman scattering, and the second condition is likely to cause amplification of the Raman shifted photons by population inversion existing between the excitonic first excited state and ground state.

A notable feature of the DOO-PPV emission under high excitation intensity is the relative scaling of the SNE band and Raman gain peaks with increasing intensities, as illustrated in Fig. 3 for excitation at 563.5 nm. In this case the threshold excitation intensity for the Raman peak is about one order of magnitude higher than the intensity needed to obtain SNE, occurring at 8 and  $0.5 \mu\text{J}$ , respectively. The Raman amplification, however, reveals a higher slope effi-

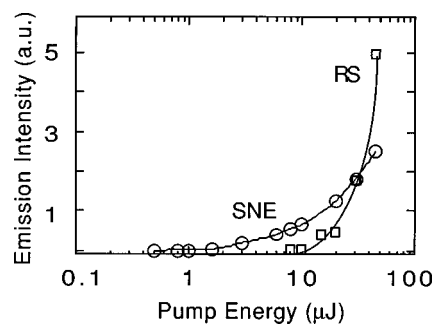


FIG. 3. Emission intensity of DOO-PPV film vs excitation intensity, showing relative strength of SNE band and amplified  $1584 \text{ cm}^{-1}$  Raman scattering mode for 563.5 nm excitation. At highest used excitation intensities, the amplified Raman scattering gain dominates the emission spectrum.

ciency compared to SNE. At the highest used excitation intensities it is therefore possible to generate an emission behavior where Raman scattering is dominant. In this case, highly monochromatic narrow-line laser-like emission is realized in the polymer films, in addition to a residual smaller and much broader emission background due to the usual spectral narrowing.

In conclusion, we have investigated DOO-PPV film emission spectra at high excitation intensities ( $1\text{--}90\text{ MW/cm}^2$ ) and discovered narrow ( $\sim 3\text{ \AA}$ ) laser-like emission lines superimposed on a relatively broad SNE band of  $\sim 10\text{ nm}$  width. As evidenced by the following observed properties, the line spectra suggest the presence of amplified resonant Raman scattering:

- (i) the spectral positions of the emission lines change with the shift of excitation wavelength;
- (ii) the output intensity varies superlinearly with the pump intensity over a large intensity range;
- (iii) the effect shows an excitation intensity threshold;
- (iv) the Raman lines are observable not only in first order but also in higher orders.

Finally, we would like to note that the narrow resonant amplified Raman emission lines may be used as mirrorless laser-like emission in conducting polymer thin films, without the need of a complicated optical resonator.

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