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Exciton versus band description of the absorption and luminescence spectra in poly(*p*-phenylenevinylene)

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The fluorescence spectra of poly(*p*-phenylenevinylene) have been investigated at 6 K employing site-selective laser spectroscopy. They delineate the existence of a well-defined energy in the tail of the absorption edge below which the fluorescence emission is quasiresonant with an excitation featuring a Stokes shift of 100 cm^{-1} only. Above this localization threshold $\nu_{\rm loc}$ spectral diffusion is observed with the emission independent of excitation yet carrying a significant polarization memory for excitation energies up to 1.9 eV in excess of $\nu_{\rm loc}$. This is incompatible with the band picture involving photogeneration of an uncorrelated electron-hole pair, yet consistent with the concept of random walks of neutral excitations through an inhomogeneously broadened density of states. The chromophores are associated with a distribution of segments of the polymer chains along which the excitation is delocalized. Published results on time-resolved fluorescence support the exciton picture.

I. INTRODUCTION

Depending on the strength of coupling among the structural elements, optical transitions in insulating solids are appropriately described in terms of either the exciton or the semiconductor band model. Weak intersite coupling in conjunction with a low dielectric constant favors the generation of strongly correlated electron-hole pairs (excitons) upon photon absorption, while strong coupling leads to the formation of uncorrelated electron-hole pairs. In view of the large anisotropy regarding inter- versus intramolecular coupling, conjugated polymers could, in principle, fall into either category. In fact, both approaches have been applied to treat the lowest $\pi \rightarrow \pi^*$ transition in quite similar systems. Spectroscopic, in particular, electroreflectance,[1,2] studies combined with photoconduction work[3,4] established the excitonic nature of the lowest allowed optical transition of crystalline polydiacetylene. Recent site-selective fluorescence work on luminescent matrix-isolated polydiacetylene chains supported this notion.[5,6] On the other hand, it became common practice to apply the band-to-band (BB) transition approach to conjugated polymers such as polyacetylene,[7] poly-phenylenevinylene,[8-10] poly-*p*-phenylene,[11] or polythiophene[12,13] using single-chain one-electron models based upon the Su-Schrieffer-Heeger Hamiltonian. Doing so is suggested by the observation of a semiconductor-metal transition upon doping and the apparent success of these theories[14,15] for understanding a variety of spectroscopic observations, for instance, photoinduced absorption[16] attributed to either solitons, polarons, or bipolarons. Within the framework of the BB approach, photoluminscence (PL) has been interpreted in terms of the recombination of electron-hole pairs, the appearance of a Stokes shift between absorption and emission being considered as evidence for polaron formation prior to recombination.[10,17,18]

The applicability of the BB approach to PPV has recently been challenged by Rauscher *et al.*[19] Based on site-selective fluorescence studies on a soluble PPV derivative (poly-phenylphenylenevinylene) dispersed in a low-temperature 2-methyltetrahydrofuran (MTHF) glass, they argued that fluorescence spectra ought to be interpreted in terms of the transfer of neutral excitations among segments of the polymer chain that differ with regard to their excitation energy. The conclusion of Furukawa *et al.*[20] that the main luminescence features of PPV should be indentified as free-exciton luminescence is in accord with this idea, although these authors retain the band approach for interpreting the main absorption band. In their model the Stokes shift reflects the exciton binding energy.

The main purpose of this work was to clarify the nature of the lowest optically allowed transition in PPV, both in absorption and emission employing steady-state site-selective spectroscopy[21] and fluorescence polarization[22,23] studies. The results support the exciton concept and indicate the failure of one-electron theories for treating the lowest excitation states of conjugated polymers like PPV.

II. EXPERIMENT

Experiments were performed with unoriented polyphenylenevinylene films prepared at the Cavendish Laboratory using the sulfonium polyelectrolyte precursor route.[24,25] A thin sample of optical density ~ 0.3 appropriate for absorption measurements was synthesized at Marburg. The sample was mounted onto the cold finger of a He-flow cryostat and kept at a temperature of $\simeq 6$ K. Site-selective cw-fluorescence (SSF) spectra were recorded using a tunable pulsed dye laser of spectral bandwidth $\simeq 0.2$ cm^{-1} and employing time-averaging detection techniques. The spectral resolution of the monochromator was < 10 cm^{-1}.

For measurements of fluorescence polarization, thin films of approximately 50-nm thickness were prepared by spin coating the precursor on a quartz substrate. The converted films show no birefringence in the polarization microscope. The optical density was 0.35 at 450 nm and 0.15 at 496 nm. The substrate carrying the PPV film was mounted at the hypotenuse area of a 30°-90°-60° quartz prism using a drop of glycerol as the immersion liquid; this arrangement reduces stray light and facilitates the correction mentioned below. The sample holder was placed on a linear translator, the sample being positioned to the center of the fluorescent light path of the spectrometer by means of a micrometer screw.

Corrected polarized excitation and fluorescence spectra were obtained by means of a specially equipped, computer-controlled, spectrometer (90° geometry, based on the Perkin Elmer[23] MPF 44). The normalized total fluorescence intensity I and the degree of anisotropy r were calculated according to Eqs. (1) and (2) (Ref. 23). Indices v and h denote the vertical and horizontal position of the polarizer in the excitation and the fluorescence beam, respectively,

$$I = I_{vv} + 2I_{vh} \ , \tag{1}$$

$$r = \frac{I_{vv} - I_{vh}}{I_{vv} + 2I_{vh}} \ . \tag{2}$$

Both quantities are corrected for wavelength- and polarization-dependent instrumental effects.

III. RESULTS

The room-temperature absorption spectrum of a thin PPV film, shown in Fig. 1, consists of a main band centered at 20 260 cm^{-1} (2.51 eV), followed by a vibronic component at the high-energy side. A low-energy tail extends to $\simeq 17\,000$ cm^{-1}. Spectral deconvolution indicates that main band can be mapped by a Gaussian profile with standard deviation $\sigma = 650$ cm^{-1}, equivalent to a full width at half maximum (FWHM) of 1430 cm^{-1}. As far as the appearance of the absorption spectra is concerned, PPV is, thus, not principally different from pendent group polymers like polyvinylcarbazole[26] or molecular organic glasses prepared by vapor deposition[27] and known to feature inhomogeneously broadened absorption bands.[28]

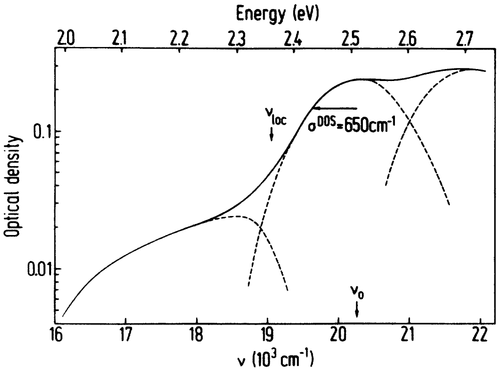

FIG. 1. Low-energy portion of the room-temperature absorption spectrum of a thin poly(p-phenylenevinylene) film on a semilogarithmic scale. It can be deconvoluted into a main band of Gaussian shape, centered at 20 260 cm^{-1}. It is followed by a vibronic band at higher energies and a defect band at lower energies.

Low-temperature fluorescence spectra depend on the spectral position of the excitation laser within the absorption band (Fig. 2). For $\nu_{exc} > 19\,020$ cm^{-1} (2.36 eV), the emission spectrum is independent of excitation. It consists of a moderately broad $S_1 \rightarrow S_0$ 0-0 band (FWHM $\simeq 500$ cm^{-1}) followed by a vibronic progression. Upon scanning the excitation laser beyond 19 020 cm^{-1}, the emission spectrum narrows and begins shifting linearly with ν_{exc}. The dominant vibronic band splits into a doublet with peak energies $\simeq 1170$ and 1535 cm^{-1} to the red of the maximum of the high-energy 0-0 band. The latter is offset from the laser energy by ≈ 100 cm^{-1}. A compilation of data for the position of the center of the $S_1 \rightarrow S_0$ 0-0 and $0 \rightarrow 1535$ bands, respectively, as a function of ν_{exc} is presented in Fig. 3. It clearly delineates a break in the emission versus excitation energy plot at $\nu_{loc} = 19\,020$ cm^{-1}. Operationally ν_{loc}, henceforth called the localization threshold, is defined as the intersection of the asymptotes of the $\nu_{em}(\nu_{exc})$ plot. Figure 3 also demonstrates that genuine resonant emission has, in no case, been observed. There is a constant Stokes shift of $\delta \simeq 100$ cm^{-1} between the laser energy and the peak of

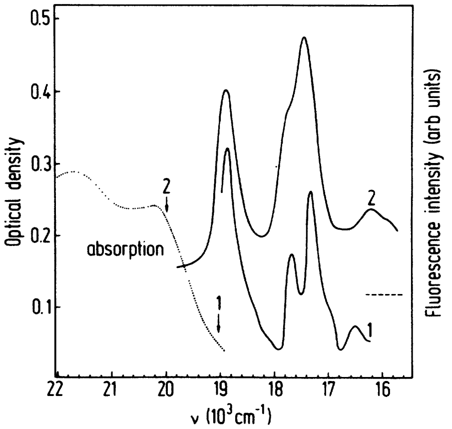

FIG. 2. 6-K-fluorescence spectra of PPV excited at the indicated spectral positions.

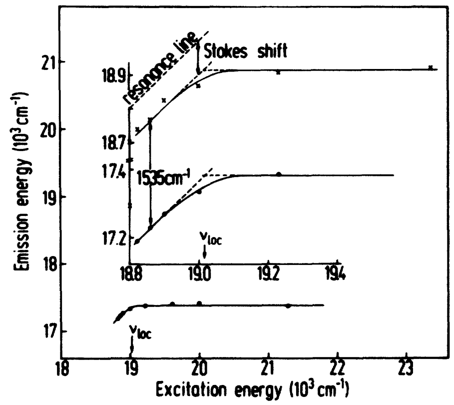

FIG. 3. Variation of the spectral position of the 1535-cm^{-1} vibronic fluorescence band, recorded at 6 K, with excitation energy. The inset shows plots of emission vs excitation energies for the $S_1 \rightarrow S_0$ 0-0 and 0–1535 cm^{-1} bands, respectively, on an expanded scale.

the $S_1 \rightarrow S_0$ 0-0 band upon excitation below ν_{loc}.

Polarized fluorescence and fluorescence excitation spectra recorded at 298 K are shown in Fig. 4 together with the dependence of the degree of polarization r [Eq. (2)] on excitation and emission energy, respectively. Since the refractive index of PPV in the region of absorption, needed to correct r with respect to instrumental effects, is not precisely known, absolute numbers of r have to be considered with caution. This does not, however, affect the following qualitative conclusions: (i) The fluorescence carries a polarization memory upon scanning ν_{exc} across the entire absorption band, (ii) r increases as ν_{exc} approaches the tail of the absorption profile, and (iii) the degree of polarization of the fluorescence emission recorded at fixed ν_{exc} decreases towards lower emission energies and becomes constant for $\nu_{\mathrm{em}} \leq 19\,000$ cm^{-1}.

IV. DISCUSSION

Since the following discussion will be largely based on the concept of incoherent excitation transport in a random medium, it appears to be appropriate to delineate its key elements first. For more detailed information the reader is referred to earlier work.[29–33] Consider a Gaussian density of localized states (DOS) coupled by exchange or multipolar interaction. A packet of independent elementary excitation generated at a specified site will execute a random walk in whose course it will relax within the DOS and spread in energy space provided that its width σ is $\gg kT$. As time progresses, a relaxation excitation will find fewer and fewer acceptor sites it can jump to without significant activation. The mean-square displacement must, therefore, decrease with time, i.e., motion will be dispersive. Eventually the excitation will reach a site from which the jump rate to a site of equal or lower energy is less than the intrinsic decay rate. The energy of those sites defines a localization threshold ν_{loc} separating states that participate in incoherent transport from states that do not. For short-lived singlet excitations and three-dimensional jump topology, ν_{loc} is located at an energy $\simeq -2\sigma$ below the center of the DOS. Exciting at $\nu < \nu_{\mathrm{loc}}$ generates excitations that have little or no change to leave their initial site during their lifetime. Scanning a narrow excitation laser across an inhomogeneously broadened DOS profile should, therefore, produce luminescence that is independent of excitation, yet

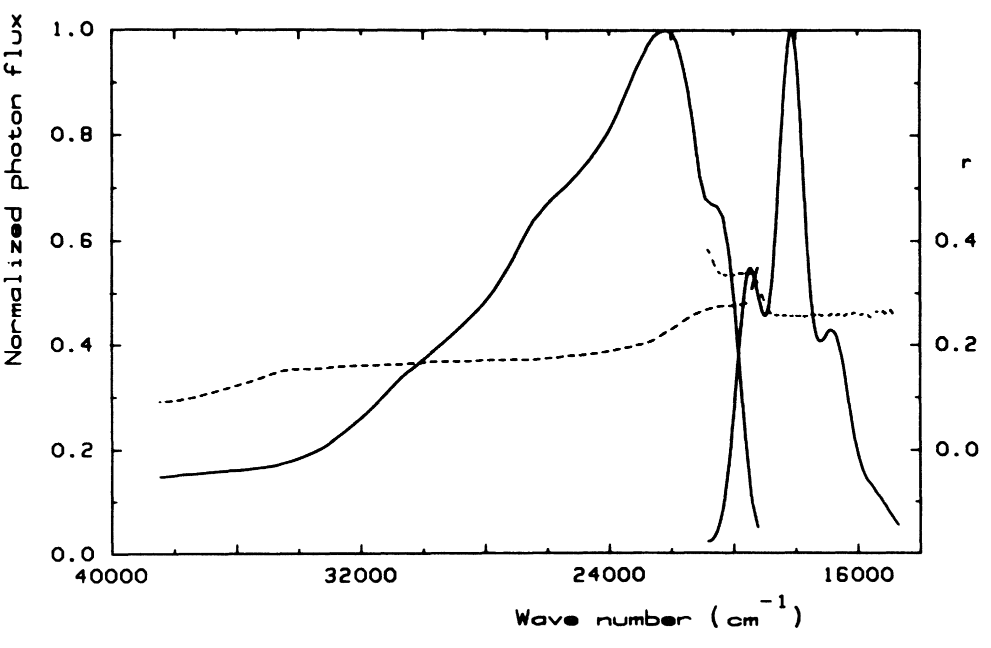

FIG. 4. Normalized excitation and fluorescence spectra of PPV film at room temperature; the thickness of the film is 50 nm. Wave number of fluorescence $\bar{\nu}_{\mathrm{flu}} = 18\,120$ cm^{-1} for the excitation spectrum, wave number of excitation $\bar{\nu}_{\mathrm{exc}} = 21\,510$ cm^{-1} for the fluorescence spectrum. The slit width is 3 nm. Dashed curves: degree of polarization r [Eq. (2)], right-hand side ordinate.

subject to spectral diffusion as long as $\nu_{\mathrm{exc}} > \nu_{\mathrm{loc}}$, and shift linearly with ν_{exc} for $\nu_{\mathrm{exc}} < \nu_{\mathrm{loc}}$ as depicted schematically in Fig. 5. In the latter case, resonant emission will, however, be observed only if electron-phonon coupling of the chromophore is weak. Otherwise, structural relaxation of the chromophore-solvent ensemble will occur leading to a Stokes shift between absorption and emission. Since site selectivity is, nevertheless, preserved, this case will be referred to as quasiresonant emission, its signature being a linear shift with excitation energy and a constant energy separation (Stokes shift) from the resonance line. Spectra recorded under quasiresonant conditions can, therefore, be used to determine the strength of electron-phonon coupling of an emitter unaffected by spectral diffusion due to excitation migration.[21]

Excitation relaxation within a Gaussian DOS has been treated by Monte Carlo simulation and analytically employing the effective medium approach [appropriate for $\sigma/kT \lesssim 5$ (Ref. 29)] and an exact theory[33] describing the pure hopping down regime attained in the $T \rightarrow 0$ limit. In accord with intuition, those treatments indicate that excitation relaxation is slowed down in the $T \rightarrow 0$ limit because, at finite T, intervening thermal activation helps an excitation to find additional pathways for relaxation. Further, the amount of site energy an excitation has lost after a certain time normalized to the dwell time t_0 of an excitation on a site in an energetically ordered counterpart structure turns out to depend on the dimensionality of the system. In one dimension, relaxation occurs much slower.[6] On average, excitations become immobilized after having executed only a few jumps. Recent site-selective fluorescence studies on a matrix-isolated polydiacetylene molecule showed quantitative agreement with the predictions of the theory for one-dimensional (1D) systems.[6] In that case, the sites were identified as the segments of the polymer chain subject to disorder because of wormlike distortion.[34]

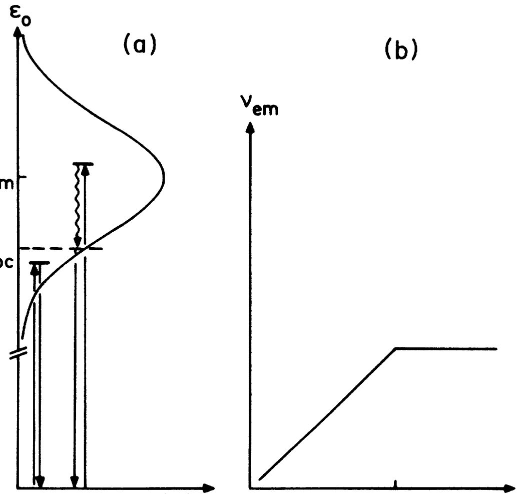

FIG. 5. (a) Schematic view of the electronic density of states distribution (DOS) of a disordered solid. The energy $\varepsilon_{\mathrm{loc}}$ separates states that participate in incoherent excitation transfer from those that do not. (b) Schematic view of the emission (ν_{em}) energy as a function of excitation (ν_{exc}) energy upon scanning a spectrally narrow excitation source across the DOS.

The results of the present site-selective fluorescence work are in accord with the above concept. Exciting above $\nu_{\mathrm{loc}} = 19\,020$ cm^{-1} produces fluorescence that is independent of excitation yet subject to inhomogeneous broadening, while excitation below ν_{loc} generates fluorescence that shifts quasiresonantly with excitation and exhibits a Stokes shift of 100 cm^{-1} independent of ν_{exc}. ν_{loc} is located $\simeq 1300$ cm^{-1} below the center of the absorption peak. This energy shift is twice the Gaussian width of the low-energy wing of the absorption band as suggested by theory.

Further support for the random-walk concept stems from the recent time-resolved fluorescence study of Furukawa *et al.*[20] These authors excited a stretch-oriented PPV film, held at a temperature of 50 K, with 303-nm (33 000 cm^{-1}) pulses of a ps laser. The photons excite vibrationally hot singlet states that decay rapidly to the manifold of zero vibronic S_1 states by vibrational cooling thereby producing a random distribution of excited states matching the density of states profile. Monitoring the emission at variable delay times after excitation revealed a shift of the emission bands as indicated in Fig. 6. This result can be directly compared with Monte Carlo computer simulations of the relaxation of excitations executing a random walk in an energetically disordered hopping system. The solid curve in Fig. 6 is the simula-

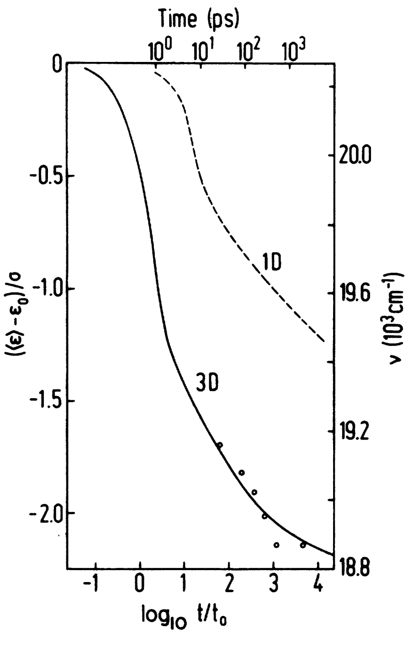

FIG. 6. Solid curve: Monte Carlo result for the decay of the mean energy $\langle \varepsilon \rangle$ of an ensemble of excitations started at random within a 3D Gaussian DOS of width $\sigma = 650$ cm^{-1} at $T = 48$ K ($\sigma/kT = 18.7$). t_0 is the dwell time of an excitation in a hypothetical ordered counterpart structure and ε_0 indicates the energy of the center of the DOS. The dashed curve is for 1D topology. Data points (left scale) are taken from Fig. 5(a) of Ref. 20. The coincidence between experiment and simulation has been achieved by choosing $t_0 = 4 \times 10^{-13}$ s.

tion result for the energetic decay of an ensemble of excitations started randomly within a 3D-DOS of width $\sigma = 650\ \mathrm{cm}^{-1}$ at a temperature $T = 48$ K, equivalent to a disorder parameter $\sigma/kT = 18.7$. For comparison, the result of 1D topology has also been included. The difference in dimensionality is clearly revealed by the different rates of relaxation.

Since position and width of the DOS profile are known from absorption spectra, the only adjustable parameter for comparing experimental and simulation data is the dwell time t_0 of an excitation in an hypothetical ordered counterpart structure which fixes the time scale in the computation. (Adopting the 295-K absorption data is not strictly correct. A fluorescence excitation spectrum recorded at 6 K indicated that sample cooling results in both a slight red shift of the absorption and a 20% reduction of the width of the absorption tail. On the level of accuracy set by the experiments, both effects cancel as far as the energy shifts relative to the band center and normalized to the bandwidths are concerned.) Identifying the time origin in the data of Furukawa *et al.* with the shortest time of delay of indicated yields $t_0 \simeq 4 \times 10^{-13}$ s. It is comparable to the hopping time of singlet excitons in molecular crystals,[35] e.g., crystalline anthracene, as expected if the rate-limiting step for excitation migration was interchain transfer. Not only does this analysis demonstrate the success of the random-walk model in explaining the short-time dynamics of the PPV photoluminescence, it also testifies on the 3D topology of the random walk.

In principle, the observed variation of the emission energy with ν_{exc}, particularly the occurrence of the localization threshold (see Fig. 3) could be the signature of a mobility edge separating localized states from band states as known from amorphous inorganic semiconductors.[36] By exciting above ν_{loc}, one would create uncorrelated electron-hole pairs that recombine without retaining a memory about their generation, while exciting below ν_{loc} woud create excitonic states that decay quasiresonantly. The fluorescence polarization experiments argue against this notion. Figure 4 indicates a constant degree of polarization $r \approx 0.2$ for $35\,000 > \nu_{\mathrm{exc}} > 24\,000$ followed by a slight increase as ν_{exc} approaches $20\,000\ \mathrm{cm}^{-1}$. This is incompatible with the band picture. Carriers excited $15\,000\ \mathrm{cm}^{-1}$ (1.8 eV) above the band gap should be subject to efficient intraband scattering and interchain transfer erasing the polarization memory completely. The polarization measurements are, however, in accord with the exciton concept. In the case of an isotropic film containing noninteracting molecular emitters, one expects to observe the fundamental anisotropy r_0 of the fluorophores that is entirely determined by the anisotropy of the molecular absorption and emission tensors.[22] Its theoretical upper limit is $r_0 = 0.4$. If the excitation is allowed to migrate during its lifetime, r will be smaller and be related to the probability g^s that the excitation remains on its starting position and on the mutual orientational correlation between the absorbing and emitting state. A crude approximation[23] yields

$$r = r_0[g^s + (1-g^s)^2P_2] , \tag{3}$$

where $^2P_2$ $(0 < {}^2P_2 < 1)$ is a second-order coefficient describing orientational pair correlation weighted by the normalized site fluorescence intensity. In case of an isotropic solid, $^2P_2 = 0$.

The strong anisotropy of the optical absorption in conjugated polymers suggests that the transition moments for absorption and emissions be virtually parallel to the polymer chain yielding $r_0 = 0.4$ in agreement with experiments on a matrix-isolated model compound, bis-1,4-(2-methylstyryl)benzene.[37] Upon decreasing the excitation energy towards ν_{loc}, one would expect r to increase from a value close to zero to $r = 0.4$ because g^s approaches unity as energy transfer is gradually eliminated. The fact that r is as large as $\simeq 0.2$ way above ν_{loc} is a consequence of the microstructure present in PPV and the fact that only very few elementary transfer steps are required for an excitation to get rid of its extra site energy. It is also important to recall that, within the framework of molecular excitations, most of the excess energy is due to the excitation of molecular vibrations or higher electronic states which both relax very quickly by coupling to the phonon bath without involving electronic jump processes.

In molecular glasses or polymers where the chromophores are the pendant groups, e.g., polyvinylcarbazole, the inhomogeneous broadening of molecular transitions is the result of the statistical local variation of the van der Waals interaction energy of an excited molecule with its polarizable environment reflecting variations in the local packing. In conjugated polymers the chromophores, e.g., sites, have to be identified with segments of the polymer backbone over which the excitation is delocalized. Their length, called the effective conjugation length, may be limited by chain distortion or local chain defects. By virtue of Kuhn's particle in a box model,[38,39] variations translate into a variation of the excitation energies of the segments and, hence, contribute to inhomogeneous broadening. Extrapolating the peak energies of the inhomogeneously broadened $S_1 \leftarrow S_0$ 0-0 bands of phenylene vinylene oligomers as models of PPV (Ref. 40) suggests an effective conjugative length of $\simeq 11$ units for PPV rather than 3–4 units as suggested before.[41,42] A variation by ±1 unit would easily account for the observed $650\text{-}\mathrm{cm}^{-1}$ (0.08-eV) Gaussian width of the DOS without requiring any contribution arising from packing. This concurs with the indication of electron and x-ray diffraction studies that even unoriented PPV has a significant degree of crystallinity and that stretch-oriented PPV does not affect the luminescence profile noticeably.[20]

Combining the above ideas, we end up with the following concept for rationalizing excitation dynamics in PPV. A photon is absorbed by a segment of a polymer chain and generates a singlet excitation. It can jump to another segment of the same chain or of a neighbor chain whose excitation energy is lower. At the end of its random walk, which does not involve more than a few jumps at low temperatures, the excitation will arrive at an acceptor site at which it decays radiatively or nonradiatively because there are no other sites with still lower energy available as acceptors. Due to local chain ordering, the polarization memory will partially be retained and approaches the theoretical value if excitation occurs into the tail states of the DOS which cannot transfer within their intrinsic lifetime. The random-walk concept also offers a straightforward explanation for the nonexponential time dependence of the exciton luminescence seen by Furukawa *et al.*[20] upon recording at 19 047 cm^{-1} (525 nm). This energy is above ν_{loc}. Therefore, excitations pass through the spectral observation window upon relaxing to deeper states of the DOS to finally establish an occupational density of states centered around ν_{loc}. The emission must exhibit a fast initial decay determined by rapid spectral diffusion across the spectral window and merge into a slower decay at longer times than are due to those excitations that accumulate in the upper portion of the occupational DOS and decay with the intrinsic lifetime. The concept can also account for the appearance of a second red-shifted emission band upon raising the temperature above ~ 100 K. The absorption suggests the existence of traps of unidentified origin—chemical or physical—that may be populated via exciton hopping. Since, with increasing temperature, the number of sites an excitation can visit increases, the probability of becoming trapped also increases. Thermally activated self-localization would, of course, lead to a similar dependence.[20] For reasons to be discussed below, we consider this interpretation unlikely, however.

The site-selective fluorescence spectra recorded upon exciting at $\nu_{\mathrm{exc}} < \nu_{\mathrm{loc}}$ are characteristic of the individual absorber or emitter and reflect its electron-phonon coupling. They delineate a Stokes shift of $\delta \simeq 100\ \mathrm{cm}^{-1}$ at 6 K, comparable to what has been measured for polydiacetylenes. It indicates quite moderate electron-phonon coupling only—from $\delta = 2S\hbar w_{\mathrm{ph}}$ $S \simeq 2, \ldots, 3$ is obtained assuming 20 cm^{-1} for the energy of the dominant phonon—and demonstrates that the formation of the weak excitonic polaron is not impeded by an energy barrier.

We conclude this discussion by addressing two observations known from the literature that might argue in favor of the band approach. The first one relates to the action spectrum of photoconductivity. Tokito *et al.*[43] report on a peak at 2.5 eV (20 000 cm^{-1}) which might indicate onset intrinsic carrier generation via a band to band transition. However, according to a recent reinvestigation in this laboratory, this peak is an artifact caused by the onset of bimolecular carrier recombination as the penetration depth of the exciting light becomes small.[44] The corrected action spectrum shows no singularity. The second comment relates to the electron-energy-loss spectra Fink reported for PPV.[45] He noted a distinct increase of a low-energy transition with significant dispersion as polymerization proceeds and which must be related to the conjugated chains. It need not be associated with transition among valence- and conduction-band states. Note that the particle in the box model also predicts a series of excited states for a chain consisting of $\gtrsim 11$ elements. Its dispersion must be large because of strong π bonding among the elementary units. For optical transitions the **k** selection rule applies ensuring that the absorption spectrum resembles that of a molecular absorber, while in electron-loss spectroscopy, the full set of states becomes accessible.

V. CONCLUDING REMARKS

The present results demonstrate the inadequacy of one-electron theories for understanding the spectroscopy of a conjugated model polymer in the spectral range of the lowest allowed electronic transitions. They indicate that, instead, the transition involves strongly correlated electron-hole pairs both in absorption and emission. Obviously transitions between valence and conduction bands of the polymer backbone carry little oscillator strength and are, therefore, buried underneath the exciton transition as they are in conventional molecular solids and, notably, in polydiacetylenes. The results should have a strong implication on the interpretation of photoinduced features observed in the optical gap of conjugated polymers usually attributed to the transition among polaronic and free-carrier states. It is by no means surprising that difficulties are encountered upon interpreting photoluminescence and photoinduced absorption measurements in terms of polaron or bipolaron models[10,45] if input parameters are derived on the basis of evaluation procedures that turn out to be inappropriate.

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