Role of structural fluctuations and environmental noise in the electron/hole separation kinetics at organic polymer bulk-heterojunction interfaces.

Eric R. Bittner and Allen Kelley

We investigate the electronic dynamics of model organic photovoltaic (OPV) system consisting of polyphenylene vinylene (PPV) oligomers and [6,6]-phenyl C61-butyric acid methylester (PCBM) blend using a mixed molecular mechanics/quantum mechanics (MM/QM) approach. Using a heuristic model that connects energy gap fluctuations to the average electronic couplings and decoherence times, we provide an estimate of the state-to-state internal conversion rates within the manifold of the lowest few electronic excitations. We find that the lowest few excited states of a model interface are rapidly mixed by C=C bond fluctuations such that the system can sample both intermolecular charge-transfer and charge-separated electronic configurations on a time scale of 20fs. Our simulations support an emerging picture of carrier generation in OPV systems in which interfacial electronic states can rapidly decay into charge-separated and current producing states via coupling to vibronic degrees of freedom.

1 Introduction.

The power conversion efficiencies of highly optimized organic polymer-based photovoltaic (OPV) cells exceeds 10% under standard solar illumination with reports of efficiencies as high as 12% in multi-junction OPVs. This boost in efficiency indicates that mobile charge carriers can be generated efficiently in well-optimized organic heterostructures; however, the underlying mechanism for converting highly-bound Frenkel excitons into mobile and asymptotically free photocarriers remains elusive in spite of vigorous, multidisciplinary research activity. Much of the difficulty in developing a comprehensive picture stems from our lack of detailed understanding of the electronic energy states at the interface between donor and acceptor materials and how these states are influenced by small–but significant–fluctuations in the molecular structure.

The generic photophysical pathways that underlie the generation of mobile charge carriers in an OPV solar cell are sketched in Fig. 1. The absorption of a photon by the material produces a \( \pi - \pi^* \) excitation (exciton) within the bulk (a) that can migrate and diffuse via Förster energy transfer processes. Once in close proximity to a bulk-heterojunction interface, energetic off-sets between the respective HOMO and LUMO levels of adjacent donor and acceptor molecules provide the necessary driving force to separate an exciton into a localized charge transfer (CT) state (b) which typically lies 0.25 to 0.4 eV lower in energy. Alternatively, an exciton may dissociate directly via tunneling into charge-separated (CS) or polaron states (c) which may subsequently evolve to contribute to the photocurrent or undergo geminate or non-geminate recombination to form CT states (d).
We distinguish CT states from CS states by whether or not the donor and acceptor species are in direct contact (CT) or separated by one or more intermediate molecules (CS).

Ultrafast spectroscopic measurements on OPV systems have reported that charged photoexcitations are generated on ≤ 100-fs timescales, however, full charge separation to produce free photocarriers is expected to be energetically expensive given the strong Coulombic attraction between electrons and holes due to the low dielectric constant in molecular semiconductors. Nonetheless, experiments by Gélinas et al., in which Stark-effect signatures in transient absorption spectra were analysed to probe the local electric field as charge separation proceeds, indicate that electrons and holes separate by as much as 40 Å over the first 100 fs and evolve further on picosecond timescales to produce unbound and hence freely mobile charge pairs. Concurrently, transient resonance-Raman measurements by Provencher et al. demonstrate clear polaronic vibrational signatures on sub-100-fs on the polymer backbone, with very limited molecular reorganization or vibrational relaxation following the ultrafast step. Such rapid through-space charge transfer between excitons on the polymer backbone and acceptors across the heterojunction would be difficult to rationalize within Marcus theory using a localised basis without invoking unphysical distance dependence of tunnelling rate constants and appear to be a common feature of organic polymer bulk heterojunction systems.

Polymer microstructural probes have revealed general relationships between disorder, aggregation and electronic properties in polymeric semiconductors. Moreover, aggregation (ordering) can be perturbed by varying the blend-ratio and composition of donor and acceptor polymers. On one hand, energetic disorder at the interface would provide a free-energy gradient for localised charge-transfer states to escape to the asymptotic regions. In essence, the localised polarons in the interfacial region could escape into bands of highly mobile polarons away from the heterojunction region. It has also been suggested that in polymer/fullerene blends, interfacial exciton fission is facilitated by charge-delocalisation along the interface which provide a lower barrier for fission with the excess energy provided by thermally-hot vibronic dynamics.

Finally, we recently presented a fully quantum dynamical model of photo-induced charge-fission at a polymeric type-II heterojunction interface. Our model supposes that the energy level fluctuations due to bulk atomic motions create resonant conditions for coherent separation of electrons and holes via long-range tunnelling. Simulations based upon lattice models reveal that such fluctuations lead to strong quantum mechanical coupling between excitonic states produced near the interface and unbound electron/hole scattering states resulting in a strong enhancement of the decay rate of photo excitations into unbound polaronic states.

In this work, we employ the our model in conjunction with an atomistic quantum/molecular dynamics study of a model donor-acceptor blend to provide an estimate of the interstate transition rates with the excited-state manifold. Our simulations combine a molecular dynamics description of the atomic motions coupled to an on the fly description of the excited state π-electronic structure. By analysing the energy gap fluctuations between excited states, we provide a robust estimate of both the interstate electronic couplings, decoherence times, and transition rates. We begin with a brief overview of our model and then describe our results.

1.1 Heuristic model

A simple model for considering the role of the environment can be developed as follows. Consider a two-state quantum system with coupling λ in which the energy gap Δ(τ) fluctuates in time about its average Δσ, and (Δ(τ)Δ(0)) = σΔ2. In a two-state basis of {0},|1⟩ the Hamiltonian for this can be written as

\[ H = \frac{\Delta(t)}{2} \hat{\sigma}_z + \lambda \hat{\sigma}_x \]  

(1)
where $\hat{\sigma}_z$ are Pauli matrices. Note that Eq. 1 can be transformed such that fluctuations are in the off-diagonal coupling

$$H = \frac{\Delta_0}{2} \hat{\sigma}_z + \delta V(t) \hat{\sigma}_x$$

(2)

where $\Delta_0 = \Delta + \lambda$ and $\delta V(t) = 0$. The fluctuations in the electronic energy levels are attributed to thermal and bond-vibrational motions of polymer chains and can be related to the spectral density, $S(\omega)$ via

$$\bar{V}^2 = \frac{1}{2\pi} S(\omega).$$

(3)

Averaging over the environmental noise, we can write the average energy gap as $\hbar \bar{\Omega} = \sqrt{\bar{V}^2 + \bar{V}^2}$ with eigenstates

$$\vert \psi_+ \rangle = \cos \theta \vert 0 \rangle + \sin \theta \vert 1 \rangle$$

(4)

$$\vert \psi_- \rangle = -\sin \theta \vert 0 \rangle + \cos \theta \vert 1 \rangle$$

(5)

where $\tan 2\theta = \bar{V}/\Delta_0$ defines mixing angle between original kets. Consequently, by analysing energy gap fluctuations, we can obtain an estimate of both the coupling between states as well as transition rates.

1.2 Noise-averaged kinetics

To estimate the average transition rate between states, we first write the equations of motion for the reduced density matrix for a two level system coupled to a dissipative environment,

$$\rho_{11} = -\frac{i}{\hbar} \bar{V} (\rho_{21} - \rho_{12}) - \frac{1}{\tau_1} \rho_{11}$$

$$\rho_{22} = \frac{i}{\hbar} \bar{V} (\rho_{21} - \rho_{12}) - \frac{1}{\tau_2} \rho_{22}$$

$$\rho_{12} = \frac{i}{\hbar} \bar{V} (\rho_{22} - \rho_{11}) - \frac{1}{T_d} \rho_{12} - \frac{i\Delta_0}{\hbar} \rho_{12}$$

$$\rho_{21} = \frac{i}{\hbar} \bar{V} (\rho_{22} - \rho_{11}) - \frac{1}{T_d} \rho_{21} - \frac{i\Delta_0}{\hbar} \rho_{21}$$

(6)

where we have introduced $\tau_1$ and $\tau_2$ as the natural lifetimes of each state and $T_d$ as the decoherence time for the quantum superposition, which in turn, can be related to the spectral density via $T_d^{-1} = \bar{V}/\hbar$. Taking $T_d$ to be short compared to the lifetimes of each state, we can write the population of the initial state as

$$\rho_{11}(t) = \exp \left[ -\left( \frac{1}{\tau_1} + k \right) t \right]$$

(7)

where $k$ is average state-to-state transition rate. Integrating this over time, we obtain an equation of the form

$$\int_0^\infty \rho_{11}(t) dt = \left( \frac{1}{\tau_1} + k \right)^{-1}$$

(8)

suggesting a form for the exact solution of Eqs. 5. Taking the Laplace transform of Eqs. 5 and assuming that our initial population is in state 1 ($\rho_{11}(0) = 1$), Eqs. 6 become a series of algebraic
The average rate vanishes in the limit of rapid decoherence (fluctuations are weak, to a CT state and the other corresponds to a CS state. When the average gap, even low-lying CT states may be brought into strong coupling and the coupling can be treated as a weak perturbation. However, when the off-diagonal couplings are comparable to the average gap, even low-lying CT states may be brought into strong coupling with the CS states.

The implication of this heuristic model is that one can obtain the input to the rate equation (Eq. 10) from mixed quantum classical simulations that take into account the excited state populations. Here we report on such simulations of a model OPV system consisting of a blend of fullerenes and polyphenylene vinylic oligomers as depicted in Fig. 2. Our simulation method employs an atomistic description of the nuclear dynamics described by a force-field that responds to changes in the local bond-order. We specifically chose 1 PCBM and 3 nearby PPV oligomers to represent a model bulk-heterojunction in order to study the penetration of extended intramolecular electronic states into the bulk region. The remaining molecules in the simulation were treated using purely classical force-field. At each step of the simulation, we compute the Hartree-Fock (HF) ground-state for the π system and use configuration interaction (singles) (SCI) to describe the lowest few \( \pi \rightarrow \pi^* \) excitations. Inter-molecular interactions within the active space were introduced via non-bonding Coulombic coupling terms and static dispersion interactions contained within the MM3 forcefield.

Fig. 2 shows a snapshot of the periodic simulation cell containing 50 PCMB molecules and 25 PPV oligomers following equilibration at 100K and 1bar of pressure using classical molecular dynamics (MD) within the NPT ensemble. The molecules surrounding the 4 \( \pi \)-active molecules serve as a thermal bath and electronic excitations are confined to the \( \pi \)-active orbitals. In total, our \( \pi \)-active space included a total of 172 carbon 2p, orbitals and we used a total of 10 occupied and 10 unoccupied orbitals to construct electron/hole configurations for the CI calculations. During the equilibration steps, we assume the system to be in its electronic ground state, after which we excite the system to the first SCI excited state and allow the system to respond to the change in the electronic density within the adiabatic/Born-Oppenheimer approximation. It is important to note that the excited state we prepare is not the state which carries the most oscillator strength to the ground nor do we account for non-adiabatic surface hopping-type transitions in our approach. Our dynamics and simulations reflect the longer-time fate of the lowest-lying excited state populations as depicted in step (d) in Fig. 2. The combination of a classical MD forcefield with a semi-empirical description of a select few molecules within the system seems to be a suitable compromise between a fully \( \text{ab initio} \) approach which would be limited to only a few molecules and short simulation times and a fully classical MD description which would neglect any transient changes in the local electronic density. In spite of the relative simplicity of our model, the simulations remain quite formidable.

3 Results

Over the course of a 50 ps simulation, the lowest lying SCI excitation samples a variety of electronic configurations ranging from localized PCBM excitons to charge-separated and charge-transfer states with varying degrees of charge separation. In Fig. 3, we show the lowest few SCI excitation energies following excitation at \( t = 0 \) fs to the lowest SCI state for one representative simulation. The labels refer to snap-shots taken at 50fs intervals to visualize the various electronic configurations sampled by our approach in Fig. 4. First, we note that following promotion to the lowest lying SCI at \( t = 0 \) there is very little energetic reorganization or relaxation compared to the the overall thermal fluctuations that modulate the SCI eigenvalues. This can be rationalized...
since the excitation to the $\pi^*$ orbitals at any given time is largely
delocalised over one or more molecular units and hence the av-
erage electron-phonon coupling per C=C bond is quite small.
The number of avoided crossings that occur between lowest ly-
ing states is highly striking, signalling that the internal molecular
dynamics even at 100K is sufficient to bring these states into re-
gions of strong electronic coupling.

In Fig. 3b we show a histogram of the energies of the lowest 5
SCI energies accumulated over 50 ps of simulation time follow-
ing promotion to the lowest SCI state. Focusing upon the lowest
lying state (in blue), fluctuations due to molecular dynamics can
account for nearly 0.25eV of inhomogeneous broadening of this
state bringing it (and similarly for the other states) into regions
of strong electronic coupling with nearby states which dramatically
changes the overall electronic character of the state from purely
charge-transfer to purely excitonic on a rapid time-scale.

We next consider the origins of the energy fluctuations evi-
denced in Fig. 3b. While we only show a 200fs segment of a much
longer 50ps simulation, over this period one can see that the CI
energies are modulated with a time-period of about 20 fs. Indeed,
the Fourier transform of the average CI excitation energy reveals
a series of peaks between 1400-1700 cm$^{-1}$ which corresponds
to the C=C stretching modes present in the polymer chains and
fullerene molecules. We conclude that small-scale vibronic fluctua-
tions in the molecular structures and orientations produce sig-
nificant energetic overlap between different electronic configu-
rations in organic polymer-fullerene heterojunction systems and
speculate that this may be the origins of efficient charge separa-
tion in such systems.

A variety of states are produced by our model and we cate-
gorize them as excitonic (electron/hole on the same molecular
unit) occupying $\approx 50\%$ of the states, charge-transfer (electron on
PCMB/hole on PPV#1 (nearest to PCBM)) occupying $\approx 15\%$ of
the states, or charge separated (electron on PCBM/hole on PPV
#2 or #3) occupying $\approx 25\%$ of the states. These are shown in
Fig. 5 where we indicate the local charge-density of each C2$p_z$
orbital by a blue (positive) or red (negative) sphere scaled in pro-
portion to the local charge on each site.

In Fig. 4 we show a sequences of snap shots taken every 50
fs following the initial excitation. These figures reveal the highly
dynamical nature of the lowest lying excitation in which the sys-
ystem samples excitonic configurations (a), charge-transfer configu-
ratings (b,c), charge-separated states in which the electron and
hole are separated by at least one polymer chain (d,e), and highly
mixed charge-transfer/excitonic states as in (e,f). The scenario
depicted here is not an exceptional case within our simulation.
Here, the initial excited state is clearly localized on the PCBM unit
with a high degree of excitonic character. There is clearly some
charge separation within the PCBM; however, both the electron
and hole clearly reside on the PCBM. After 50 fs (c.f. Fig. 4b),
structural fluctuations in part induced by changes in electronic
density and in part by the thermal fluctuations of the surrounding
medium bring this state nearly into resonance with the second SCI
state inducing charge separation between the PCBM and a nearby
Fig. 5 A 6 fs time history from 51 to 56 fs of the first excited CI state is shown in Fig. 3. This series resides around an avoided crossing between the first and second excited state. Showing how a CT state at the interface can evolve into exciton states farther into the bulk around one avoided crossing points. After the excited states diverge, the exciton in the bulk collapses back into an exciton localised on the PCBM.

**Fig. 3c** shows a histogram of the energy gaps between the first and higher-lying excited excited states of our system. According to our heuristic model, the mean ($\mu$) and variance ($\sigma^2$) of the gap distributions can be used as input to estimate the state-to-state rate for this system under the mapping that $\mu = \Delta_o$ and $\sigma^2 = \delta V^2$ as per Eq. 3. Furthermore, we take $T_d^{-1} \approx \bar{V}/\hbar$ as an estimate of the decoherence time. The results are shown in Table 1. The estimated transition rates are consistent with the observation that the system rapidly samples a wide number possible configurations over the course of the molecular dynamics simulation. On average, the state-to-state coupling of 70 meV is comparable to the average energy gaps between the lowest states. This brings the system into the regime of strong electronic coupling. However, larger couplings also imply shorter electronic decoherence times—which dramatically limit the the ability of charges to separate by tunnelling. In this case, any superposition CI states resulting from the quantum mechanical time-evolution of the system would collapse to single eigenstate on a sub-10 fs time-scale due to the interaction with the vibronic degrees of freedom. Based upon our model and simulations, we estimate that within 20 fs, population in any low-lying electronic state is effectively mixed with nearby states simply due to the underlying vibrations of the lattice.

**Table 1** Estimated interstate transition rates from Eq. 10 and vibronic couplings.

| Transition | $\Delta_o$ (eV) | $\bar{V}$ (eV) | $T_d$ (fs) | $\bar{k}^{-1}$ (fs) |
|------------|----------------|----------------|------------|-------------------|
| 1 $\rightarrow$ 2 | 0.11 | 0.06 | 11.41 | 21.8 |
| 1 $\rightarrow$ 3 | 0.18 | 0.08 | 8.66 | 16.6 |
| 1 $\rightarrow$ 4 | 0.26 | 0.08 | 8.70 | 16.7 |

**4 Conclusions**

We present here the results of hybrid quantum/classical simulations of the excited states of a model polymer/fullerene heterojunction interface. Our results indicate that dynamical fluctuations due to both the response of the system to the initial excitation and to thermal noise can rapidly change the character of the lowest lying excited states from purely excitonic to purely charge separated over a time scale on the order of 100 fs. In many cases, an exciton localised on the fullerene will dissociate into a charge-transfer state with the hole (or electron) delocalised over multiple polymer units before localizing to form a charge-separated state. While the finite size of our system prevents further dissociation of the charges, the results are clearly suggestive that such interstate excitation changes over a short time period. Shown here are the excess charge-densities at each atomic site taken at 1 fs intervals. At each 1 fs time-step, the electronic character changes wildly due to strong coupling between the electronic and vibrational degrees of freedom.

PPV oligomer. Further fluctuations bring this state into resonance with other charge separated states as shown in Fig. 4c, d, and f. Because our quantum subspace is restricted to the molecules shown in Fig. 4 charge separation to more distant regions can not occur.
crossing events driven by bond-fluctuations can efficiently separate charges to a distance to where their Coulombic attraction is comparable to the thermal energy.

The nuclear motions most strongly coupled to the electronic degrees of freedom correspond to C=C bond stretching modes implying that small changes in the local lengths have a dramatic role in modulating the electronic couplings between excited states. Since $kT \ll \hbar \omega$ for these modes, they should be treated quantumindependently rather than as classical motions. Generally speaking, including quantum zero-point effects into calculation of Fermi golden-rule rates leads to slower transition rates than those computed using classical correlation functions which implies that the values estimated here are the upper bounds for the actual transition rates. The results presented here corroborate recent ultrafast experimental evidence suggesting that free polarons can form on ultrafast timescales (sub 100fs) and underscore the dynamical nature of the bulk-heterojunction interface.

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