Hot Charge Transfer States and Charge Generation in Donor Acceptor Blends

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In an organic blend the vibrational normal mode excited by exciton splitting is the same as the one coupled to charge hopping. Excess driving force for exciton splitting can therefore aid charge transfer, if vibrational relaxation is slow compared to charge transfer. A model is developed that takes this into account and hence explains the experimentally observed relation of driving force for exciton splitting and charge yield and that high charge yields can be achieved with the observed fast rates of recombination.

Keywords: charge generation, solar cell, electron phonon coupling

INTRODUCTION

In an organic blend, charges are generated by splitting excitons at the interface between materials with different electron affinities: the donor material is typically responsible for absorbing light and has a greater affinity for holes; the acceptor has greater affinity for electrons. Charges must escape each other’s Coulomb attraction without recombining. Exciton splitting is typically driven by a large (> 0.5 eV) driving force [1]. We develop a model where this excess energy aids charges escape from the Coulomb well. This can happen because the polaron pair formed by exciton splitting is in a vibrational excited state. The mode excited is the superposition of the modes that change the donor from the exciton to the charged geometry and the acceptor from the neutral to the charged geometry. This second mode is also coupled to charge transfer in the acceptor molecule, hence, if the mode is sufficiently long lived, the states formed just after exciton splitting are able to separate more efficiently if extra energy is available.

That hot states are involved in charge separation is not a new idea. Peumans et al. need to assume very large thermalization radii to reproduce experimental charge yields [2]. Models involving hot excitons have been used to describe charge generation in pure polymers [3]. Models by Offermans et al. predict increased charge yields if charges are generated hot [4]. Experiments have also shown that charge mobilities are higher immediately after charge generation [5], suggesting that charge transfer is fastest immediately after exciton splitting. However, how thermalization lengths are connected to molecular properties is not yet understood.

Understanding the link between the driving force for charge separation and quantum yield will help determine the limiting efficiency of organic solar cells (OSC). OSCs can have high quantum efficiencies [6], however open circuit voltages (Voc) are still substantially smaller than the band gap. The Voc for several materials is less than half the maximum of external quantum efficiencies [1]. Until recently, designing better OSC materials was thought to require reducing the energy lost in exciton splitting [7]. Recent measurements by Okhita et al. [8] relate the energy loss and the yield of charges: bad news for OSC as increasing the Voc would also lower quantum yields.

Modeling generation without thermalization requires recombination rates in the microsecond range [4, 9–11] in order to achieve high yields of charges (> 10%). But experimental measurements of the rate of recombination have found it to be faster than nanoseconds [12, 13]. Here high yields are obtained with fast recombination by including the effect of charge transfer from hot states.

The theoretical background for the model developed is given by the Marcus Levitch Jortner (MLJ) equation [14]. The rate of charge transfer becomes:

\[
\Gamma = \frac{\langle i|H|j \rangle^2}{\hbar} \sqrt{\frac{\pi}{\lambda_o kT}} \Sigma_f \langle 0|f \rangle^2 e^{-\frac{4\lambda o kT}{h\omega} + \frac{\Delta G}{kT} + \frac{\Delta \bar{G}}{kT}}
\]

where \( \langle i|H|j \rangle \) is the matrix element for charge tunneling between the diabatic electronic states \( i \) and \( j \), \( \lambda_o \) is the outer sphere reorganization energy four coupling to a classical bath, \( \omega \) is the frequency of the quantum mode and \( \langle 0|f \rangle \) is the Franck Condon overlap between the initial vibrational state (the ground state) and the final one (with quantum number \( f \)). The Franck Condon factor is computed assuming that the initial and final vibrational states are wavefunction of simple harmonic oscillators with identical frequencies but shifted in mass weighted coordinates by \( \sqrt{\Delta} \), the Huang Rhys factor. \( \Delta G \) represents the difference in free energy between the initial and final diabatic states. Each term in the summation represents the probability of resonant electron tunneling occurring between the ground vibrational state of the initial state and the \( f^{th} \) vibrational state of the final states. This equation can be used to model all three processes of interest in the paper: exciton splitting, charge transfer and charge recombination. A caveat is that charge transfer must occur in the non-adiabatic regime, i.e. the transfer integral must be small compared to the electron \( \lambda_o \) and to \( \Delta \omega \).

Figure 1 shows the processes modeled in the paper. Each column of energy levels represents an electronic state, labeled by the distance \( d \) between electron and
hole. At a distance 0 the system is in the neutral ground state (black energy levels) or in the excited state (red energy level). The processes competing are: i) exciton dissociation; ii) charge transfer from a vibrationally excited state; iii) decay of the vibrational energy by internal conversion; and iv) charge recombination to the ground state. Exciton splitting is not modeled explicitly, but is used to provide the initial excited vibrational state.

**METHOD**

The vibronic state \(|i, \nu\rangle\) of the system is described by the outer product of the electronic state \(|i\rangle\) and of the vector describing the vibrational state of the oscillators \(|\nu\rangle\). Each mode in \(|\nu\rangle\) is coupled to the energy of a single electronic state \(|i\rangle\).

When charge transfer occurs between two electronic states \(i\) and \(j\), only the modes of the oscillators coupled to each of those two states will be able to change. If the mode associated with electronic state \(i\) changes from quantum number \(\mu\) to \(\rho\) and the mode associated to \(j\) changes from \(\nu\) to \(\sigma\), the rate of charge transfer can be written as:

\[
\Gamma(\ i, \mu, \nu \rightarrow j, \rho, \sigma) = \sum_{S',S} P(S, A|\nu, \mu) \Gamma(i, S \rightarrow j, S') P(S', A|\rho, \sigma)
\]

where \(\Gamma(i, S \rightarrow j, S')\) represents the rate of transfer between electronic states \(i\) and \(j\) and symmetric combination of the vibrational modes \(S\) to \(S'\). Only symmetric combinations of modes contribute to charge transfer, as the energy difference between two oscillators depends only on the difference of the distortions of each oscillator. The probability terms \(P(S, A|\nu, \mu)\) represent the probability of a system of two simple harmonic oscillators in localised modes \(\nu\) and \(\mu\) to be in a symmetric mode \(S\) and an antisymmetric mode \(A\). By using a probability term, rather than explicitly considering the wavefunction, we implicitly assume that with each charge hop, coherence is lost.

The rate term \(\Gamma(i, S \rightarrow j, S')\) can be computed with a trivial generalisation of the MLJ equation:

\[
\Gamma(i, S \rightarrow j, S') = \langle i| H |j \rangle^2 \frac{\pi}{\lambda_s k T} (S|S')^2 \exp \left( -\frac{(G_{i,j} + \lambda_s + \hbar \omega (S' - S))^2}{4 \lambda_s k T} \right)
\]

where all symbols have the same meaning as in equation 1.

The probabilities \(P(S, A|\mu, \nu)\) can be determined by assuming that the ladder operators for the symmetric/antisymmetric modes are given by combinations of the appropriate localised ladder operators \(a_i^+\) and \(a_i^{-}\):

\[
a_{s/\pi} = \frac{a_i^+ + a_i^{-}}{\sqrt{2}}
\]

The amplitude of the projection of such a state into the corresponding localised modes is:

\[
P(S, A|\mu, \nu) = 2^{-(\mu - \nu)} \left( \sum_{0 \leq m \leq \mu, \nu \leq m} (m + n)! (\mu + \nu - m - n)! \mu! \nu! \delta(A, (m + n)) \delta(S, (\mu + \nu - m - n)) \right)^2
\]

where the \(\delta\) functions ensures that the probability is non-zero only if \(\mu + \nu = A + S\).

As well as charge hopping between vibronic states, a state is also allowed to lose a vibrational quantum by internal conversion at a rate \(k_{VR}\) without changing its electronic state.

The dynamical system defined by these equations is linear and could be solved by writing a master equation, but since the total vibronic phase space is large it is more efficient to solve it by generating a starting state vector \(|1, \nu\rangle\) and updating it using a continuous time random walk algorithm [15]. Rates are then computed only for states as they are needed. The simulation is stopped if either the charges recombines, or if they reaches a certain distance \(d\). We do not explicitly model exciton dissociation, but use the parameters for exciton dissociation to determine the probability of starting the simulation from a particular vibrational level, given by:

\[
P(\nu) = \frac{\Gamma(0, S \rightarrow 1, S') P(S, 0|S' - \nu, \nu)}{\sum_{S'} \Gamma(0, S \rightarrow 1, S') P(S, 0|S' - S)}
\]

where each term in the summation represents the probability of producing a certain symmetric state \(S\) and the probability that the state gives rise to localised state \(\nu\). The excited neutral state is labeled \(0^+\). Note that this expression depends on the difference in energy between the excited state and the first charged state (labelled \(\Delta G\) in figure 1) on \(\lambda_o\), on the Huang Rhys factor and on \(\hbar \omega\), but not on the matrix element.

We apply this model to a one dimensional chain of acceptors, with the hole localised at one end of the chain. Electronic states are uniquely labeled by the distance between hole and electron \(|\bar{i}\rangle\), for example state \(|1\rangle\) will have the electron and hole one lattice apart spacing. State \(|0\rangle\) is the neutral ground state reached if the electron and hole recombine. Each state \(|i\rangle\) is connected to its neighbors \(|i + 1\rangle\) and \(|i - 1\rangle\) with the same transfer integral for charge separation \(V_{CS}\), with the exception of states \(|1\rangle\) and \(|0\rangle\), which are connected by the transfer integral for charge recombination \(V_{CR}\), this allows the timescales for charge transfer and recombination to be controlled independently.

The energy \(E(i)\) of a particular electronic state \(|\bar{i}\rangle\) is determined only by the applied electric field \(F\) and the
Coulomb potential: \( E(i) = \frac{e^2}{4\pi\varepsilon_0 a i} - F a i \), where \( a \) is the lattice constant, \( \varepsilon \) and \( \varepsilon_0 \) are respectively the relative and vacuum permittivities and \( e \) is the charge of an electron. The energy of state \( |0\rangle \) is a fixed value \( E_b \) below the zero of this potential. \( E_b \) is the the pseudo band gap between the highest occupied molecular orbital of the donor and the lowest unoccupied molecular orbital of the acceptor. \( E_b \) and \( \Delta G \) (the driving force for exciton splitting) are shown schematically in figure 1.

RESULTS

All our modeling uses the following parameters for the energetics: \( a = 1 \) nm, \( E_b = -0.9 \) eV, \( \varepsilon = 4 \) and \( F = 5 \times 10^4 \) V/cm. The electric field employed is rather large, smaller fields would be necessary if more subtle models of the polarization of the interface \[16\] [17] lowered the barrier do charge separation, or if a three dimensional model which allowed both charges to move was employed \[8\] [11].

The parameters of the charge transfer equation used are: \( \Delta = 1 \), \( h\omega = 0.17 \) eV, \( \lambda_o = 0.1 \) eV, \( V_{CS} = 0.05 \) eV, and \( k_{VR} = 10^{12} \) s\(^{-1}\), a set of values typical for fullerene \[18\]. The parameters for recombination are the same as above, but with a transfer integral \( V_{CR} = 0.01 \) eV and an energy defined by \( E_b = -1 \) eV. This puts the recombination rate in the sub ps regime. Panel a) in figure 2 shows the conditional probability of the system reaching a certain distance \( d \) given that it has already reached a distance \( d - 1 \) for a range of initial vibrational quanta.

Showing the conditional probability helps identify the thermalization distance, because once the system thermalizes all the curves fall onto each other. Increasing the number of phonons in the initial state massively increases the probability that the charge is able to escape recombination, for example in the initial state state the probability of recombining immediately is 60\%, but with just one quantum of vibrational energy this probability decreases to less than 1\%. Simulations with one extra phonon thermalise after just one hop. The higher excited states thermalise at a distance of 4nm, showing that (for these parameters) thermalization is complete after three or four hops. The inset of panel a) shows the probability of a particular vibrational excited state being created given a certain \( \Delta G \). Clearly highly excited states are more likely for greater \( \Delta G \). Weighing the probabilities computed by the probability that that starting number of phonons is achieved for a certain \( \Delta G \) gives the charge yield as a function of \( \Delta G \).

Panels b), c) and d) show the effect on charge yield at 5 nm as a function of \( \Delta G \) of: the transfer integrals for charge transport (b), the rate of vibrational relaxation (c) and \( \lambda_o \) for charge transport (d). Loss of vibrational excitation can occur in two ways: by internal vibrational relaxation or by losing energy to the classical modes through the external reorganization energy. The yield of charges is therefore the result of competition of three basic process: charge transport, internal vibrational relaxation and charge recombination. Decreasing the transfer integral not only reduces the yield of charges, it also decreases the dependence of yield on \( \Delta G \). This is because slowing down charge transfer not only makes recombination more likely (reducing the yield) it also makes vibrational relaxation faster (reducing the dependence on \( \Delta G \)). Increasing the rate of vibrational relaxation reduces the yield because it causes relaxation to occur faster. \( \lambda_o \) has a large effect because it dictates how much energy is lost to the classical bath with each hop: making it larger makes the system thermalise more effectively through charge transfer.

CONCLUSION

Explicitly modeling charge transfer and vibrational excited states allows high charge yields with fast recombination and explains the dependence of charge yield on the driving force for exciton splitting. Improving charge transport improves charge generation because of more effective competition of charge separation with both charge recombination and vibrational relaxation.

Three conditions must be fulfilled for vibrational excitation to aid charge generation: 1) the vibrational mode excited by exciton splitting must be the same as that coupled to charge separation, 2) vibrational relaxation must be slow compared to charge tunneling, 3) \( \lambda_o \) must
be small to ensure low losses to the classical bath.

The present model makes two fundamental by two assumptions: that coherence is lost at each hop and that the coupling is non-adiabatic. Future work concentrate on tackling these problems. The model allows us to predict that the quantum efficiency of a blend should increase with photon energy. We have assumed that vibrational excitation aids charge separation only in the acceptor molecule. If the modes that lead to exciton splitting are not orthogonal to those coupled to charge transfer also in the donor molecule, the effect of the initial energy would be increased. This provides a design rule for good donor materials.

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FIG. 2: Panel a) The conditional probability of the system reaching a certain distance \( d \) given that it has reached distance \( d - 1 \) for different initial quanta of vibrational excitation. The inset shows the probability distribution of producing a certain number of quanta for various values of the driving force for exciton splitting. The curves are offset for clarity. The value of \( \Delta G \) in eV is shown below each curve. Panels b), c) and d) show the yield of charges at 5 nm as a function of the following parameters: b) the transfer integral for charge separation, c) the rate of internal relaxation, d) the outer sphere reorganization energy. Each curve is labelled by the value of the parameter used in that simulation.

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