

Energy dependence of electronic energy relaxation in poly(*p*-phenylenevinylene)

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Femtosecond time-resolved photoluminescence spectroscopy is used to study the dynamics of optical emission from poly(*p*-phenylenevinylene) at 77 K over an energy range of 2.19–2.37 eV. All of the decay curves in this energy range can be described by the summation of two exponential functions. Analysis of the spectral dependence of the time constants extracted from these fits indicates that the transient photoluminescence at any given wavelength is due in general to the superposition of three transitions emanating from a single set of inhomogeneously broadened excitons. The three distinct transitions correspond to processes in which two, one, or zero phonons are excited in the host polymer during the emission event. By separating out these three contributions, it is determined that the effective lifetime of the inhomogeneously broadened excitons increases monotonically from 980 fs at 280 meV above the peak in the density of states (DOS), to 114 ps near the peak in the DOS. © 2001 American Institute of Physics.
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I. INTRODUCTION

Conjugated polymers such as poly(*p*-phenylenevinylene) (PPV) have been the subject of intense study in the last decade due to their semiconductor-like properties. Their visible band gaps, light emission efficiency, and ease of production make them attractive for use in electroluminescent devices. Recently, significant advances have been made in the design of light-emitting diodes based on organic polymers such as PPV.^{1,2} The emission wavelength of these polymers can be tuned by chemically modifying the backbone, and they are more compatible with flexible substrates than conventional semiconducting inorganics.

The ultimate utility of these materials in optoelectronic applications will depend on the dynamical behavior of their nonequilibrium electron-hole excitations. The quest to understand the nature of electronic excitations in these materials has fueled research from a fundamental standpoint. Much of the early work on PPV was devoted to resolving the issue of whether the photoexcitations are best described by a semiconductor band model or a molecular approach. In the semiconductor model,³ the polymer is viewed as an infinite one-dimensional (1D) chain with strong electron-phonon coupling, but Coulombic forces and electron-electron correlations are ignored. The excited species are delocalized singlet polaron excitons which decay either radiatively or nonradiatively. More recently, the evidence has pointed toward the molecular approach as being the more accurate one.⁴ Because of the significant disorder present in the PPV chains, there is a distribution of conjugation lengths and corresponding excitation energies. The excitations are Coulombically bound electron-hole pairs, and the broad line shapes seen in

the absorption and emission spectra are described in terms of an inhomogeneously broadened density of states (DOS).

Using this molecular picture, an exciton associated with a given conjugated segment of the polymer may (i) emit a photon (with a certain likelihood of simultaneously exciting a molecular vibration), (ii) scatter to a nonradiative state from which it can effectively never emit a photon, or (iii) scatter to a different conjugated segment of the polymer, where it still has the opportunity to emit a photon. The corresponding timescales depend on the conjugation length, and it is important to determine what this dependence is.

Time-resolved photoluminescence studies have proven effective for probing these dynamics in PPV and in other conjugated polymers. The radiative lifetime in PPV can be slightly over a nanosecond in carefully prepared and preserved samples. Nonradiative “trapping” rates vary considerably depending upon the synthetic method used and on any photochemistry which may have occurred within the irradiated sample. Although the analysis of quantum efficiencies is complicated by branching effects, it seems that the best nonradiative lifetimes are on the order of the radiative lifetime. We are unaware of any evidence that suggests that either the radiative or nonradiative decay rate varies substantially over energies within the DOS that contribute significantly to the total luminescence yield.

In contrast, Kersting *et al.*⁴ have convincingly demonstrated that the site-to-site transfer process between relatively short conjugated segments lying high in the DOS is nonexponential, and that its effective rate decreases as the energy approaches the peak of the DOS. They accomplished this by time resolving the luminescence emitted at energies high above those where there is an appreciable signal in the time-integrated luminescence spectrum of PPV, and comparing

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the results with detailed numerical simulations of the complicated scattering processes. They experienced difficulties in the analysis of data taken close to the high energy side of the peak in the DOS, which they attributed to the overlapping contribution of luminescence from two different parts of the DOS, separated by the first vibrational overtone observed in the time-integrated spectrum. They made no attempt to perform a detailed analysis of data taken at energies at or below the main peak in the time-integrated luminescence spectrum.

The work of Kersting *et al.*⁴ demonstrated that an elaborate model is required to accurately account for the detailed dynamics of scattering excitons. From the practical point of view of an optoelectronic device designer, it would be useful to have a simple phenomenological description of the approximate, effective scattering rate as a function of energy within the DOS. We have achieved this objective by analyzing the decay of time-resolved photoluminescence data at energies that span the two main peaks in the time-integrated luminescence spectrum from PPV. By interpreting the two exponential time constants extracted from each data set in terms of the overlapping contributions from zero-, one-, and two-phonon-assisted transitions from a single DOS, we show that the effective scattering time increases from 980 fs, 280 meV above the peak in the DOS, to 114 ps, near the peak in the DOS. The effective time constant varies exponentially with the excess energy above the peak in the DOS.

II. EXPERIMENT

The PPV precursor was synthesized following the procedure of Papadimitrakopoulos *et al.*⁵ PPV thin films were prepared by dissolving the precursor in 1:1 water:methanol, then transferring a small drop of the solution onto a quartz slide with a pipette, followed by heating to 190 °C under vacuum for 6 h.

The experiment was carried out at 77 K using a time-resolved photoluminescence technique.⁶ The 100 fs output pulse of a Ti:sapphire laser tuned to 1.55 eV was split at a 50–50 beamsplitter into a gate pulse and an excitation pulse. The gate pulse was delayed using a translation stage with a spatial resolution of 1 μm , and the excitation pulse was frequency doubled in a 1 mm thick BBO crystal and focused onto the sample in a reflection geometry with an average power limited to 1 mW to mitigate sample degradation. The PPV photoluminescence was collimated and recombined with the delayed gate pulse in a 0.5 mm thick crystal of LiIO_3 . The upconverted light was spectrally dispersed in a monochromator and detected with a photomultiplier tube.

III. RESULTS AND DISCUSSION

Figure 1 shows the 77 K photoluminescence (PL) spectrum as a function of energy. The highest peak at 2.33 eV results from the purely electronic transition, denoted $S_1 \rightarrow S_0/0 \rightarrow 0$, while the peak at 2.20 eV and the shoulder at 2.03 eV are attributed to the phonon-assisted $S_1 \rightarrow S_0/0 \rightarrow 1$ and $S_1 \rightarrow S_0/0 \rightarrow 2$ transitions, respectively. The central mean of the DOS, as determined by a Gaussian fit to the zero-phonon peak in the continuous wave (cw) spectrum, is at an energy of 2.33 eV and it has a width of $2\sigma=0.14$ eV.

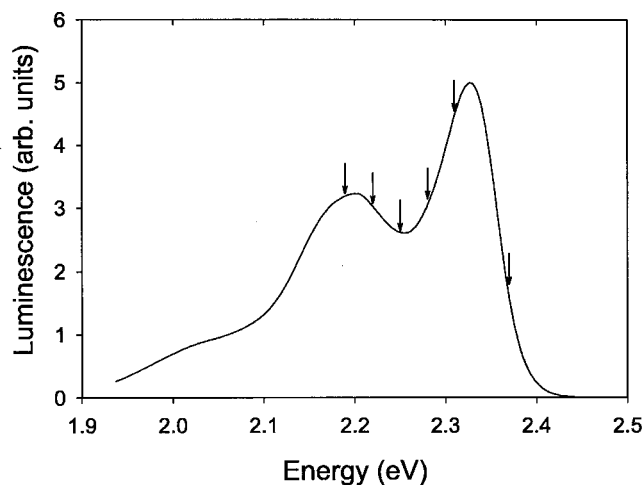


FIG. 1. Photoluminescence spectrum of a thin film of PPV at 77 K, where the arrows denote the spectral position of the time-resolved measurements (2.19, 2.22, 2.25, 2.28, 2.31, and 2.37 eV). The data are not corrected for the spectral response of the system.

The 77 K upconverted PPV luminescence is plotted in Fig. 2 for the six detection energies, 2.19, 2.22, 2.25, 2.28, 2.31, and 2.37 eV. From the data we can see evidence of two distinct regimes: a fast decay, which occurs within 20 ps, followed by a slower tail which extends to several hundred picoseconds.

The data that decrease monotonically with delay were fit to a biexponential of the form

$$I = I_0 + w_1 e^{-t/t_1} + w_2 e^{-t/t_2}, \quad (1)$$

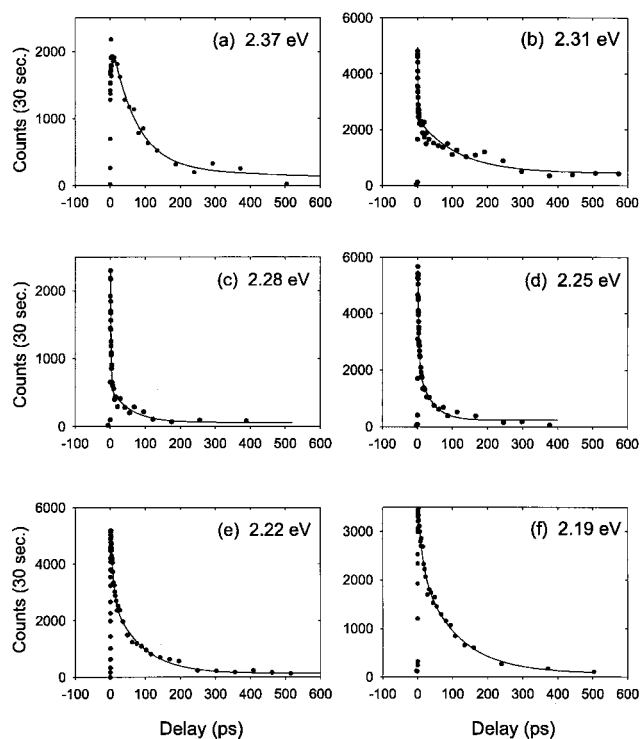


FIG. 2. Long timescale regime of upconverted PPV luminescence at 77 K. The solid lines represent biexponential fits.

TABLE I. Short and long time constants extracted from the fits to the luminescence transients of Fig. 2. The data at all energies were fit to biexponential functions except the 2.37 eV data, which were fit to a single exponential. All times are in units of picoseconds.

Energy (eV)	t_1	t_2
2.19	14 ± 3	110 ± 21
2.22	7.1 ± 0.9	85 ± 9
2.25	3.1 ± 0.2	38 ± 7
2.28	1.9 ± 0.1	49 ± 14
2.31	0.98 ± 0.1	114 ± 18
2.37	...	77 ± 7

where I_0 is a constant background, t_1 and t_2 represent the short and long time constants, respectively, and w_1 and w_2 are the respective weighting factors. The offset I_0 effectively accounts for the contribution from PL on nanosecond timescales, as has been observed by many authors.^{4,7,8} The highest energy data set (2.37 eV) is fit to a single exponential function, because the short time constant at this energy is less than the time resolution of the system. The fits are shown superimposed on the data in Fig. 2, and they reproduce the data effectively.

The two time constants extracted from the fits are summarized in Table I. As is clear from inspection of the decay curves in Fig. 2, the fast time constant, t_1 , monotonically becomes faster with increasing detection energy until, for the highest energy data (2.37 eV), it is not observable within the time resolution of our system. The long time constant exhibits a more complicated, nonmonotonic dependence on the detection energy. It is longest at the luminescence maxima, and assumes its shortest value (38 ps) at 2.25 eV, in the valley between the zero- and one-phonon transitions.

As mentioned above, Kersting *et al.*⁴ analyzed the data they obtained on the high energy shoulder of the no-phonon luminescence peak in terms of overlapping contributions from direct and one-phonon-assisted transitions originating from different portions of the DOS. If we adopt a similar interpretation of our data, the short, monotonically decreasing time constants (the t_1 's in Table I) correspond to luminescence from conjugated segments lying high out in the DOS, shifted downward in energy by an amount equal to the two-phonon overtone. To the extent that it is possible to compare our time constants with a forced exponential fit to Kersting *et al.*'s (nonexponential) data, this assignment is consistent with their work. This strongly suggests that the longer time constants that do not vary monotonically with the detection energy (the t_2 's in Table I) are likely associated with one-phonon and zero-phonon assisted emission processes.

To test this hypothesis, in Fig. 3 we use different symbols to label the various time constants from Table I, as a function of the detection energy. (The second time constant at the highest detection energy was omitted because it is less than our temporal resolution of ~ 300 fs; if it had been included, it would be consistent with the set of data labeled with open circles.) The dashed lines in Fig. 3 represent the best fit to the data shown as open circles, shifted by zero-,

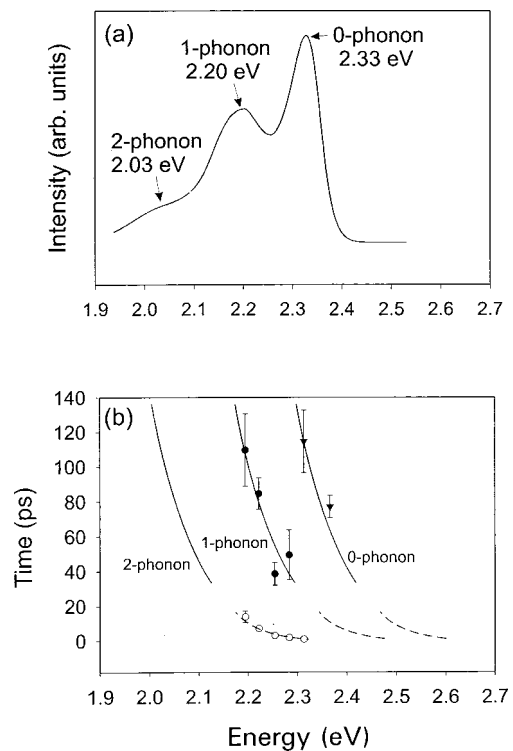


FIG. 3. Time constants extracted from the 77 K luminescence transients. The open circles represent the fast time constant data, and the closed symbols the slow time constant data. The lines in (b) were added by hand and translated by the zero-one and one-two phonon separations measured from the cw spectrum in (a). All of the decay constants therefore fit onto a single line when shifted by the appropriate phonon energies.

one-, and two-phonon energies. The solid lines in Fig. 3 represent the best fit to the data shown in solid circles, again shifted by zero-, one-, and two-phonon energies.

Looking at the data plotted in Fig. 3, we propose that only the triangular data actually represent the time constant associated with emission from excitons having an energy equal to the detection energy. The closed circles actually sample the same set of excitons, but at lower detection energies, via a one-phonon-assisted emission process. As postulated above, the open circles reflect the dynamics of excitons at much higher energies, in the tail of the DOS where there is no significant luminescence evident in the time-integrated spectrum.

With this interpretation of our data, it is possible to deduce the effective scattering rate of excitons at energies ranging from -7 to $\sim +280$ meV with respect to the peak in the DOS, as shown in Fig. 4. The open and closed circles correspond to the fast and slow (2.19–2.3 eV) time constant data from Fig. 3. The slow time constant data points at 2.31 and 2.37 eV are shown as triangles, and are consistent with this assignment. Although the time constants in Fig. 4 have been obtained by forcing an exponential fit to what is almost certainly a nonexponential process, this result serves the purpose of providing a ‘‘rule of thumb’’ guide for the way in which the effective net scattering rate of highly nonequilibrium excitons depends on their excess energy. Note that the effective time constant increases roughly exponentially with decreasing excess energy, then saturates at ~ 114 ps at an

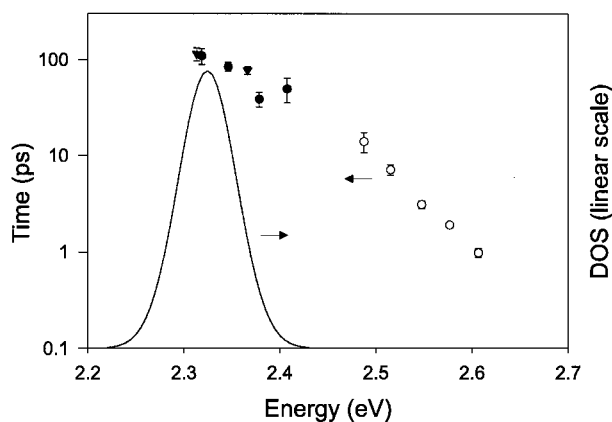


FIG. 4. Inhomogeneously broadened exciton DOS determined from a Gaussian fit to the zero-phonon peak of the PL data (right axis) shown with the decay time determined from fits to the luminescence transients (left axis).

excess energy where the excitons accumulate and begin to contribute to the integrated luminescence spectrum (see Fig. 1). The 114 ps time constant appears to reflect the nonradiative decay time for excitons near the peak of the DOS. It is relatively short, likely because of some photochemical degradation induced by the 1 mW UV excitation beam, despite the fact that the sample was kept in a nitrogen environment.

IV. CONCLUSION

Time-resolved photoluminescence decay curves obtained from PPV at energies spanning the zero- and one-

phonon time-integrated luminescence peaks were analyzed in terms of overlapping contributions from zero-, one-, and two-phonon transitions from a single inhomogeneously broadened exciton DOS. At 77 K we deduce that the effective scattering time of high-energy excitons increases approximately exponentially from ~ 980 fs at 280 meV above the peak in the DOS, to 114 ps near the peak in the DOS. These results should be of interest to those involved in modeling and designing light emitting devices based on PPV.

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- ¹P. K. Ho, J. Kim, J. H. Burroughes, H. Becker, S. F. Li, T. M. Brown, F. Cacialli, and R. H. Friend, *Nature (London)* **404**, 481 (2000).
- ²H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.-Y. Lin, and A. Dodabalapur, *Nature (London)* **404**, 478 (2000).
- ³A. J. Heeger, S. Kivelson, R. J. Schrieffer, and W. P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).
- ⁴R. Kersting, B. Mollay, M. Rusch, J. Wenisch, G. Leising, and H. F. Kauffmann, *J. Chem. Phys.* **106**, 2850 (1997).
- ⁵F. Papadimitrakopoulos, K. Konstadinidis, T. M. Miller, R. Opila, E. A. Chandross, and M. E. Galvin, *Chem. Mater.* **6**, 1563 (1994).
- ⁶J. Shah, *IEEE J. Quantum Electron.* **24**, 276 (1988).
- ⁷I. D. W. Samuel, B. Crystall, G. Rumbles, P. L. Burn, A. B. Holmes, and R. H. Friend, *Synth. Met.* **54**, 281 (1993).
- ⁸M. Yan, L. J. Rothberg, F. Papadimitrakopoulos, M. E. Galvin, and T. M. Miller, *Phys. Rev. Lett.* **73**, 744 (1994).