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Theory of non-Condon emission from the interchain exciton in conjugated polymer aggregates

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The authors present here a simple analysis that explains the apparent strengthening of electron phonon interaction upon aggregation in conjugated polymer materials. The overall scheme is that of an intermolecular Herzberg-Teller effect whereby sidebands of a forbidden transition are activated by oppositely phased vibrations. The authors show that upon aggregation, the 0-0 emission becomes symmetry forbidden and the apparent redshift and remaining vibronic structure are due to sideband (0-1,0-2, etc.) emission. At higher temperatures, the 0-0 peak is due to thermal population in a higher lying even-parity vibronic state rather than direct emission from the odd-paritied lowest intermolecular vibronic state. © 2007 American Institute of Physics. [DOI: 10.1063/1.2741250]

Conjugated polymers are quasi-one-dimensional semiconductors of current interest for use in electro-optical devices such as light-emitting diodes and photovoltaic cells.¹ The light emitting species in these materials-the intrachain exciton-is essentially molecular in nature. Interchain aggregation in the solid state reduces the luminescence quantum yield by giving rise to lower lying interchain electronic states. Aggregation has also been observed in many polymer materials with close chain packing.²⁻⁹ Since an interchain state is delocalized over two or more chains, the interchain exciton is more diffuse with substantially weaker electron/ phonon coupling compared to its intrachain counterpart. However, in apparent contradiction to this notion, the C = Cstretching progression in the luminescence appears to strengthen rather than weaken upon aggregation in polyindenofluorenes⁵ and in the highly ordered β phase of polyfluorenes.¹⁰ However, in the latter case, the vibronic shifts may be the result of completely different geometries with the adjacent monomer for the two phases since the peaks in the emission from the β phase do not quite overlap with the peaks in the glassy phase. Photoluminescence studies of silica diluted poly-p-phenylenevinylene (PPV) show that the intrachain and interchain emissions have nearly identical vibronic structure, but the latter is redshifted relative to the former by about one vibrational quanta.⁶ Kobayashi et al.¹¹ have reported similar dual luminescence in polythiophene films, attributing a long-lived component to a molecular 2 ${}^{1}A_{o}$ with a faster component attributed to a higher lying $1B_u$ state both decaying to a symmetric $1 {}^{1}A_{o}$ ground state. Finally, Franck-Condon analysis of the spectra of highly regioregular poly-(3 hexylthiophene) indicates that the dipole-forbidden state has the same interchain nature as in PPV.² However, the authors here invoke a two emitter model with contributions from both intra- and interchain electronic species. The fact that the dark state in question appears at the same position and has the same Franck-Condon coupling as the intrachain exciton casts doubt on the adiabatic separation between these electronic states.

This compels us to develop a model that treats both the electronic and vibrational motions on equal quantum mechanical footing. In this paper, we propose a nonadiabatic interchain exciton transfer model that rationalizes the dual luminescence in terms of an anomalously strong non-Condon sideband emission from the lower dipole-forbidden interchain state. We consider two equivalent polymer chains and use an electronic basis consisting of two states, one in which the exciton is on chain a: $|a\rangle$ and the other in which the exciton is on chain b: $|b\rangle$. For simplicity, we assume that the localized exciton on each chain is coupled to a single vibrational mode on the chain. For this we define our dimer hamiltonian as

$$H = \sum_{n=a,b} |n\rangle \langle n| \left(\epsilon_n + \sum_k \left(\hbar \omega_k a_k^{\dagger} a_k + g_{nk} (a_k^{\dagger} + a_k) \right) \right) + V_{ab} (|a\rangle \langle b| + \text{H.c.}),$$
(1)

where $\epsilon_{a,b}$ are the vertical electronic excitation energies relative to the ground state of the undimerized system with $|a\rangle$ and $|b\rangle$ being localized excitonic states on chain *a* and *b*, respectively. The $\{a_k, a_k^{\dagger}\}$ are annihilation/creation operators for intramolecular phonon mode *k* with frequency ω_k . Our model assumes one intramolecular phonon mode on each chain. The intermolecular off-diagonal term V_{ab} mitigates the transfer of an electronic excitation from molecule *a* to *b*.

The relevant diabatic potentials can be written as

$$U_a(\mathbf{q}) = \hbar \,\omega (\mathbf{q} - \mathbf{q}_a)^2,\tag{2}$$

126, 191102-1

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$$U_b(\mathbf{q}) = \hbar \,\omega (\mathbf{q} - \mathbf{q}_b)^2,\tag{3}$$

taking the origin q=0 to be the equilibrium geometry of the ground electronic state. If the chains are equivalent, the harmonic frequencies and equilibrium displacements are the same for both chains. To put this into parameters suitable for conjugated polymers, we take $\hbar\omega=0.18$ eV as the C=C stretching frequency, which is a typical value for polymers such as PPV.¹² The distortions can be deduced from the intensity ratios of the vibronic sidebands. Assuming the emission is largely from the lowest vibronic level (n=0) in the excited state to the *n*th vibronic level in the ground state, the 0-n intensity ratio is approximately given by I_{0-n} $\propto S^n e^{-S}/n!$, where S is the dimensionless Huang-Rhys factor. For frequency scaled coordinates, $q_a = S^{1/2}$ is the displacement of the mode in the excited state. Moreover, the localization energy of the exciton E_r is equivalent to the Stokes shift $E_r = E_s = \hbar \omega q_a^2 = \hbar \omega S$. For conjugated polymers, such as PPV, the higher frequency modes are usually well resolved with equal intensity in the 0-1 and 0-0 vibronic emission peaks giving a Huang-Rhys factor of S=1.^{13,14}

As in molecular H aggregates, the nearly forbidden lower energy interchain component observed in close-packed polymers is consistent with an electronic interaction $V_{ab} > 0$. However, the magnitude of this interaction is elusive and varies with structure and morphology. Interchain interactions can be covalent electron-transfer-type couplings^{9,15} or noncovalent, exciton-transfer-type couplings mediated by Coulomb coupling between transition densities on the separate chains.^{16,17} Here, we consider the dominant interaction to be transition dipole-dipole interactions not only because the resulting Förster transfer is ubiquitous in polymer films¹⁸ but also because the head-to-head alignment of the monomeric transition moments in adjacent chains warrants the positive sign of the interaction. Moreover, accurate quantum chemical computations^{19,20} of the Davydov splitting $(2V_{ab})$ for molecular dimers show that it roughly follows the dipole-dipole interaction behavior. Using a Frenkel exciton model developed for PPV and a local dipole approximation derived from configuration interaction theory, we obtain $V_{ab} \approx 0.06$ eV or about $\hbar\omega/3$ for parallel PPV oligomers cofacially stacked 4 Å apart. This is consistent with values obtained using more accurate levels of theory.²⁰

Assuming V_{ab} is independent of the intramolecular coordinates, we can write the adiabatic potential energy surfaces for the upper and lower states as

$$U_{\pm} = \frac{1}{2}(U_a + U_b \pm \sqrt{(U_a - U_b)^2 + 4V_{ab}^2})$$

A sketch of the adiabatic potentials along the q_1 - q_2 coordinate is shown in Fig. 1. So long as $E_r > V_{ab}$, the lower energy potential surface has two minima separated by a barrier. Consequently, with the parameters adopted here, it may seem appropriate to treat the interchain exciton as an incoherent hopping process. However, the regime of exciton hopping can at best be qualified as nonadiabatic since the hopping frequency V_{ab}/\hbar is lower, but comparable to the frequency of the Franck-Condon mode, ω . Consequently, we cannot totally separate the electronic and vibrational degrees of freedom (Condon approximation) in estimating the optical trans-



FIG. 1. Adiabatic potential for the interchain vibronic states along the q_1 - q_2 direction.

sitions to the ground state since in going from one potential minima to the other, the electronic wave function changes from one single exciton to the other, passing over the saddle point as the dipole-forbidden antisymmetric combination of the two. The presence of two electronic origins rules expansion in terms of the vibronic coupling (i.e., Herzberg-Teller coefficient) as well.^{21,22}

We can transform to a shifted representation by the unitary transformation $\tilde{H} = U^{\dagger}(H_o + V)U$ where H_o and V are the diagonal and off-diagonal term in H, and U is the unitary transformation operator

$$U = \exp\left[-\sum_{ak} |a\rangle \langle a| \frac{g_{ak}}{\hbar \omega_k} (a_k^{\dagger} - a_k)\right]$$
(4)

$$=\sum_{n} |n\rangle \langle n| \exp\left[-\sum_{k} \frac{g_{ak}}{\hbar \omega_{k}} (a_{k}^{\dagger} - a_{k})\right].$$
(5)

In the transformed representation

$$\widetilde{H}_0 = \sum_a \widetilde{\epsilon}_a |a\rangle \langle a| + \sum_k \hbar \omega_k a_k^{\dagger} a_k,$$

where

$$\widetilde{\boldsymbol{\epsilon}}_{a} = \boldsymbol{\epsilon}_{a} - \sum_{k} \frac{g_{ak}^{2}}{\hbar \omega_{k}}$$

and the quantity $E_s = \sum_k g_{ak}^2 / \hbar \omega_k$ is the Stokes shift. The coupling matrix can be expressed as

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FIG. 2. (Top) Lowest two vibronic states for the dimer. The dashed line along $q_1=q_2$ contains the plane defining the *A* or *B* symmetry of the vibronic wave functions. (Bottom) Energy splitting of vibronic levels vs interchain coupling. The long-dashed lines at $E=\hbar\omega$ and $E=2\hbar\omega$ are the energies of the degenerate uncoupled levels. A_n and B_n indicate the symmetry of the final vibronic state under reflection between the two chains.

$$\widetilde{V} = \sum_{a \neq b} V_{ab} |a\rangle \langle b|$$

$$\times \exp\left[\sum_{k} \frac{g_{ak}}{\hbar \omega_{k}} (a_{k}^{\dagger} - a_{k}) - \sum_{k'} \frac{g_{bk'}}{\hbar \omega_{k'}} (a_{k'}^{\dagger} - a_{k'})\right]$$

$$= \sum_{a \neq b} V_{ab} |a\rangle \langle b| M_{ab}.$$
(6)

The matrix M_{ab} in this last equation is the matrix of Franck-Condon factors between a vibrational level of chain *a* with a vibrational level on chain *b*.

For the molecular dimer, we can solve the eigenvalue problem $H\psi = E\psi$ to obtain the fully coupled vibronic states of the system.²⁶ The resulting eigenstates are either symmetric (A) or antisymmetric (B) under the twofold symmetry of the dimer. The lowest two of these are shown in the upper panel of Fig. 2 with the dashed line containing the symmetry mirror plane between the two phonon coordinates. In the lower panel of Fig. 2, we plot the vibronic sublevels versus the interchain coupling. Since the vibrational overlap is small, the splitting of the components is small compared to V_{ab} . Moreover, in general, the *antisymmetric* states are lower in energy than the corresponding symmetric states. Also, the redshift of the B_0 state from the zero-phonon exciton level is greater than the corresponding blueshift of the A_0 state, indicating that the multiphonon coupling exerts some downward pressure on the low-lying interchain states.

We next turn our attention towards the allowed optical transition between the dimer exciton states and the dimer ground state. The vibrational levels in the ground state are



FIG. 3. (Top) Emission (solid) and absorption (dashed) spectra for model dimer system at T=1 K and T=300 K. Note that the electronic origin has been set at E=0. (Bottom) Absorption and emission spectra for isolated single chain.

simply those of a two dimensional isotropic harmonic oscillator centered at the origin (corresponding to the undistorted ground-state geometries of the two molecular chains). Of these *only* the lowest lying level is the result of a state that is totally symmetric. The remaining levels with increasing degeneracy contain both symmetric, asymmetric, and nonsymmetric wave functions. For example, the (2,0) and (0,2)states are neither symmetric nor asymmetric while the (1,1)is symmetric. For notation, let us refer to these states as G_n where n indicates the total number of vibrational quanta. Consequently, dipole transitions from the lowest B_0 exciton vibronic level to the G_0 is forbidden, while transitions between the B_0 to the other vibrational levels should give rise to vibrational sidebands comparable in strength to transitions from the A_n levels. This is akin to the Herzberg-Teller effect in molecules whereby the sidebands of a forbidden transition are activated by oppositely phased intramolecular vibrations. Small statistical variations of the single exciton electronic origins will weakly allow the A_0 to G_0 transition and strengthen its sidebands.

In order to highlight the spectroscopic signatures of the interchain coupling mechanism we propose, we calculated the absorption and emission spectra of an isolated chain and a chain dimer. The intrachain (isolated) spectrum is given in Fig. 3. The spectra show the typical vibrational fine structure one expects for a simple single oscillator mode system. The absorption and emission spectra are mirror images about the central 0-0 peak. The aggregate spectra is quite a bit differ-

ent. As shown in Fig. 3, we no longer see mirror symmetry about the 0-0 peak. In fact, at low temperature, the 0-0 peak is completely absent in the emission spectra. As indicated above, this is due to the fact that at low temperature, only the B_0 has any thermal population and the B_0 - G_0 transition is forbidden. The remaining features are the sidebands. Increasing the temperature to T=300 K (for the parameters above, T=300 K $\approx \hbar \omega/7k_B$) imparts some population to the A_0 state and we begin to see the A_0 - G_0 feature in the emission spectra. The resulting strengthening of the sidebands upon aggregation is wholly consistent with emission bands reported for ordered films of a number of conjugated polymer systems.^{3,4,6,10}

In short, our model resolves a crucial and perhaps controversial issue regarding whether the emission spectrum of conjugated polymer dimers is molecular or intermolecular in origin. Our analysis indicates that the lowest energy intermolecular excited vibronic state (B_0) is of odd parity with respect to the intermolecular mirror plane. Hence, the vibronic transition from this state to the even parity ground state are forbidden by symmetry. However, thermal population of higher lying vibronic states can give rise to emission at approximately the 0-0 energy giving what appears to be a weakening of the 0-0 transition compared to the photoemission spectrum of an isolated chain. Hence, the emission features typically labeled 0-1 and 0-0 are interchain in nature.

Our approach, however, does leave open the question of morphology and aggregation in the bulk. It is not clear whether the survival of the 0-0 peak in the emission is due to a short lived S_0 transient, to breaking of symmetry in the stacking, or to disorder. A small A_0 - G_0 coupling is likely since the corresponding feature appears in the absorption spectrum.² It is entirely possible that in a three-dimensional stacking configuration, the Davydov splitting, and symmetry of the states at the Γ point may be quite different than that of the dimer, as may be the case with the different phases found in polyfluorene films.⁵ We note that the issue of disorder in polymer aggregates has been recently explored by Spano and co-worker²³⁻²⁵ using a generalized Holstein model with disorder introduced as Gaussian noise in the intermolecular couplings. Increasing disorder breaks symmetry within the aggregate leading to an increase of the 0-0 line strength with increasing disorder in H aggregates. Consequently, in the disordered limit, the 0-0 emission is molecular in origin.

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