Femtosecond Energy Relaxation in π-Conjugated Polymers

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Ultrafast relaxation processes in poly(p-phenylenevinylene) and its oligomers are investigated using femtosecond luminescence spectroscopy. A quasi-instantaneous luminescence rise and the absence of luminescence near the excitation energy indicate very rapid vibronic relaxation. The subsequent transient redshift of the spectra is attributed to ultrafast energy relaxation of optical excitations within an inhomogeneously broadened density of states.

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The fundamental interest in the dynamics of optical excitations in conjugated polymers combined with their growing technological importance has increasingly stimulated efforts to understand the static and in particular the dynamic electronic properties of this class of solids [1,2]. In spite of many investigations addressing the linear and nonlinear optical properties, the basic models are still heavily debated. One-dimensional semiconductor models based on the work by Su, Schrieffer, and Heeger [3] have been applied for the interpretation of optical experiments on conjugated polymers [4]. They ignore Coulombic (exciton) effects and invoke strong electron-phonon coupling leading to rapid self-localization of charged excitations. However, the characterization of the polymer backbone as an infinite one-dimensional system is questionable for conjugated polymers forming amorphous films. The neglect of Coulombic effects is even more problematic in systems with low dielectric constant as recent theoretical work indicated [5,6]. Examples of such polymers are poly(p-phenylenevinylene) (PPV) and its soluble derivative poly(p-phenyl-phenylenevinylene) (PPPV) which exhibit a high photoluminescence and electroluminescence quantum yield rendering them attractive for optoelectronic applications [7,8]. The photoluminescence (PL) of these materials is characterized by broad emission bands significantly redshifted with respect to the absorption. The PL has been attributed to radiative recombination of oppositely charged polarons formed after photoexcitation of an electron from the π-type valence band into the conduction band [9]. However, the comparison of the optical properties of the polymer with oligomers of different chain length and site selective fluorescence spectroscopy has supported an alternative interpretation [10,11]. Disordered polymers should rather be considered as arrays of chromophores originating from subunits of the polymer chain separated by topological faults. The broad absorption spectra are then explained in terms of inhomogeneity effects arising from variations of length and environment of the conjugated segments, with the elementary excitations being Coulombically bound electron-hole pairs [5,6]. In this concept, the redshift between the absorption and the luminescence spectra is explained by energy relaxation of the optical excitations in the inhomogenously broadened density of states distribution (DOS). Strong coupling of the electronic transitions to the molecular vibrations gives rise to sidebands in the optical spectra.

Time-resolved optical studies like transient absorption spectroscopy have already provided some information on the initial relaxation processes [12,13]. However, the signals obtained in transient absorption measurements are a superposition of several nonlinear optical processes. For instance, the interplay of bleaching and excited state absorption leads to complicated features in the pump-probe measurements. An alternative approach to the initial relaxation of photoexcitations is the temporal evolution of luminescence, which opens a more direct access to the ultrafast relaxation processes.

In this Letter, we report on femtosecond time-resolved luminescence experiments to study the initial relaxation processes in π-conjugated polymers. Our work is focused on the subpicosecond luminescence of PPV and related oligomers. Analogous results are obtained with phenyl-substituted PPPV and with polymer blends. We demonstrate that the vibronic relaxation occurs on a time scale of less than 100 fs. In the polymer, additionally a transient redshift of the photoluminescence spectrum is observed due to electronic energy relaxation of the optical excitations. It is absent in the oligomer spectra. The luminescence decay yields time constants ranging from less than 1 ps for higher-energy transitions to more than 100 ps at lower energy. Both observations are incompatible with polaron formation since this process is expected to occur on a subpicosecond time scale independent of spectral position [14]. All data can be quantitatively understood by ultrafast energy relaxation via an incoherent random walk within the DOS.

Experiments are performed at 295 K on a set of solution cast films of PPV prepared via the sulphonium polyelectrolyte precursor route [9] and microcrystalline samples of oligomers of phenylenevinylene (OPVs) prepared via Wittig condensation. The average chain length of the polymer is about 50 000 repeat units whereas the effective conjugation length is estimated to be about 10 repeat units [11]. The picosecond luminescence response

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has been studied previously [15,16]. An overall luminescence lifetime in the order of 100 ps was obtained. To distinguish between electronic and vibronic relaxation processes, we compare the transient luminescence of the polymer with oligomer model compounds consisting of three (OPV3) and four (OPV4) repeat units. The spectral shapes of the time-integrated luminescence spectra of these oligomers are similar to those of PPV. However, the maxima are slightly blueshifted due to the smaller conjugation length in the oligomers. The vibrations responsible for the vibronic progressions in the optical spectra are the same in the oligomers and the polymer. Therefore, differences in the relaxation behavior have to be attributed to electronic processes. Additionally, the well-defined conjugation length of the oligomers results in smaller inhomogeneous broadening of the spectra.

We apply femtosecond luminescence up-conversion spectroscopy as an experimental technique [17]. The laser source is a Kerr lens mode-locked Ti-sapphire laser producing 150 fs pulses at 1.56 eV and a repetition rate of 76 MHz. The samples are excited by frequency-doubled laser pulses at 3.12 eV. The excitation power is reduced to 0.8 mW on a spot size diameter of about 100 μm to avoid nonlinear annihilation processes and sample degradation. The luminescence emitted from the sample is focused dispersion-free with a mirror optic onto an optical nonlinear crystal of beta-barium borate (BBO). Sum frequency light is generated if the luminescence and the reference pulse (1.56 eV) temporally overlap within the crystal. This signal is dispersed by a monochromator and detected by a single photon counting system. The temporal evolution of the luminescence is mapped by delaying the reference pulse with respect to the pulse exciting the sample. The time resolution is limited by the pulse width of the laser and group velocity dispersion within the BBO between luminescence and the reference pulse. For the spectral range investigated in the present measurements, the time resolution of the setup is between 160 fs at 1.8 eV and 300 fs at 2.8 eV. The energy resolution of the system is limited by the spectral width of the laser pulses of about 15 meV and the resolution of the monochromator of about 20 meV. All experiments presented in this work are performed at room temperature.

Time-resolved luminescence spectra of PPV recorded at very early time delays are presented in Fig. 1(a). Even during the excitation pulse, broad luminescence extending down to energies lower than 2 eV is observed. Within 2 ps the spectrum evolves into a shape very similar to the cw spectrum, which is depicted in the inset. The purely electronic transition at 2.4 eV is followed by vibronic progressions at lower energies. The optical excitations are generated in the vibronic progressions of the $S_1 \leftarrow S_0$ transitions with an excess energy of about 600 meV as compared to the absorption edge. Even during excitation, no significant luminescence is observed from these initially excited states energetically above the purely electronic transition. The luminescence of the electronic transition with the vibronic progressions at lower energies rises quasi-instantaneous with the exciting laser pulse. Thus the vibronic relaxation occurs on a time scale much shorter than our time resolution. We explain this ultrafast vibrational relaxation by the large vibrational mode density in polymers. This leads to an ultrafast vibrational redistribution faster than the subpicosecond vibrational relaxation observed in smaller organic molecules [18,19]. The time-resolved luminescence spectra of the oligomer are shown in Fig. 1(b) for comparison. Again a rapid evolution into a spectrum similar to the steady-state luminescence is observed.

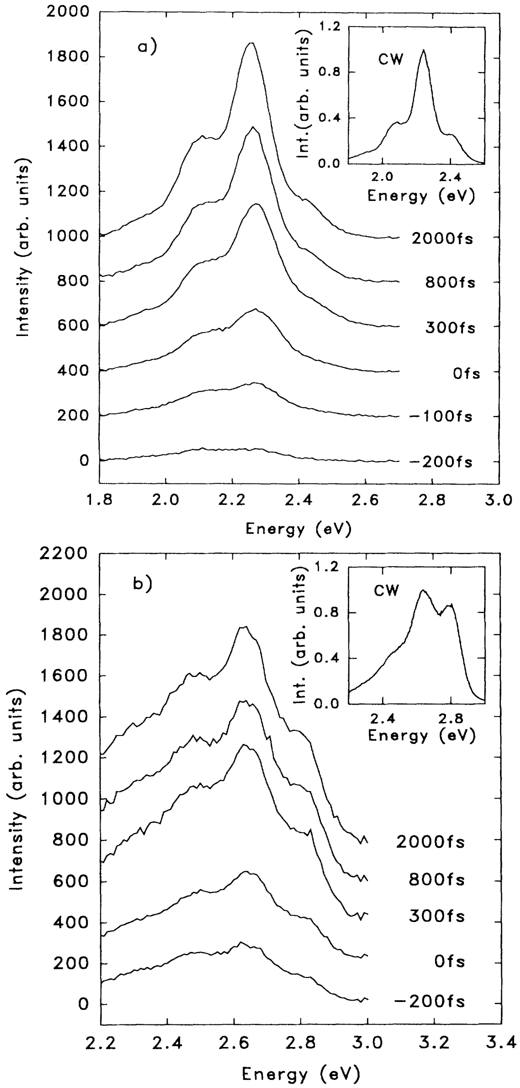

FIG. 1. (a) Time-resolved luminescence spectra of PPV after excitation with 150 fs laser pulses at 3.12 eV. (b) Time-resolved luminescence spectra of OPV3 for the same excitation. The slight differences between time-resolved and cw spectra result from the response functions of the setup.

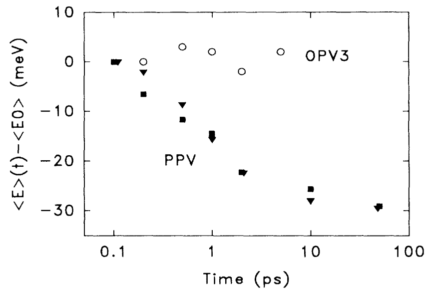

FIG. 2. Energetic positions of the main emission bands in PPV and OPV3 versus delay time. Squares and triangles depict the transient positions of the emission bands in PPV around 2.07 and 2.24 eV, respectively. The circles depict the transient positions of the main emission band in OPV3 at about 2.63 eV.

However, after this similar ultrafast initial rise the time-resolved spectra of OPV and PPV reveal a *distinctly different* relaxation behavior: The polymer exhibits a significant transient redshift not observed with the oligomers. The transient luminescence spectra are fitted by a superposition of several Gaussian bands. In Fig. 2, we have plotted the peak positions of the strongest vibronic sidebands versus time. A redshift $\langle E\rangle(t) - \langle E_0\rangle$ of about 30 meV is measured within the first few picoseconds after optical excitation in the case of PPV. In contrast, *none* of the OPV samples show a measurable redshift of the luminescence peaks as shown in Fig. 2 for OPV3. We therefore conclude that the redshift cannot be explained by vibronic relaxation but is rather related to migration of photoexcitations to emission sites with lower energies, absent in oligomer samples.

Further insight into the relaxation processes is deduced from luminescence transients monitored at different spectral positions. In Fig. 3(a), the luminescence rise at 2.4 eV is plotted together with the cross correlation between the 3.12 eV excitation pulse and the 1.56 eV reference pulse. The luminescence rise follows the response function of the experimental setup. Similar results are found in the entire spectral range between 1.8 and 2.4 eV. Nevertheless, a slight increase of the intensity is observed up to 1.5 ps, which we attribute to accumulation of excitations in the tail portion of the DOS due to their spectral relaxation. In the data of Fig. 3(b) spectral relaxation is evident from the luminescence decay as a function of spectral position. The time scale of the decay at photon energies corresponding to the $S_1 \rightarrow S_0$ 0-0 cw-fluorescence band is about 200 ps (see, for example, the trace for 2.4 eV). It decreases by more than 2 orders of magnitude upon shifting the monitor energy to 2.7 eV, which is above the center of the $S_1 \leftarrow S_0$ absorption band. This pronounced dependence of decay time on photon energy is again not observed in oligomer samples.

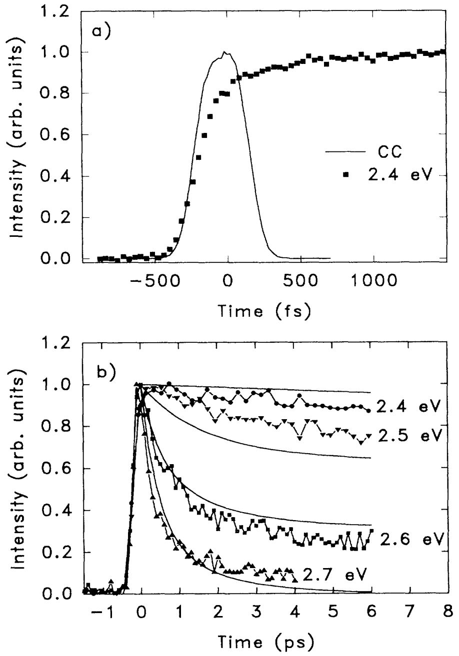

FIG. 3. Transient luminescence traces in PPV, detected at different luminescence energies. (a) Rise of the luminescence at 2.4 eV (symbols). CC denotes the cross correlation (solid line). (b) Normalized luminescence decays at different energies. The solid lines are calculated as described in the text.

In the following, we demonstrate that our experimental observations can be well interpreted by the concept of random walk of excitations within the DOS, elaborated by Monte Carlo studies and an effective medium approach [20,21]. In a crude approximation, the temporal decay of the mean energy $\langle E\rangle(t)$ of photoexcitations generated at random within a Gaussian DOS should follow [21]:

$$\langle E\rangle(t) \sim \ln\left(\frac{t}{t_0}\right), \tag{1}$$

with t_0 being the dwell time, which characterizes the average time for a single hop. This predicted logarithmic dependence is reflected clearly in the temporal shift of the emission maximum in the case of the polymer sample (see Fig. 2). An upper limit for t_0 of about 250 fs (time resolution of the setup) can be obtained from the very fast decay of the luminescence at 2.7 eV [see Fig. 3(b)]. Therefore considerable energy relaxation has occurred already on the time scale on which the spectra of Fig. 1 were recorded. The estimate of t_0 concurs with values reported for the hopping time of singlet excitons in molecular crystals [22]. At the high-energy side of the DOS, the population decay is determined by fast hopping to sites with lower energy. The strong dependence of the decay times on energy reflects the energy dependence of the hopping rate, which decreases gradually as the excitation moves further into the low-energy tail of the DOS. The most significant contribution to the subpicosecond and picosecond energy relaxation at room temperature is expected to arise from nearest neighbor downward hopping [23]. In this approximation the rate ν_i for leaving a site with energy E_i is proportional to the number of sites in the DOS with lower energies:

$$\nu_i(E_i) \sim \int_{-\infty}^{E_i} \rho(E)dE\,. \tag{2}$$

The DOS can be mapped by a Gaussian distribution of site energies E_i [10] centered at 2.536 eV with a Gaussian width of 0.046 eV as derived from absorption spectra. For comparison with the experimental data, both the finite time and energy resolution of the setup are considered. The basic experimental trends are reproduced by the model (see solid lines in Fig. 3), which confirms once more the concept of a random walk within the DOS.

Our results on PPV and its oligomers cannot be explained with the concept of self-trapping of excitons, which has previously been used to explain spectral relaxation in other conjugated polymers, such as polydiacetylenes [12,16]. Self-trapping effects are incompatible with (i) the strong increase of the relaxation time for decreasing the monitor energy (300 fs to 200 ps), (ii) the different behavior of polymer and oligomer luminescence at the same monitor energy (2.7 eV) corresponding to chromophores of the same length, and (iii) the nonexponential long time decay of the spectrally integrated emission reflecting the statistics of excitation trapping by extrinsic traps [24].

In conclusion, we have performed for the first time femtosecond luminescence studies of conjugated polymers. The results in poly(p-phenylenevinylene) show an ultrafast onset of the luminescence, demonstrating a rapid vibronic relaxation. Transient luminescence spectra reveal a redshift on femtosecond and picosecond time scales in PPV absent in its oligomers. This strongly indicates that the elementary excitations in PPV are of the Frenkel-Wannier type executing an incoherent random walk within an inhomogeneously broadened density of states distribution. It gives rise to an energy dependent luminescence decay and to a dynamic Stokes shift of electronic origin.

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