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Hot exciton dissociation in conjugated polymers

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We consider on-chain dissociation of an exciton created on a conjugated polymer chain by optical excitation above the absorption edge. Assuming that the excess excitation energy is stored in several phonons, we estimate the rate of dissociation by phonon absorption when one of the carriers (electron or hole) is ejected into a delocalized state of the conduction or valence band. We obtain the characteristic time for this process to be less than 100 fs.

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I. INTRODUCTION

An important process that decreases the efficiency of photoluminescence in conjugated polymers is the dissociation of the singlet excitons produced by photoexcitation into interchain polaron pairs.[1,2] There is experimental evidence that the dissociation of initially hot excitons occurs on a time scale of several picoseconds at most. This follows from the studies of dynamics of electric-field-induced luminescence quenching,[3] studies of photocurrent generation kinetics by two-pulse exciton depletion,[4] experiments on femtosecond dynamics of photoinduced polaron-pair absorption.[5] Time-resolved microwave conductivity measurements for a polymer in dilute solution and in aggregate showed that polaron pairs can be generated on a single-polymer chain, although presence of nearby chains increases the yield of polaron-pair generation.[6] An experiment on photocurrent generation kinetics with different polarizations of the pump and probe pulses also provides evidence for intrachain polaron pair generation as the initial stage of dissociation.[7] The characteristic time reported in most of these works is about 1–2 ps. Experiments on transient infrared absorption[8,9] give times as short as 100 fs.

It seems natural to associate this time scale with ‘‘cooling down’’ of the exciton, i. e., with the relaxation of vibronic degrees of freedom. However, the experimental situation in this field is not clear either. On the one hand, vibronic coherence on a picosecond time scale was observed directly in poly(*p*-phenylenevinylene) (PPV).[10] On the other hand, femtosecond luminescence spectroscopy studies of PPV have given 100 fs as an approximate upper limit of the vibronic relaxation time.[3,11]

The only theory of the hot-exciton dissociation we are aware of is that of Arkhipov *et al.*[12,13] The main idea of these works is that the excess energy of the excitation photon is quickly distributed over the conjugation segment of the chain, leading to a local quasiequilibrium heat bath with high effective temperature that gradually decreases as the energy is dissipated into the environment. The exciton has a chance to dissociate as long as the effective temperature is high enough to provide the activation energy. Fitting the experimental data for the photocarrier generation yield in methyl-substituted ladder-type poly-para-phenylene (MeLPPP) led to a value of 35 fs for the effective cooling time of the vibrational heat bath.[13] On the one hand, this can be considered additional evidence for ultrafast vibrational relaxation. On the other, such a short time is hardly compatible with the very idea of the quasiequilibrium, which makes the description of Refs. 12 and 13 unsatisfactory.

In the present paper we make an attempt to attack the problem from the opposite limit. Namely, we assume that the vibrational degrees of freedom that were excited by the pump photon remain excited for some time, the excess photon energy being stored in several phonons corresponding to these degrees of freedom. Given this as the initial state (exciton + several phonons), we calculate the rate of exciton dissociation by phonon absorption when one of the carriers (electron or hole) is detrapped, i. e., ejected into a delocalized state of the conduction or valence band.

Our approach as well as that of Refs. 12 and 13 implies the existence of a threshold excess photon energy for charge photogeneration. The issue of the excitation energy dependence of the charge photogeneration is controversial: on the one hand, the photocurrent has been reported to increase strongly at excitation energies about 1 eV above the absorption edge;[14,15] on the other hand, a recent experiment casts doubt on these results by showing that the current could be due to electrons emitted from the sample into the surrounding space, i. e., photoemission.[16] As will be seen later, our results for the dissociation rate are not strongly sensitive to the value of the threshold, given that sufficient energy is provided.

The problem of threshold excess photon energy for charge photogeneration is closely related to the problem of the exciton binding energy in conjugated polymers. The latter has been subject to much debate; most experimental studies give a number of ~ 0.3 eV (see Ref. 17, and references therein). We note that, generally speaking, in our picture the two energies are different: while the exciton binding energy E_{exc} is defined as the difference between the energy of a pair of separated electron and hole polarons and the energy of a bound exciton (all of them with the lattice relaxed, i. e., self-trapped), the dissociation threshold E_{diss} in our picture would be the energy required to eject an electron (hole) from the excitonic bound state into the one-particle continuous spectrum of delocalized states (one might call it single-particle binding energy). Thus the difference $E_{diss} - E_{exc}$ should be approximately equal to the binding energy of a single-electron (hole) polaron.

In principle, the exciton polaron can decay into two polarons, which would formally correspond to another decay channel. However, the the typical length of a conjugation segment, commonly believed to be about 10–20 sites, is at most several times larger than the polaron size. In this case the two-polaron channel is less relevant because two large polarons confined to the same conjugation segment "feel" each other very well and would immediately recombine back; the final state is not well defined and such a calculation would not make much sense. At the same time, the state "polaron + carrier" on the same conjugation segment is not so badly defined as two polarons.

It is worth noting that intrasegment exciton dissociation (here and below "segment" means a conjugation segment) that we are going to consider, does not necessarily lead to charge separation, as the two carriers can form an exciton again. Clearly, this is quite probable if they stay on the same conjugation segment after cooling down, so charge separation requires an interchain or an intersegment hopping. However, it should be easier for a carrier to hop from an unbound state in the conduction or valence band than from a bound exciton state, as in the latter case it is held by Coulomb attraction. Dissociation of a thermal exciton due to the presence of an acceptor impurity with a level deeper than the exciton binding energy was considered by Rice and Gartstein.[18] An analogous phenomenon can occur for two polymer chains if the conduction or valence band of one of them is higher than that of the other.[19] However, if the chains are nearly identical, the intrasegment dissociated state may serve as a precursor for interchain charge separation. Of course, one can consider direct phonon-assisted interchain hopping from the bound-exciton state, but this is beyond the scope of the present paper.

In our calculations we assume zero external electric field and do not address the problem of electric-field dependence of the dissociation quantum yield. Again, experimental results reported so far are controversial: a yield of $\sim 10^{-4}$ was reported for MeLPPP in the fields $\sim 10^4$–10^5 V/cm in Ref. 13, while the authors of Ref. 7 obtain a yield of ~ 0.1 in a field of $4 \cdot 10^4$ V/cm, and in Refs. 8 and 9 a similar value (~ 0.1) was reported for the yield at zero field. In view of these contradictions we restrict ourselves to the case of zero field.

We perform calculations having in mind MeLPPP, which is known to be one of the least disordered conjugated polymers and for which detailed spectroscopic information is available.[20] The 0-0 electronic transition (i. e., the transition between the relaxed vibrational states) is located at 2.73 eV. The vibronic progression observed in the spectra corresponds to two vibrational modes coupled to the exciton: one with the energy $\hbar\Omega = 0.18$ eV and the Huang-Rhys factor $S \approx 0.86$, and the other one whose energy and Huang-Rhys factor are $\hbar\omega = 0.08$ eV and $s \approx 0.72$, respectively. Excitation by the second harmonic of a Ti:sapphire laser (3.18 eV) used in many experiments corresponds to an excess energy of about $2\hbar\Omega + \hbar\omega$. We assume these vibrations to be dispersionless and intraring.

II. CALCULATION OF THE DISSOCIATION RATE

A. Initial state

The state of the polymer chain immediately after excitation above the absorption edge is assumed to correspond to an exciton and several phonons. As already mentioned, properties of excitons in conjugated polymers were widely debated in the past 10 years. Most of the theoretical work was done on PPV (for a review see, Ref. 21). We take the electron states of a phenyl ring as a starting point for describing the excitations in the polymer, considering the phenyl ring as a lattice site. As the characteristic vibrational relaxation energy $S\hbar\Omega + s\hbar\omega \sim 0.2$ eV, the self-localization effect should be significant.

First we consider the completely relaxed excitonic state, i. e., the zero-phonon state of the displaced oscillators. Let us denote the coordinates corresponding to the normal modes with frequencies $\hbar\Omega$ and $\hbar\omega$ by Q_n and q_n, respectively, for each monomer unit n. The presence of the exciton results in static displacements $\tilde{Q}_n$ and $\tilde{q}_n$. The profile of displacements along the chain corresponds to a potential well felt by the electron and the hole, which results in a self-trapped excitonic state of characteristic size denoted by κ_{ex}^{-1}.

One can imagine two limiting cases for the electron and the hole motion in a self-trapped exciton. The first is the case when Coulomb attraction between the electron and the hole is much stronger than their coupling to the phonons. In this case the total electron-hole wave function $\Psi_{ex}(n_e, n_h)$ can be factorized into the product of the wave functions describing the electron-hole relative motion and the exciton center-of-mass motion. The relative motion is then governed by the Coulomb attraction and is characterized by a certain length scale a_B, the excitonic Bohr radius. The center-of-mass motion of this tightly bound exciton is coupled to the lattice displacements, which results in exciton self-localization on a length scale $\kappa_{ex}^{-1} \gg a_B$. This case is favored by the fact that in the purely one-dimensional Coulomb problem the binding energy is infinite and $a_B \to 0$.

However, in reality this infinity is cut off for many reasons, e.g., the band nonparabolicity,[22] or discreteness of the lattice and finiteness of the electron-hole interaction energy on one monomer. This results in a Bohr radius of several monomer units. Detailed calculations of exciton states in polyacetylene[23] show that the two lengths are of the same order: $\kappa_{ex}^{-1} \sim a_B$. Calculations of Ref. 24 for PPV gave the value of $a_B \approx 6$ monomer units without taking into account the lattice relaxation. Experiments on PPV oligomers of different lengths[25] gave the extent of the excitonic state of about five monomer units, which means that the exciton is "squeezed" more than was predicted in Ref. 24, possibly due to self-trapping. In these conditions the exciton state is characterized by a single length scale κ_{ex}^{-1}. We choose a simple model wave function of the form

$$\Psi_{ex}(n_e, n_h) \approx \psi_{ex}(n_e)\psi_{ex}(n_h), \tag{1}$$

$$\psi_{ex}(n) = \frac{\sqrt{\kappa_{ex}/2}}{\cosh \kappa_{ex} n}, \tag{2}$$

where n_e and n_h are the electron and the hole coordinates on the chain (measured in the monomer units), and we take $\kappa_{ex} = 1$ which gives $\Psi_{ex}(n_e, n_h)$ significantly different from zero on approximately five sites. Strictly speaking, the normalization factor is equal to $\sqrt{\kappa_{ex}/2}$ only in the continuum limit $\kappa_{ex} \ll 1$, but for $\kappa_{ex}=1$ the error is less than 1%. The specific functional form (1), (2) is chosen for computational convenience only; any other function localized around the site $n=0$ on the scale κ_{ex}^{-1} would be suitable.

We assume charge conjugation symmetry, so that the interaction potentials due to nuclear displacements are the same for the electron and the hole. We take the electron-phonon (hole-phonon) interaction Hamiltonian to have the form

$$V_n^e = V_n^h = -FQ_n - fq_n, \tag{3}$$

where F and f are the coupling constants. Let $\tilde{Q}_n$ and $\tilde{q}_n$ describe the spatial profile of the static lattice displacements corresponding to the postulated electron-hole wave function $\Psi_{ex}(n_e, n_h)$. If the oscillator of a normal mode Q_n is displaced by $\tilde{Q}_n$, the expectation value of the vibrational potential energy corresponding to the ground state of the displaced oscillator in the presence of the exciton is given by

$$\frac{M\Omega^2\tilde{Q}_n^2}{2} - F\tilde{Q}_n \sum_{n'} [|\Psi_{ex}(n,n')|^2 + |\Psi_{ex}(n',n)|^2],$$

where the first term is the harmonic part of the potential energy (M being the mass associated with the vibration), and the second term is due to the interaction (3) with the electron and the hole. The sum over the second and the first argument (n') of $|\Psi_{ex}|^2$ gives the probability density for the electron and the hole, respectively. The constant energy corresponding to the zero oscillations has been omitted.

The displacements can be found by minimizing the energy with respect to $\tilde{Q}_n$ and $\tilde{q}_n$, which gives

$$\tilde{Q}_n = 2|\psi_{ex}(n)|^2 \frac{F}{M\Omega^2}, \quad \tilde{q}_n = 2|\psi_{ex}(n)|^2 \frac{f}{m\omega^2}, \tag{4}$$

where m is the mass associated with the vibration $\hbar\omega$. The excitonic Huang-Rhys factors S_n and s_n for each vibrational mode on each monomer are defined as[26]

$$S_n = \frac{M\Omega^2\tilde{Q}_n^2}{2\hbar\Omega}, \quad s_n = \frac{m\omega^2\tilde{q}_n^2}{2\hbar\omega}. \tag{5}$$

The full Huang-Rhys factors that determine the oscillator strength of the zero-phonon excitonic transition are given by the sum over all lattice sites,

$$S = \sum_n S_n \approx \frac{2\kappa_{ex}}{3\hbar\Omega}\frac{F^2}{M\Omega^2}, \quad s = \sum_n s_n \approx \frac{2\kappa_{ex}}{3\hbar\omega}\frac{f^2}{m\omega^2}, \tag{6}$$

where we used the continuum approximation

$$\sum_n 4|\psi_{ex}(n)|^4 \approx \int_{-\infty}^{+\infty} \frac{\kappa_{ex}^2 dy}{\cosh^4 \kappa_{ex} y} = \frac{4\kappa_{ex}}{3}, \tag{7}$$

which introduces an error of just 2% for $\kappa_{ex}=1$. As Huang-Rhys factors are known from experiment,[20] this gives us information about coupling constants.

When the excitation occurs above the absorption edge, phonons are created. Let the vibrational excited state correspond to N_n quanta $\hbar\Omega$ and ν_n quanta $\hbar\omega$ on each monomer unit n. Then the state of the polymer immediately after the excitation can be described by the wave function

$$\psi_{ex}(n_e)\,\psi_{ex}(n_h) \prod_n \Phi_{N_n}(Q_n - \tilde{Q}_n)\,\phi_{\nu_n}(q_n - \tilde{q}_n), \tag{8}$$

where $\Phi_N(Q)$ and $\phi_\nu(q)$ are the wave functions of the two oscillators in the Nth or νth excited state, respectively, the wave function ψ_{ex} is given by Eq. (2), and the displacements $\tilde{Q}_n$ and $\tilde{q}_n$ by Eq. (4).

B. Final state

Immediately after the dissociation at least one of the carriers is assumed to be in a delocalized state belonging to the continuous energy spectrum. We do not consider its subsequent relaxation, such as self-localization (polaron formation), or transfer to a neighboring chain. In principle, the second carrier can also be promoted to the continuous spectrum, however, it will cost more energy than staying in the bound state in the well produced by the nuclear displacements. Clearly, the lowest-energy configuration corresponds to a polaron. The nuclear displacements due to the delocalized carrier are small. To be specific, we consider the electron ejected into the continuous spectrum and the hole staying in the lowest-energy self-localized state. All the phonon energy is assumed to be ‘‘spent’’ on the dissociation, and no excitations on the top of the polaron state are present. The rate of the symmetric process (i.e., the electron staying trapped and hole delocalized) is the same in our approach due to charge conjugation symmetry.

Assuming that the state of the trapped hole is determined mainly by its interaction with the nuclei, rather than with the electron, we can seek the wave function (which is a function of the hole coordinate n_h and the nuclear coordinates Q_n, q_n) in the form

$$\psi_h(n_h) \prod_n \Phi_0(Q_n - \overline{Q}_n)\,\phi_0(q_n - \overline{q}_n), \tag{9}$$

where $\overline{Q}_n, \overline{q}_n$ are the average nuclear displacements, found from the condition of the minimum total energy.

The expectation value of the total energy of the hole and the nuclei in the state (9) is given by

$$E[\psi_h(n), Q_n, q_n] = E_h + E_{h-ph} + E_{ph}, \tag{10}$$

$$E_h = -t \sum_n [\psi_h^*(n)\psi_h(n+1) + \text{c.c.}], \tag{11}$$

$$E_{h-ph} = -\sum_n (F\overline{Q}_n + f\overline{q}_n)|\psi_h(n)|^2, \tag{12}$$

$$E_{ph} = \sum_n \left[\frac{M\Omega^2\overline{Q}_n^2}{2} + \frac{m\omega^2\overline{q}_n^2}{2}\right]. \tag{13}$$

Here E_h is the free hole energy determined by the nearest-neighbor intersite hole transfer-matrix element t ("c.c." stands for the complex conjugate). The description of electrons and holes in MeLPPP in terms of a single transfer-matrix element is simplified; therefore t corresponds to an effective value (chosen, e. g., to give the correct width of the lowest single-electron band). E_{h-ph} is the energy of interaction (3) between the hole and the phonons. Finally, E_{ph} is the harmonic oscillator energy, corresponding to free phonons.

Minimization of the energy with respect to the displacements yields

$$\bar{Q}_n = \frac{F}{M\Omega^2}|\psi_h(n)|^2, \quad \bar{q}_n = \frac{f}{m\omega^2}|\psi_h(n)|^2. \tag{14}$$

Substituting these values into Eqs. (10)–(13), we obtain the total energy as a functional of $\psi_h(n)$:

$$E[\psi_h] = -t\sum_n [\psi_h^*(n)\psi_h(n+1) + \text{c.c.}] - \frac{3}{4\kappa_{ex}}(S\hbar\Omega + s\hbar\omega)\sum_n |\psi_h(n)|^4, \tag{15}$$

where we have used the relation (6). Varying this expression with respect to $\psi_h^*(n)$ one obtains the nonlinear Schrödinger equation for the wave function. In the continuum limit it has a well-known solution:[27]

$$\psi_h(n) = \frac{\sqrt{\kappa_h/2}}{\cosh \kappa_h n}, \quad \kappa_h \equiv \frac{S\hbar\Omega + s\hbar\omega}{8t\kappa_{ex}/3}. \tag{16}$$

One should not be confused by similarity of this expression to Eq. (2). The shape of $\psi_{ex}(n)$ was chosen for convenience only, while $\psi_h(n)$ is a solution of the self-consistent problem.

To estimate the effective transfer-matrix element t we use the width of the lowest single-electron band in PPP,[28,29] which is about 3 eV and corresponds to $4t$ in our description. Substituting $4t = 3$ eV into Eq. (16) gives the polaron size $\kappa_h^{-1} \approx 10$, which seems to be an overestimate. Results of calculations for[30] PPV correspond to $\kappa_h^{-1} \sim 2$–3. It is natural to expect polarons in MeLPPP to be less tightly bound than in PPV since the former is stiffer due to its ladder structure. However, in the present calculation we have not taken into account all the degrees of freedom that can contribute to the polaron binding. One obvious candidate is the acoustic mode. The polarizable environment surrounding the polymer chain also contributes to the polaron binding: for a film this corresponds to interchain phonons, for a solution one can have a significant contribution from solvent degrees of freedom.[31] Thus in the following we set $\kappa_h = 0.2$ and determine the static displacements from Eq. (14) with the wave function given by Eq. (16).

Finally, we have to specify the final state of the electron. We approximate the delocalized states by the free plane waves with wave vectors k and energies ϵ_k,

$$\psi_e(n) = \frac{e^{ikn}}{\sqrt{L}}, \quad \epsilon_k = -2t\cos k, \tag{17}$$

where $-\pi < k < \pi$ and L is the length of the conjugation segment (assumed to be large). The density of these states is given by

$$\rho(\epsilon) \equiv \int_{-\pi}^{\pi} \delta(\epsilon - \epsilon_k)\frac{L\,dk}{2\pi} = \frac{L/\pi}{\sqrt{4t^2 - \epsilon^2}}. \tag{18}$$

We note that spin multiplicity does not enter here since the electron spin cannot change during dissociation.

C. Transition-matrix element

The perturbation that causes the exciton dissociation is the electron-phonon coupling V^e given by Eq. (3). To find the transition probability in the first order of perturbation theory (Fermi golden rule) we calculate the matrix element $\langle i|\hat{V}^e|f\rangle$ between the initial and final states described in the preceding two sections. This matrix element can be written as

$$\langle i|\hat{V}^e|f\rangle = I_e I_h I_{FC}(-FX - fx), \tag{19}$$

$$I_{e(h)} = \sum_n \psi_{ex}^*(n)\psi_{e(h)}(n), \tag{20}$$

$$I_{FC} = \prod_n \int \Phi_{N_n}^*(Q_n - \tilde{Q}_n)\Phi_0(Q_n - \bar{Q}_n)\,dQ_n \times \int \phi_{\nu_n}^*(q_n - \tilde{q}_n)\phi_0(q_n - \bar{q}_n)\,dq_n, \tag{21}$$

$$X = \sum_n \frac{\int \Phi_{N_n}^*(Q_n - \tilde{Q}_n)Q_n\Phi_0(Q_n - \bar{Q}_n)\,dQ_n}{\int \Phi_{N_n}^*(Q_n - \tilde{Q}_n)\Phi_0(Q_n - \bar{Q}_n)\,dQ_n}, \tag{22}$$

$$x = \sum_n \frac{\int \phi_{\nu_n}^*(q_n - \tilde{q}_n)q_n\phi_0(q_n - \bar{q}_n)\,dq_n}{\int \phi_{\nu_n}^*(q_n - \tilde{q}_n)\phi_0(q_n - \bar{q}_n)\,dq_n}. \tag{23}$$

The origin of the different terms is the following. The first two factors $I_e I_h$ are the overlaps of the electron and the hole wave functions of the initial and final states, which were defined in Eqs. (2), (16), and (17). When calculating the contribution of each term in the Hamiltonian (3) one obtains the product of overlaps of the vibronic wave functions for each site n except that corresponding to the term considered in Eq. (3). The product I_{FC} (the Frank-Condon factor) as defined in Eq. (21) includes the overlaps for all n, but we define X and x in Eqs. (22) and (23) in such a way that their denominators just cancel the "extra" terms in the product I_{FC}. The numerators of X and x correspond to the matrix elements of the two terms in Eq. (3) between the appropriate wave functions for each n. Note that the transition considered here does not correspond to a definite number of phonons.

The electron and the hole overlaps are easily calculated. The hole overlap is given by

$$I_h = \sum_n \frac{\sqrt{\kappa_{ex}\kappa_h}/2}{\cosh \kappa_{ex} n \cosh \kappa_h n} \approx 0.67, \tag{24}$$

for $\kappa_{ex}=1$, $\kappa_h=0.2$. For the electronic overlap we have

$$I_e \approx \sqrt{\frac{\kappa_{ex}}{2}} \int \frac{e^{iky}}{\sqrt{L}} \frac{dy}{\cosh \kappa_{ex} y} = \frac{\pi}{\sqrt{2\kappa_{ex} L}} \frac{1}{\cosh[\pi k/(2\kappa_{ex})]}. \tag{25}$$

Assuming $k \lesssim \kappa_{ex}$ (i. e., that the dissociated state is not very high in the band), so that $\cosh[\pi k/(2\kappa_{ex})] \approx 1$, we obtain

$$I_e I_h \approx \frac{1.5}{\sqrt{L}}.$$

To calculate the vibrational overlap factors appearing in Eqs. (21)–(23) it is convenient to use the coherent state representation for harmonic oscillators (see, e.g., Ref. 32). The vacuum state of a displaced oscillator $\phi_0(q-\bar{q})$ corresponds to a coherent state $|\xi\rangle$ of the undisplaced oscillator which can be written in the Fock basis $|\nu\rangle$ of the undisplaced oscillator as

$$|\xi\rangle = e^{-\xi^2/2} \sum_{\nu=0}^{\infty} \frac{\xi^\nu}{\sqrt{\nu!}} |\nu\rangle, \tag{26}$$

where ξ is the dimensionless displacement

$$\xi \equiv \bar{q} \sqrt{\frac{m\omega}{2\hbar}}. \tag{27}$$

Then the scalar products appearing in Eqs. (21)–(23) can be calculated as follows

$$\begin{aligned} \int \phi^*_{\nu_n}(q_n - \tilde{q}_n)\phi_0(q_n - \bar{q}_n) dq_n &= \int \phi^*_{\nu_n}(q')\phi_0(q' - \bar{q}_n + \tilde{q}_n) dq' = \langle \nu_n | \xi_n \rangle \\ &= \frac{\xi_n^{\nu_n}}{\sqrt{\nu_n!}} e^{-\xi_n^2/2}, \end{aligned} \tag{28}$$

where

$$\xi_n \equiv (\bar{q}_n - \tilde{q}_n) \sqrt{\frac{m\omega}{2\hbar}} = [\psi_h^2(n) - 2\psi_{ex}^2(n)] \sqrt{\frac{3s}{4\kappa_{ex}}}, \tag{29}$$

and the Huang-Rhys factor appears again. Analogously, the matrix element of the displacement can be expressed as

$$\begin{aligned} \int \phi^*_{\nu_n}(q_n - \tilde{q}_n)(fq_n)\phi_0(q_n - \bar{q}_n) dq_n &= \int \phi^*_{\nu_n}(q')(fq' + f\tilde{q}_n)\phi_0(q' - \bar{q}_n + \tilde{q}_n)\, dq' \\ &= \frac{e^{-\xi_n^2/2}\xi^{\nu_n}}{\sqrt{\nu_n!}} \left(f\tilde{q}_n + \sqrt{\frac{\hbar f^2}{2m\omega}} \frac{\xi_n^2 + \nu_n}{\xi_n} \right) \\ &= \hbar\omega \frac{e^{-\xi_n^2/2}\xi_n^{\nu_n}}{\sqrt{\nu_n!}} \left(\frac{3s}{4\kappa_{ex}} [2\psi_{ex}^2(n) + \psi_h^2(n)] \right. \\ &\quad \left. + \frac{\nu_n/2}{\psi_h^2(n) - 2\psi_{ex}^2(n)} \right). \end{aligned} \tag{30}$$

We assume that in the initial state one has two phonons $\hbar\Omega$ and one phonon $\hbar\omega$, which correponds to excitation by the second harmonic of Ti:sapphire laser as mentioned in the introduction. As the probability of creating an arbitrary configuration $\{N_n, \nu_n\}$ during the excitation is proportional to the Poisson distribution[26]

$$\prod_n \frac{S_n^{N_n}}{N_n!} \frac{s_n^{\nu_n}}{\nu_n!} e^{-S_n - s_n},$$

the most probable configuration corresponds to $N_n = 2\delta_{n,0}$, $\nu_n = \delta_{n,0}$, i. e., all the phonons being on the site $n=0$ (since $S_0 S_1 < S_0^2/2$). Then the Frank-Condon factor (21) is given by

$$I_{FC} = \frac{\Xi_0^2 \xi_0}{\sqrt{2}} \exp\left[-\frac{1}{2} \sum_n (\Xi_n^2 + \xi_n^2) \right] \approx -0.13, \tag{31}$$

where Ξ_n is defined analogously to ξ_n [Eq. (29)] and is actually equal to $\Xi_n = \xi_n \sqrt{S/s}$. Finally, $FX + fx \approx 0.23$ eV. Collecting the numbers together we finally arrive at

$$\langle i | V^e | f \rangle \approx \frac{0.04 \text{ eV}}{\sqrt{L}}. \tag{32}$$

The density of states (18) has the usual singularities at the band edges, as the problem is one dimensional. In reality the band edges are smeared over a certain energy scale. Finite length of the segment produces a cutoff of $\epsilon - 2t_0 \sim t(\pi/L)^2$, which, for example, for $L=15$ is about 30 meV. Thermal dynamic disorder introduces broadening too, and if we assume the corresponding energy scale to be of the order of the temperature (26 meV at room temperature), we obtain a cutoff of the same order. Then for $2t = 1.5$ eV the peak density of states is about $\rho_{max} \approx (L/\pi)(300 \text{ meV})^{-1}$ (note that L in the numerator just cancels that in the matrix element (32) squared). Suppose the final electron states lie in the lower peak (i. e., the excess energy is not large), then the dissociation rate can be estimated as

$$\frac{1}{\tau_{diss}} = \frac{2\pi}{\hbar} 2 |\langle i | V^e | f \rangle|^2 \rho_{max} \approx \frac{0.02 \text{ eV}}{\hbar} \approx \frac{1}{30 \text{ fs}}, \tag{33}$$

where an additional factor of 2 appears, because we should add the rate of a symmetric process when the hole is ejected and the electron stays trapped.

III. DISCUSSION AND CONCLUSIONS

The estimate (33) of the exciton dissociation time obtained in the preceding section constitutes the main result of the present paper. Now we would like to discuss how reliable this result is and what its implications are.

The exciton binding energy, whose value is not known precisely, in our picture determines (i) whether the exciton can be dissociated at all, and (ii) the energy of the final state, which enters through the density of states (18). We postulate a positive answer to the first question, since exciton dissociation has been observed. As for the density of states, its dependence on the energy is rather weak: the peak value $\rho_{max}\approx(L/\pi)(300\text{ meV})^{-1}$ used for the calculations is actually an upper limit, while the lower limit (corresponding to the center of the band) is about five times smaller. Thus the actual dissociation time can be somewhat longer than 30 fs.

In our calculation we have completely neglected the possible presence of an electric field. It is clear from the calculation that as long as the field is weak enough, so that the wave functions are not strongly affected, it should not affect the dissociation rate either. This is in seeming contradiction with Refs. 12 and 13. We note, however, that the main quantity of interest in those works was the dissociation yield. In our calculation we have not considered the subsequent dynamics of the ejected carrier, in particular, the possibility of relaxing back into the bound state. Clearly, the probablity of this happening can be affected even by a weak field.

For the length L of the conjugation segment we have assumed $L\gg1$, and it dropped out of the final result. When L approaches the polaron size, the very concept of intrasegment dissociation does not make sense (however, the time scale corresponding to τ_{diss} still does—see below). Even for sufficiently large L the probability of relaxation back into the bound state increases with decreasing L, thus decreasing the dissociation yield. For L much larger than the polaron size it would be more correct to start from translationally invariant Bloch states for polarons, as the polaron band width does not have to be vanishingly small (the Huang-Rhys factors are not extremely large). In this case one might also consider the intrasegment dissociation of the exciton polaron into a pair of two charged polarons, which would represent an additional decay channel. However, as we already mentioned in the introduction, the typical value for L is commonly believed to be about 10–20 sites, so the long chain limit does not seem to be relevant.

We can imagine two possible scenarios of the excitation dynamics compatible with the value $\tau_{diss}<100$ fs and the presence of excitons several picoseconds later. First, if the excited vibrational modes decay into other degrees of freedom at least as fast as τ_{diss}, many excitons can survive. This agrees with the value of 35 fs for the effective cooling time of the vibrational heat bath obtained by Arkhipov *et al.* in a completely different model.[13].

Another possibility is that all the excitons are initially dissociated, but the electrons and the holes stay on the same conjugation segment for some time. Clearly, then they can recombine back into the bound state, and the characteristic time of this process should be of the same order as τ_{diss}. More strictly speaking, τ_{diss} in this case plays the role of equilibration time between the electronic and vibrational subsystems. After this time one should speak about the electron and the hole in quasiequilibrium with the local vibrational bath that subsequently cools down, as in the model of Refs. 12 and 13. Note that in this case it does not really matter whether the length of the segment is much larger than the polaron size. As the bath cools down, the carriers can either form an exciton again (which is likely if they stay on the same conjugation segment), or the carriers can escape to neighboring chains or to neighboring segments of the same chain. However, this picture can be valid only if the bath cooling time is longer than τ_{diss}, which disagrees with the results of femtosecond luminescence spectroscopy studies of PPV.[3,11]

In any case our result means that vibronic coherence should be lost in a time of the order of τ_{diss} at most. Although this agrees with several experiments where ultrashort relaxation times were observed, it is in apparent disagreement with experimental results of Ref. 10, where the vibronic coherence in the excited state was seen to persist for about 1 ps. Currently we do not see how these different experimental results can be reconciled.

To summarize, we have estimated the characteristic time of intrachain exciton dissociation by excited molecular vibrations in MeLPPP. Using the available information for this material we have obtained a time below 100 fs. This process alone does not necessarily lead to charge separation: as long as the two carriers stay on the same conjugation segment, they are likely to recombine and form an exciton again; interchain or intersegment carrier hopping are needed to separate them. However, it determines an important time scale of equilibration between the vibrational motion and the electron-hole motion on the segment. Our result agrees with the characteristic time obtained in Ref. 13 from a different model. Different experimental results available do not agree with each other; those corresponding to shorter time scales support our estimate. However, the picture is still far from being clear and more studies are needed, both theoretical and experimental.

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