

Supporting information for:

Hole Hopping Rates in Organic Semiconductors:

A Second Order Cumulant Approach.

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Methodology adopted in TDSE simulation

We adopted a partition of the whole Hilbert space H into subspaces h_s in which only s vibrational degrees of freedom are simultaneously excited.

$$H = \bigcup_s h_s,$$

Time dependent wavefunction is then written as the sum of all the contributions belonging

to each subspace:

$$\Psi(t) = \sum_{\ell} \left[C_{\ell,0}(t) |\ell, 0\rangle + \sum_i^N \sum_{v_i} C_{\ell,v_i}(t) |\ell, v_i\rangle + \sum_{ij}^{\binom{N}{2}} \sum_{v_i, v_j} C_{\ell,v_i, v_j}(t) |\ell, v_i, v_j\rangle + \dots \right] \quad (1)$$

and the expansion 1 is truncated when the contributions of higher dimension subspaces is lower than a given threshold. In eq.n 1, $|\ell, 0\rangle$ is the vibrational ground state of the ℓ -th electronic state and $|\ell, v_i\rangle$ and $|\ell, v_i, v_j\rangle$ denote states belonging to Hilbert subspaces in which only one and two vibrational degrees of freedom respectively are simultaneously excited; i and j run on the N active normal modes of the ℓ -th electronic state and v_i runs on vibrational quantum numbers of the i -th mode.

The above partition stems from the observation that Franck-Condon (FC) integrals usually decrease as the number of simultaneously excited modes increases.^{S1-S3} Since the coupling terms are proportional to FC integrals, it is reasonable to expect that vibronic states which are more effectively coupled to electronic motion are included in the subspaces with lower dimensions. Expansion 1 has been successfully used in spectroscopic problems,^{S1,S2} and, more recently, in quantum dynamics of hole transfer in DNA oligomers.^{S4}

Convergent time dependent populations have been usually achieved by including two subspaces (h_1 and h_2) in eq.n 1, whereas as concerns the number of basis function used for each mode seven Hermite functions for h_1 and five for h_2 guarantee convergence for the most difficult cases.

SOC and TDSE comparison

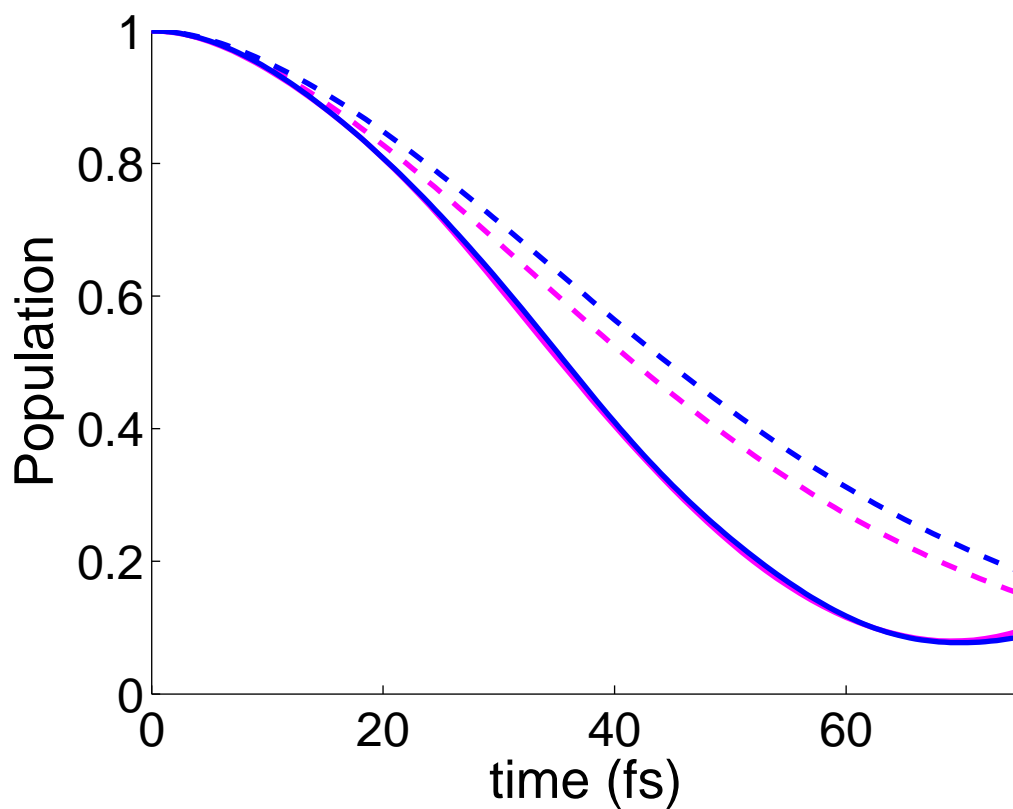


Figure S1: Comparison for the channel 2 of pentacene between time decay probabilities for hole hopping in dimers predicted by the numerical solution of the time dependent Schrödinger equation, full line, and from second order cumulant expansion of the reduced density matrix, dotted line. Initial state: equilibrium thermal population of the cationic state, magenta; equilibrium thermal population of the neutral state, blue.

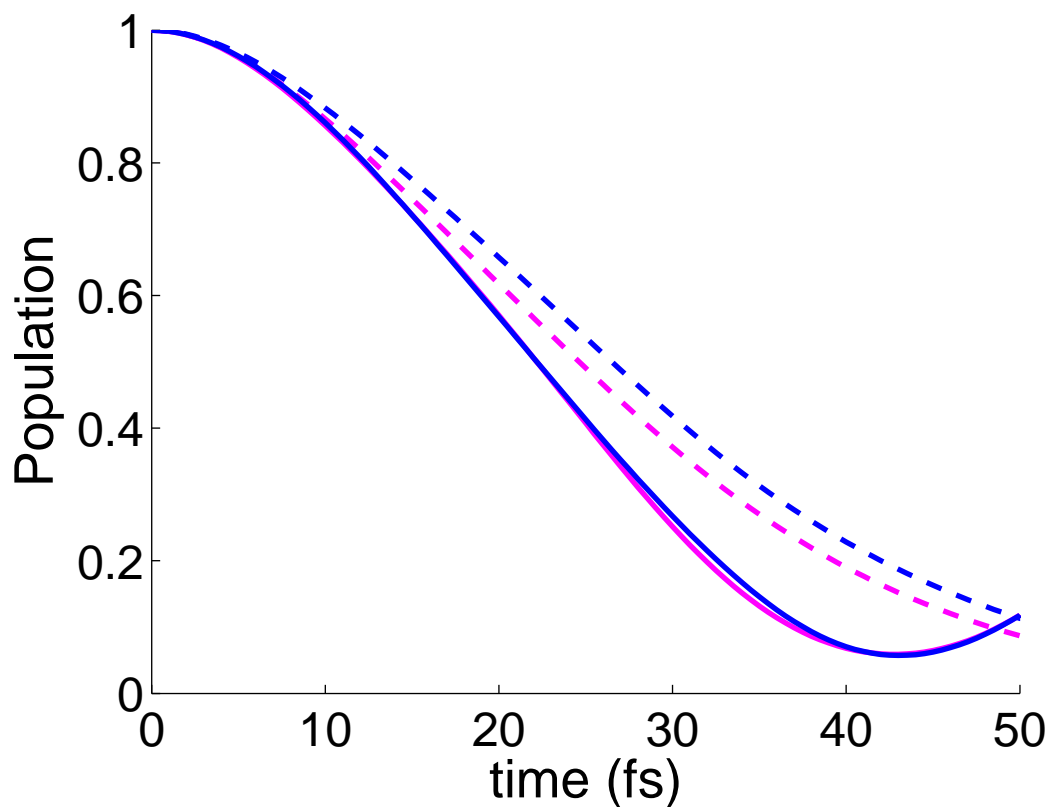


Figure S2: Comparison for the channel 3 of pentacene between time decay probabilities for hole hopping in dimers predicted by the numerical solution of the time dependent Schrödinger equation, full line, and from second order cumulant expansion of the reduced density matrix, dotted line. Initial state: equilibrium thermal population of the cationic state, magenta; equilibrium thermal population of the neutral state, blue.

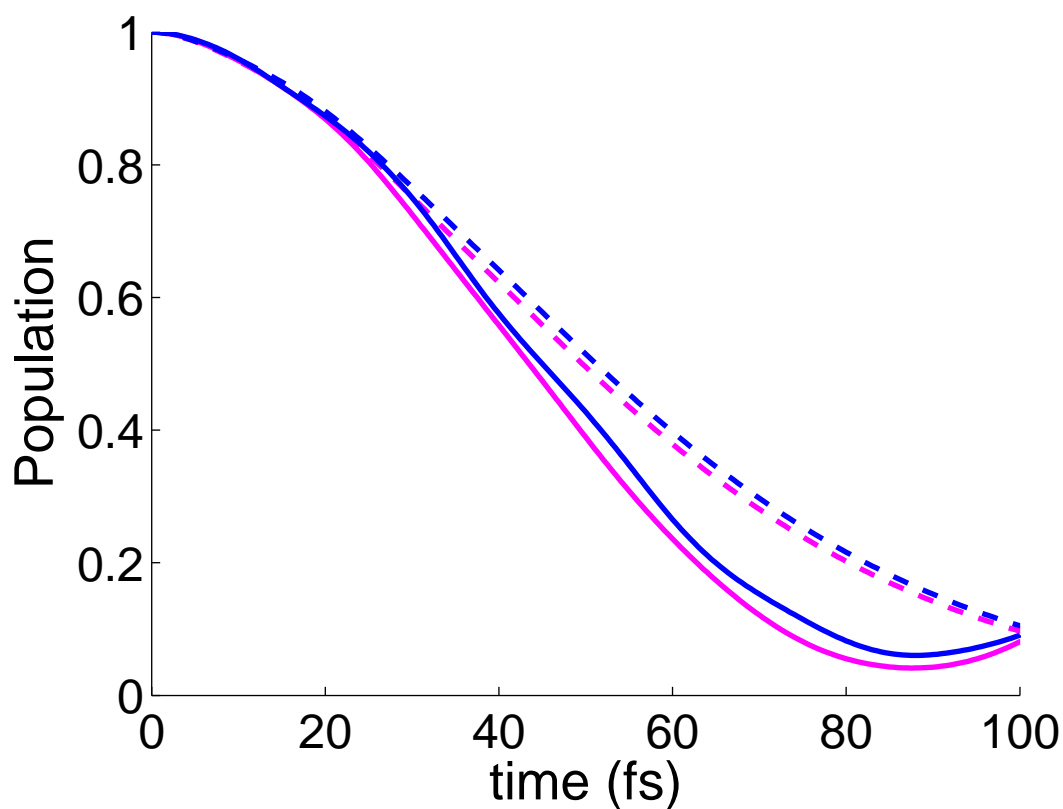


Figure S3: Comparison for the channel 1 of tetracene between time decay probabilities for hole hopping in dimers predicted by the numerical solution of the time dependent Schrödinger equation, full line, and from second order cumulant expansion of the reduced density matrix, dotted line. Initial state: equilibrium thermal population of the cationic state, magenta; equilibrium thermal population of the neutral state, blue.

Reorganization energy in gas phase

Table S1: Frequencies (ω , cm^{-1}), intramolecular reorganization energies (E_r , cm^{-1}), and equilibrium position displacements (\mathbf{K} , $\text{\AA} \text{ uma}^{-1/2}$) of the most displaced normal modes of pentacene/pentacene⁺ (P/P⁺), picene/picene⁺ (PC/PC⁺), rubrene/rubrene⁺ (R/R⁺) and tetracene/tetracene⁺ (T/T⁺) redox pairs.

P/P ⁺			PC/PC ⁺			R/R ⁺			T/T ⁺		
ω	E_r	\mathbf{K}	ω	E_r	\mathbf{K}	ω	E_r	\mathbf{K}	ω	E_r	\mathbf{K}
263	8.93	-0.26	141	2.74	-0.20	21	68.33	-2.38	318	3.54	-0.15
804	2.00	-7.1 10^{-2}	260	62.34	-0.70	68	7.76	-0.48	760	1.50	0.063
1023	4.19	-9.0 10^{-2}	426	7.86	0.19	84	32.36	0.90	1187	22.74	-0.20
1186	20.57	-0.19	595	64.32	-0.47	213	9.38	0.30	1230	52.38	0.29
1213	53.82	-0.30	1392	220.02	0.56	253	4.87	-0.20	1420	26.94	-0.20
1442	138.85	-0.44	1657	147.60	0.42	996	21.26	-0.20	1434	141.72	-0.44
1564	81.51	0.32	1665	129.02	0.40	1336	119.27	0.42	1654	117.01	-0.38
						1586	11.15	0.37			
$E_{r,\text{tot}}$	372			716			609			440	

References

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