A Simple Model For The Relaxation Dynamics in Perylene-Bisimide Dimers Excited by Femtosecond Laser Pulses

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Motivation: Energy Transport

Organic semiconductors
• promising materials in organic solar cells
• low quantum yield because of inefficient exciton energy transport in the material
• quenching processes → "self-trapping"

Investigated system: perylene bisimide (PBI) [1]
• PBI forms π-aggregates
• laser-generated excitons localize on dimer units → PBI dimers used as model system

![Figure 1: Energy transport in PBI aggregates](image)

Spectra

Absorption spectrum [2]
• dimer model
• one effective mode per monomer

![Figure 2: Absorption and emission spectra](image)

Emission spectrum [3]
• broad, red shifted band
• description by additional torsional mode

![Figure 4: Potential curves as a function of the torsional angle](image)

Transient absorption spectroscopy:
• step function → ground state bleach
• exponential decay with \( t = 215 \text{ fs} \) → stimulated emission
• oscillatory term with a period of 381 fs → quantum beats

Main result:
• ultrafast de-population of the excited (bright) state on a timescale of 215 fs [4] → self-trapping, no effective energy transport
• pathway via torsional motion not accessible
• explanation: coupling to CT states

Excitation Scheme

![Figure 8: Potential \( V_{\text{ex}} \) of the electronic ground state and diabatic potentials \( V_{\text{dd}} \) of the excited states. The black arrows depict the excitation scheme.](image)

Dimer Model and Effective Coordinate

4 coupled excited states
• 2 neutral
• 2 exciton-transfer

One effective coordinate \( q \), PBI dimers at ground state geometry
• \( q = 0 \): two neutral structures
• \( q = 1 \): one cation, one anion
• near the Franck-Condon region the CT states have higher energy than the Frenkel states → deformation along \( q \) enables coupling to CT states

![Figure 5: The four localized excited dimer states, Black: Frenkel states, Red: CT states.](image)

Determination of the potentials

• adiabatic potentials along \( q \) quantum-chemically calculated
• nonadiabatic coupling elements unknown
• diabatization using CT characters of the adiabatic potentials → diabatic Potential curves \( V_{\text{dd}} \) with \( i = 1-4 \) and couplings \( J_{12}, J_{23}, J_{34} \)

![Figure 7: Left: Adiabatic potential curves and CT characters. Right: Diabatic states and couplings](image)

Stochastic Schrödinger Equation

The employed dissipation model neglects the stochastic nature of energy transfer between system and bath. Energy dissipation is correctly described by coupling the isolated quantum system to a thermal bath. This problem can be reduced to an equation of motion for the density matrix of the system (Lindblad equation). Going back to a wavefunction based representation leads to stochastic and dissipative terms in the time-dependent Schrödinger equation. In harmonic approximation this equation can be solved by different methods like stochas-tic Schrödinger equation formalism or Monte-Carlo wavefunction simulations.

Refined dissipation model: quantum state diffusion (QSD form)

Diabatic potentials \( V_{\text{dd}} \) approximately harmonic → stochastic Schrödinger equation for harmonic system

\[
dp{\rho}(t) = -\mathcal{H}\rho(t)\frac{\text{d}}{\text{d}t} + \sum_{\alpha} C_{\alpha}(\rho(t))\frac{\text{d}}{\text{d}t} + \gamma(\rho(t)) + \mathcal{D}(\rho(t))\, ,
\]

with

\[
C_{\alpha} = \frac{1}{2} \int d\omega \left[ (\alpha_{\text{in}} - \alpha_{\text{out}}) + (\alpha_{\text{in}} - \alpha_{\text{out}})^{\circ}\right] |\omega| \mathcal{W}(t)
\]

\( \gamma \): dissipation constant
\( \mathcal{D}(\rho(t)) \): annihilation/creation operator
\( \mathcal{W}(t) \): stochastic Wigner increment

![Figure 11: Dynamics of the population \( P_{2}(t) \) of the excited bright state \( V_{\text{F}} \) for different dissipation constants \( \gamma = 1 \times 10^{-4} - 5 \times 10^{-7} \).](image)

References


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