Quantum Dynamics of Ultrafast Exciton and Charge Migration in π-Conjugated Materials: Coherence, Confinement, and Localization

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Topics

1. Photoinduced Energy & Charge Transfer in Functional Organic Materials
   - Goal: First-Principles Approach to Organic Photovoltaics
   - Electron-Hole Lattice Models & Vibronic Coupling
   - Quantum Dynamics in Many Dimensions

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   - Torsion-Induced Intra-Chain Exciton Migration
   - Ultrafast, Coherent Exciton-Polaron Dynamics
   - How Good Is Ehrenfest-Langevin Dynamics?

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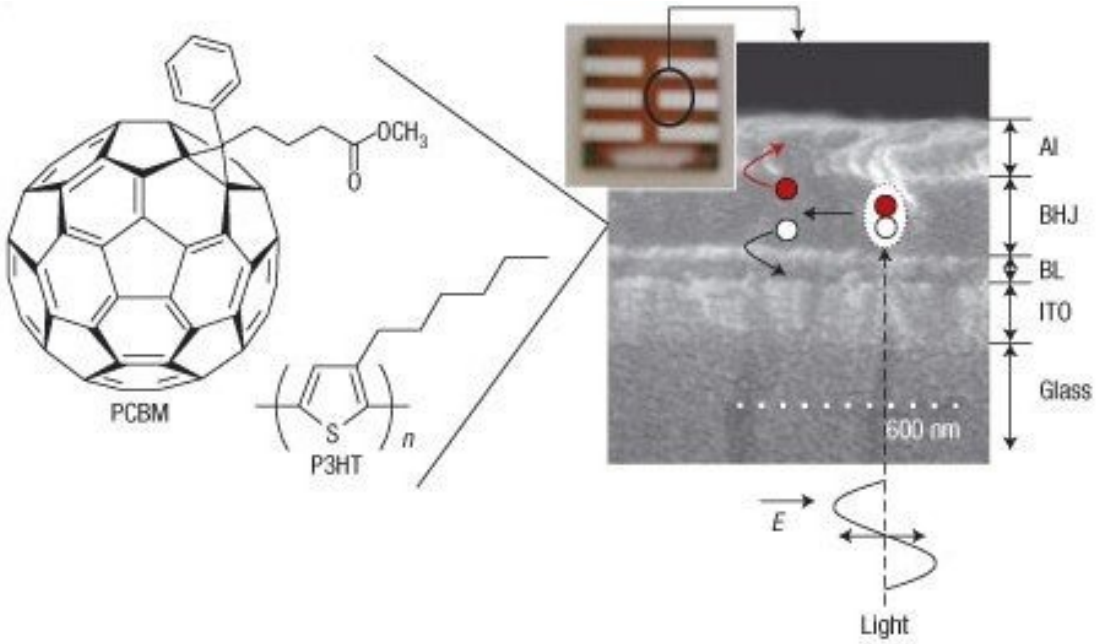
3. Case Studies II: Charge Transfer Excitons & Charge Separation
   - Charge Transfer Excitons in Neat Polythiophene
   - Charge Transfer Excitons and Interfacial Charge Separation
   - Highly Ordered Oligothiophene-Perylene Assemblies

Elementary Processes of Organic Photovoltaics



Kim et al., Nature Materials, 5, 197 (2006)

elementary steps:

- creation of electron-hole pairs (excitons)
- exciton migration to donor-acceptor interface area
- exciton dissociation at donor-acceptor junctions (here, PCBM-P3HT)[1]
- capture of charge carriers at electrodes
- potentially competing process: electron-hole recombination

[1] PCBM = phenyl-C_{61}-butyric acid methyl ester, P3HT = poly(3-hexylthiophene)

What is the Best Nano-Morphology?

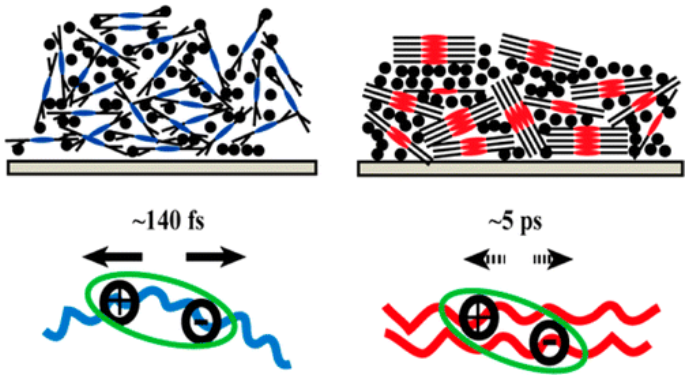
Highly ordered nanostructured domains (typically sub-10 nm) are thought to

- facilitate exciton diffusion
- favor exciton dissociation
- facilitate free carrier transport

Nanostructured domains can be achieved by

- self-assembly properties of D/A oligomers
- thin film processing methods (e.g., nanoimprint lithography)

However, the role of nanoscale ordering is controversial:

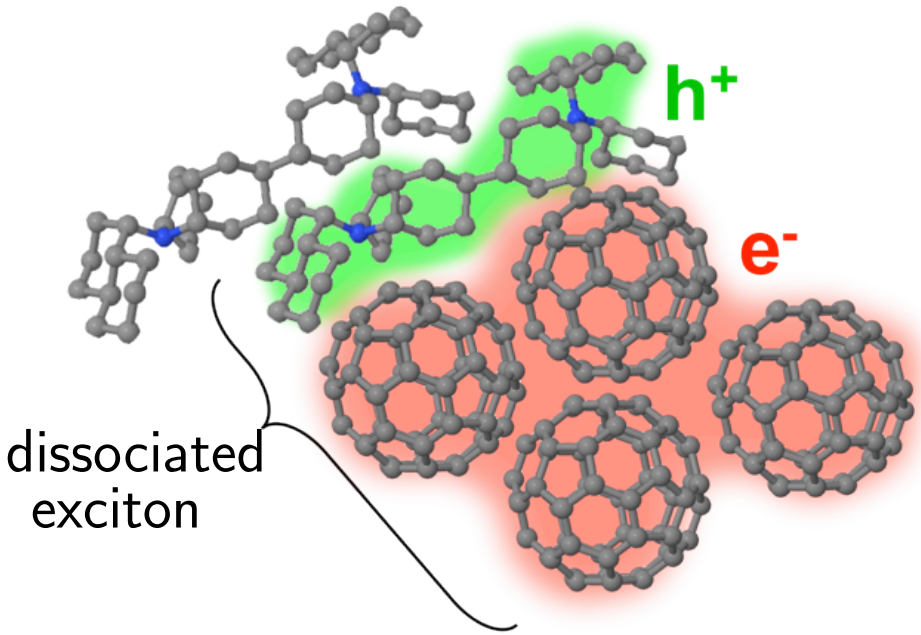


Guo et al., JACS 136, 10024 (2014)

- e.g., in a recent study of DA copolymer:fullerene systems, it is shown that the charge separation energetics changes unfavorably upon formation of crystalline domains

Which Methods, Even for a Minimal Model?

- tens to hundreds of electronic states
- aggregate-type systems
- charge transfer and excitonic couplings$^{(*)}$ required
- delocalized excitations
- strong electron-phonon coupling
- non-Markovian dynamics
- non-exponential transfer
- coherent wavepacket dynamics
- standard rate theories (Förster / Marcus) not necessarily valid



http://phys.org/news/2014-02-result-cheaper-efficient-solar-cells.html

$^{(*)}$excitonic coupling = transition density interaction:

$$V_{DA} = \frac{1}{4\pi\varepsilon_0} \int d\boldsymbol{r}_D \, d\boldsymbol{r}_A \, \frac{\rho_D^{(eg)}(\boldsymbol{r}_D)\, \rho_A^{(ge)}(\boldsymbol{r}_A)}{|\boldsymbol{r}_D - \boldsymbol{r}_A|} \longrightarrow \text{limiting case: transition dipole interaction}$$

Two Types of Approaches

approximate electron-nuclear dynamics: e.g., time-dep. Kohn-Sham equation

$$i\frac{\partial}{\partial t}\varphi_i(r,t) = (-\frac{\nabla^2}{2} + v_{\mathrm{KS}}(r,t))\varphi_i(r,t)$$

expand in adiabatic KS basis, $\varphi_i(r,t) = \sum_k c_{ik}(t)\tilde{\varphi}_k(r;R)$ such that

$$i\frac{dc_{ik}}{dt} = \sum_l c_{il}(t)(\varepsilon_l\delta_{kl} + d_{kl}\cdot\dot{R})$$

Ehrenfest or Surface Hopping dynamics

e.g., Craig, Duncan, Prezhdo, PRL 95, 163001 (2005)

pro's: no pre-computed potentials
con's: possibly poor description of excited states and nuclear dynamics

parametrized model Hamiltonian + multi-state quantum nuclear dynamics

$$i\frac{\partial}{\partial t}\psi(R,t) = \hat{H}\psi(R,t)$$

with a multi-state/site Hamiltonian

$$\hat{H} = \sum_{mn}(\hat{h}^e_{mn} + \hat{h}^{e\text{-}ph}_{mn}(R))|m\rangle\langle n| + \hat{H}^{ph}_0(R)$$

and $|\psi(R,t)\rangle = \sum_n c_n(t)\Phi_n(R,t)|n\rangle$

use (approximate) quantum dynamics

e.g., Kondov et al., JPCC 111 (2007), Tamura et al., JACS 135 (2013)

pro's: immediate physical interpretation
con's: restricted number of coordinates, electronic couplings *via* diabatization

Road Map: Model Hamiltonians & Quantum Dynamics

e-h lattice models + non-perturbative *e-ph* interaction + quantum dynamics

- electron-hole (*e-h*) lattice models including vibronic interactions
- *ab initio* (typically CC2, ADC(2)) and/or TD-DFT parametrization
- diabatization procedures to generate electronic couplings
- compute spectral densities and effective-mode decomposition
- efficient high-dimensional nonadiabatic quantum dynamics using multi-configurational methods (MCTDH) or reduced dynamics (HEOM)

- "molecular aggregate" perspective rather than "solid state" perspective: parametrization for small fragments & dynamics for larger systems

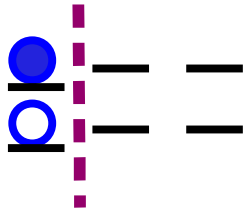
CC2 = Second-Order Approximate Coupled-Cluster

ADC(2) = Second-Order Algebraic-Diagrammatic Construction (ADC(2)) scheme

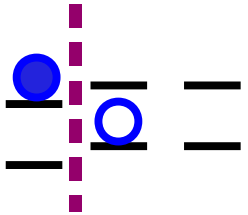
MCTDH = Multi-Configuration Time-Dependent Hartree Beck et al., Phys. Rep. **324**, 1 (2000)

HEOM = Hierarchy of Equations of Motion Tanimura, J. Phys. Soc. Jpn. **75**, 082001 (2006)

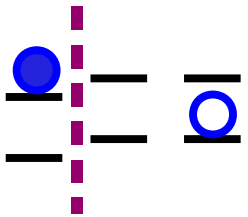
Electron-Hole Lattice Model



$|1_e\rangle_C \otimes |1_h\rangle_V$



$|1_e\rangle_C \otimes |2_h\rangle_V$



$|1_e\rangle_C \otimes |3_h\rangle_V$

- electron-hole (e-h) configurations:
  $|\mathbf{n}\rangle = |n_e n'_h\rangle = |n_e\rangle_C \otimes |n'_h\rangle_V$
- Hamiltonian in this basis:

$$\hat{H} = \sum_{\mathbf{mn}} (\hat{h}^{eh}_{\mathbf{mn}} + \hat{h}^{eh\text{-}ph}_{\mathbf{mn}}(\mathbf{x}))|\mathbf{m}\rangle\langle\mathbf{n}| + \hat{H}^{ph}_0(\mathbf{x})$$

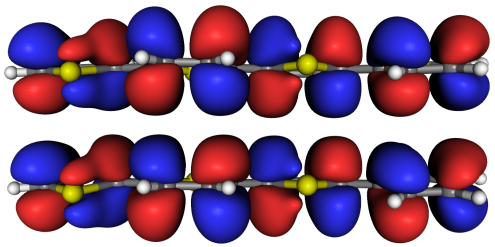
Merrifield, J. Chem. Phys. 34, 1835 (1961)
Wang and Mukamel, Chem. Phys. Lett. 192, 417 (1992)
Karabunarliev and Bittner, J. Chem. Phys. 118, 4291 (2003)
Binder, Wahl, Römer, Burghardt, Faraday Discuss, 163, 205 (2013)

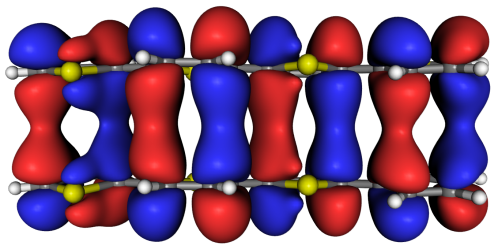
- includes Frenkel-type exciton (XT) states and charge transfer (CT) states
- oligomer (fragment) *ab initio* or TDDFT calc's: on-site energies, diabatic couplings
- vibronic couplings from Franck-Condon gradients, geometry optimization, PES cuts

Special Case: Frenkel Exciton Model

- Frenkel model ($n_e = n'_h = n$) often a good approximation to describe exciton
- exact analytic mapping of oligomer PES's to Frenkel model

  Binder, Römer, Wahl, Burghardt, J. Chem. Phys. 141, 014101 (2014)





stacked oligothiophene $(OT4)_2$: "HJ aggregate"

- delocalized states

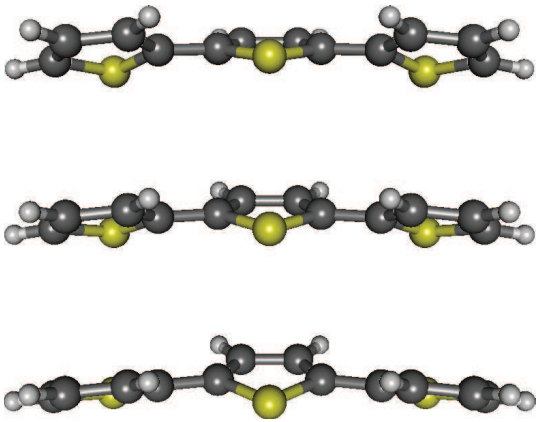
$$|\Psi_{\text{exciton}}\rangle = \sum_{n}^{N_{\text{exc}}} c_n |n\rangle$$

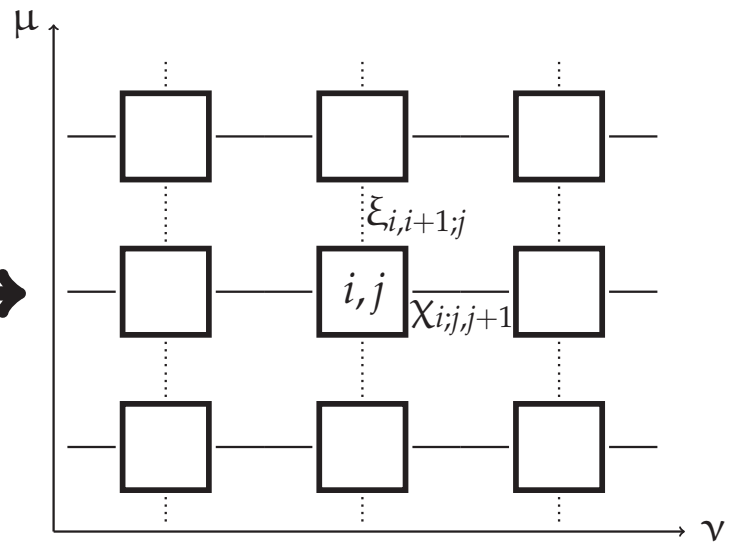
  where $N_{\text{exc}} \sim$ 5-10; $|n\rangle =$ configuration with single excitation on nth monomer
- trapping due to exciton-phonon interactions

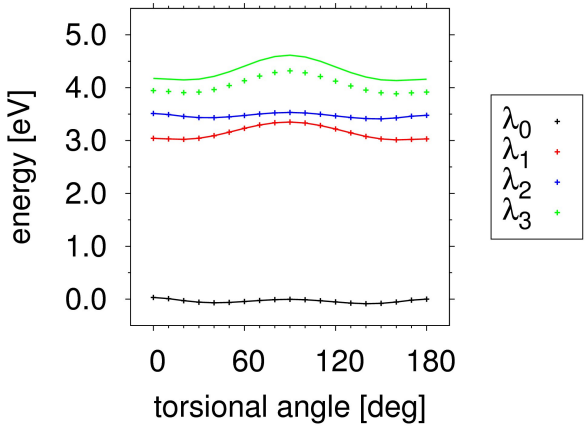
- J-aggregate: end-to-end alignment of monomer units; lowest state of the exciton manifold is the bright state
- H-aggregate: plane-to-plane stacked geometry; highest state of the exciton manifold is the bright state
- HJ-aggregate: combination of both, as in stacked oligomers

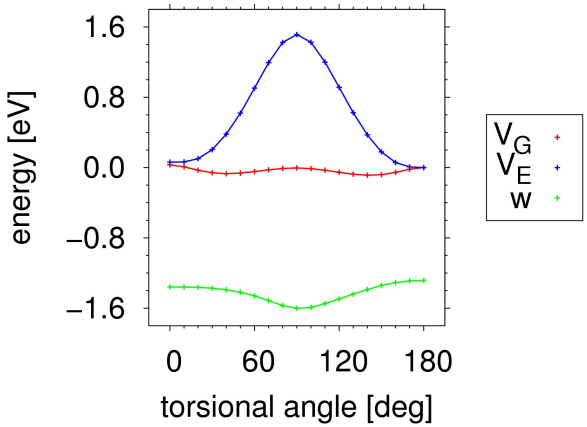
  Yamagata, Spano, JCP **136**, 184901 (2012)

HJ-Aggregate: Vibronic Lattice Model







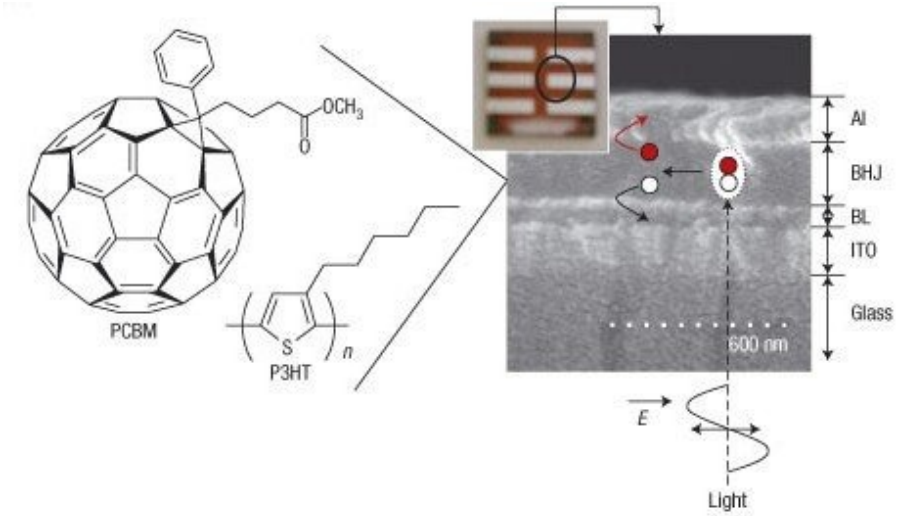


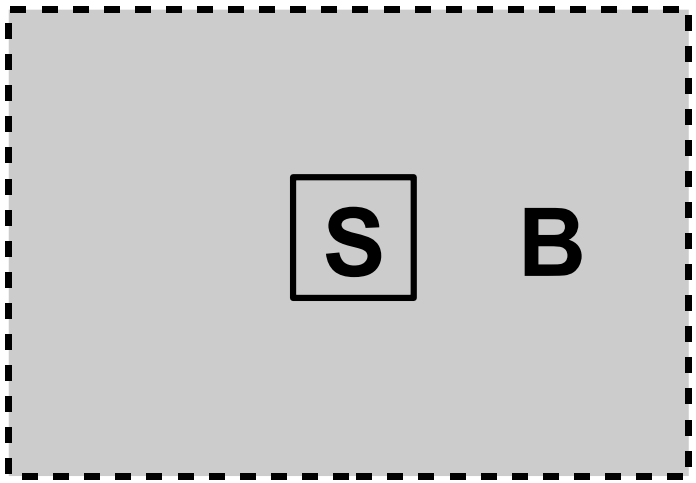
Binder, Römer, Wahl, Burghardt, J. Chem. Phys. 141, 014101 (2014)
Binder, Polkehn, Ma, Burghardt, Chem. Phys. 482, 16 (2017)

- here: analytic mapping of oligomer PES onto Hückel type model in 1D or 2D: solution to an inverse eigenvalue problem

  (NB.: V_G/V_E: monomer potentials, w: site-to-site coupling)

System-Bath Models





S region: e.g., electronic degrees of freedom (electron-hole states)

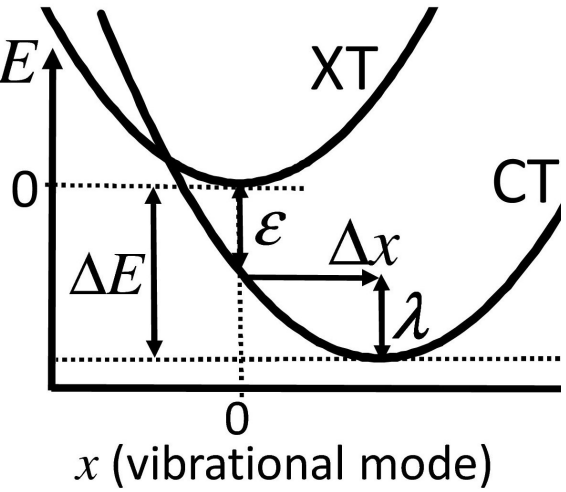
B region: all vibrations (phonons) mapped to harmonic oscillator model

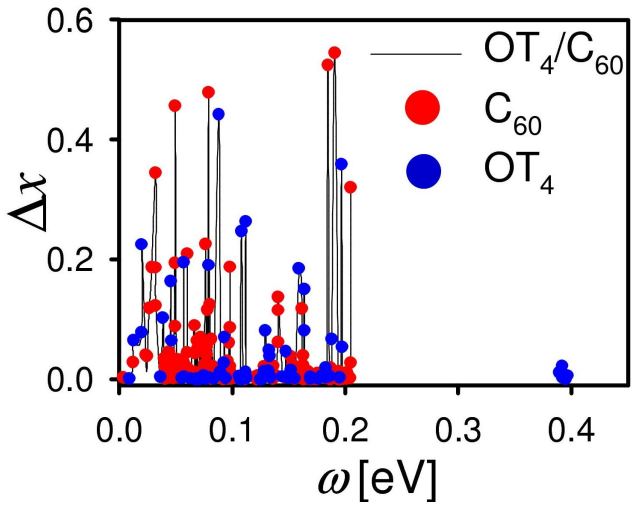
$$\hat{H}_B + \hat{H}_{SB} = \sum_n \tfrac{1}{2}(\hat{p}_n^2 + \tfrac{1}{2}\omega_n^2 \hat{x}_n^2) + \hat{s}\sum_n c_n \hat{x}_n$$

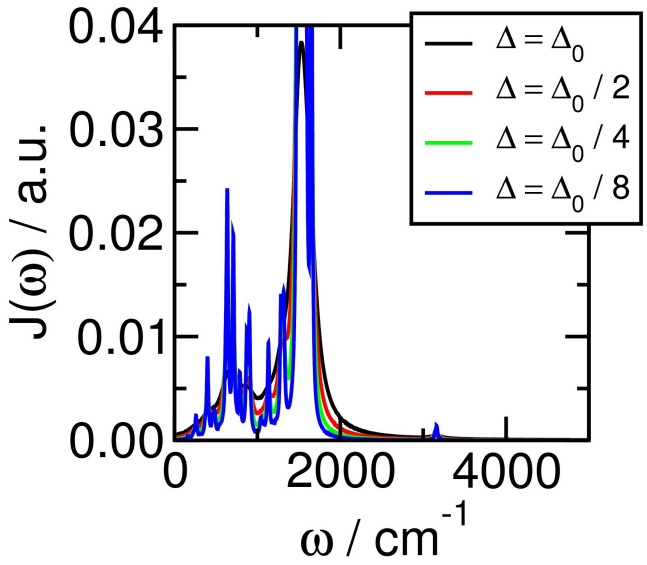
$$J(\omega) = \pi/2 \sum_n c_n^2/\omega_n \delta(\omega - \omega_n)$$

spectral density

Spectral Densities from Electronic Structure Calculations(*)







$$J(\omega) = \frac{\pi}{2} \sum_n^N \frac{c_n^2}{\omega_n} \delta(\omega - \omega_n) \simeq \frac{\pi}{2} \sum_n^N \frac{c_n^2}{\pi} \frac{\Delta}{(\omega - \omega_n)^2 + \Delta^2}$$

Tamura, Martinazzo, Ruckenbauer, Burghardt, J. Chem. Phys., 137, 22A540 (2012)

(*)NB. Alternatively: obtain SD's from correlation functions (MD, CPMD, ...)

Unitary Propagation vs. Master Equations

1. explicit, multidimensional dynamics for the full system + bath space: wavefunction $\psi_{SB}(t)$ or density operator $\hat{\rho}_{SB}(t) = \sum_n p_n |\psi_{n,SB}(t)\rangle\langle\psi_{n,SB}(t)|$

   ⟶ typically (ML-)MCTDH

   Meyer, Manthe, Cederbaum, Chem. Phys. Lett. **165**, 73 (1990), Beck et al., Phys. Rep. **324**, 1 (2000)

2. reduced dynamics (master equation) methods: $\hat{\rho}_S(t) = \mathrm{Tr}_B \hat{\rho}_{SB}(t)$

   ⟶ typically Hierarchy of Equations of Motion (HEOM)

   Tanimura, J. Phys. Soc. Jpn. **75**, 082001 (2006)

3. intermediate methods: explicit treatment of subsystem + effective-mode (E) part of the bath + master equation for residual (B') bath:[2]

$$\frac{\partial \hat{\rho}_{SE}}{\partial t} = -\frac{i}{\hbar}[\hat{H}_{SE}, \hat{\rho}_{SE}(t)] + \hat{\hat{L}}^{(B')}_{\mathrm{diss}} \hat{\rho}_{SE}(t) \quad ; \quad \hat{\rho}_{SE}(t) = \mathrm{Tr}_{B'} \hat{\rho}_{SEB'}(t)$$

[2] e.g., Caldeira-Leggett: $\hat{\hat{L}}^{(B')}_{\mathrm{diss}} \hat{\rho}_{SE} = -i\frac{\gamma}{\hbar}[\hat{X}_E, [\hat{P}_E, \hat{\rho}_{SE}]_+] - \frac{2\gamma MkT}{\hbar^2}[\hat{X}_E, [\hat{X}_E, \hat{\rho}_{SE}]]$

Unitary Dynamics: MCTDH

$$\Psi(r,t) = \sum_J A_J(t)\ \Phi_J(r,t) \equiv \sum_{j_1=1}^{n_1} \dots \sum_{j_N=1}^{n_N} A_{j_1 \dots j_N}(t) \prod_{\kappa=1}^{N} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)$$

- Multi-Configuration Time-Dependent Hartree: tensor approximation scheme
  Meyer, Manthe, Cederbaum, Chem. Phys. Lett. **165**, 73 (1990), Beck et al., Phys. Rep. **324**, 1 (2000)
- EoM's from the Dirac-Frenkel variational principle: $\langle \delta\Psi | \hat{H} - i\frac{\partial}{\partial t} | \Psi \rangle = 0$
- MCTDH takes one to 50-100 modes; exponential scaling alleviated
- restriction on the form of the potential: sums over products

- related multi-layer variant (ML-MCTDH) goes up to 1000 modes
  Wang, Thoss, J. Chem. Phys. 119, 1289 (2003), Manthe, J. Chem. Phys. 128, 164116 (2008), Vendrell, Meyer, *ibid* 134, 044135 (2011)
- related MCTDH-F (fermion) and MCTDH-B (boson) methods
  Kato, Kono, Chem. Phys. Lett. 392, 533 (2004), Nest, Klamroth, Saalfrank, J. Chem. Phys. 122, 124102 (2005)
  Alon, Streltsov, Cederbaum, Phys. Lett. A 362, 453 (2007)
- density matrix variant
  Raab, Burghardt, Meyer, J. Chem. Phys. 111, 8759 (1999)
- hybrid approaches: e.g., Gaussian-based variant (G-MCTDH, vMCG)
  Burghardt, Meyer, Cederbaum, J. Chem. Phys. 111, 2927 (1999), Worth, Burghardt, Chem. Phys. Lett. 368, 502 (2003)

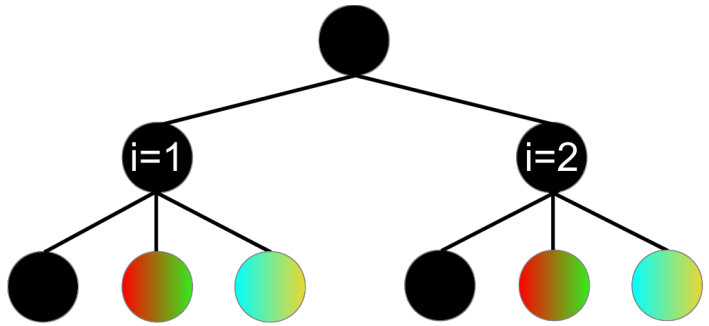
Multi-Layer(ML)-MCTDH: Hierarchical Tensor Form

$$\Psi(r,t) = \sum_J A_J(t)\Phi_J(r,t) \;\; = \sum_J A_J(t) \prod_{\kappa=1}^{M} \varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t)$$

where the 1st-layer SPFs $\varphi_{j_\kappa}^{(\kappa)}$ are now built as superpositions of 2nd-layer SPFs,

$$\varphi_{j_\kappa}^{(\kappa)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa)}(t)\Phi_L^{(\kappa)}(r_\kappa,t) = \sum_L B_{j,L}^{(\kappa)}(t) \prod_\mu \varphi_{l_\mu}^{(\kappa,\mu)}(r_{\kappa_\mu},t)$$

. . . and so on . . .

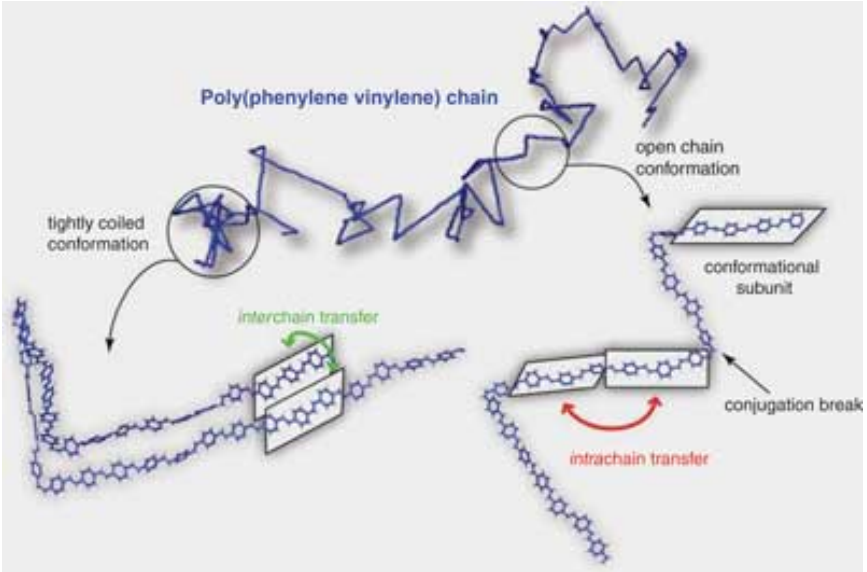


- intra-SPF correlations *via* MCTDH form
- continue to higher orders: ML-MCTDH
- "hierarchical Tucker format"
- recent Gaussian-based variant Römer, Ruckenbauer, Burghardt, J. Chem. Phys. 138, 064106 (2013)

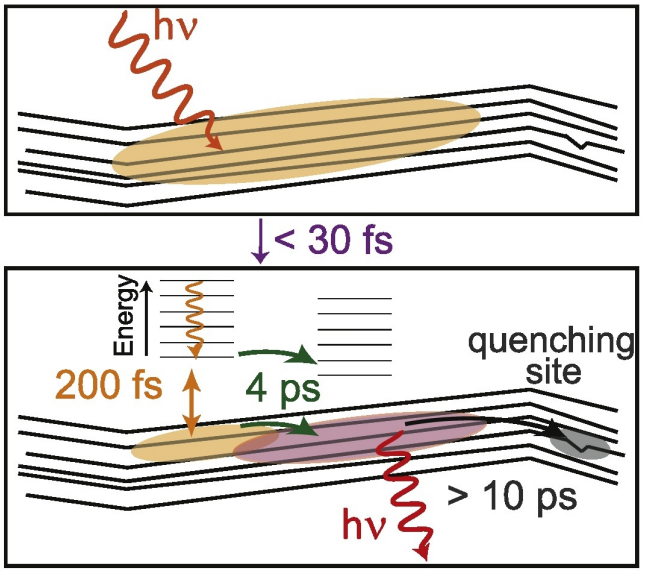
Wang, Thoss, J. Chem. Phys. 119, 1289 (2003), Manthe, J. Chem. Phys. 128, 164116 (2008), Vendrell, Meyer, J. Chem. Phys. 134, 044135 (2011)

Topics

Exciton Dynamics in Organic Semiconducting Polymers



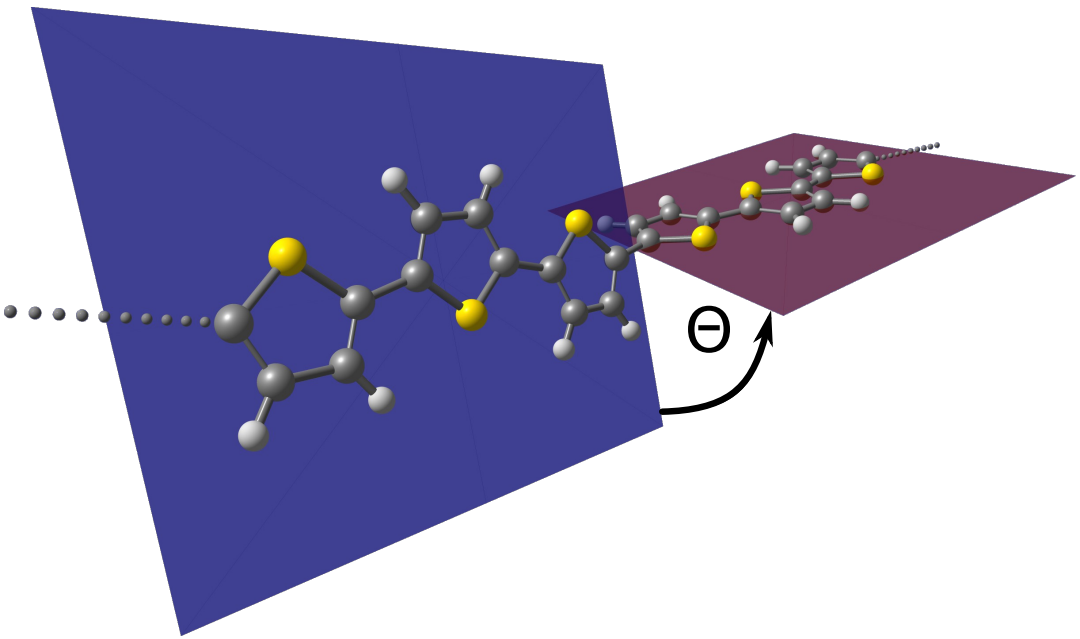
Collini, Scholes, Science 323, 369 (2009)



Consani et al., JCP 142, 212429 (2015)

∼0.1-1 ps: coherent intra-chain excitation energy transfer (EET) dynamics
∼0.1-1 ps: self-trapped exciton-polaron states
∼0.1-few ps: torsional geometry relaxation interfering with EET
∼1-10 ps: inter-chain EET
∼ps-ns: thermally assisted hopping

Test Case: Exciton Migration at a Torsional Defect



- full quantum dynamical study for small oligomers (5-20 units)
- Oligothiophene (OT) and Oligo-Phenylenevinylene (OPV)
- ML-MCTDH (up to 50 states, 100 vibrational modes)
- monomer-based, *ab initio* parametrized Hamiltonian

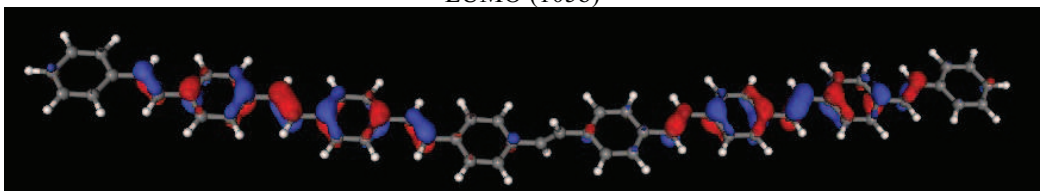
Binder, Wahl, Römer, Burghardt,
Faraday Discuss 163, 205 (2013)
Panda, Plasser, Aquino, Burghardt, Lischka
J. Phys. Chem. A, 117, 2181 (2013)
Wahl, Binder, Burghardt
Comp. Theor. Chem. 1040, 167 (2014)

- Is the transfer dynamics on ultrafast time scales coherent or of hopping type?
- Is a trapped exciton-polaron generated and if so, on which time scale?

Electronic Structure: Trapping in OPV Oligomers

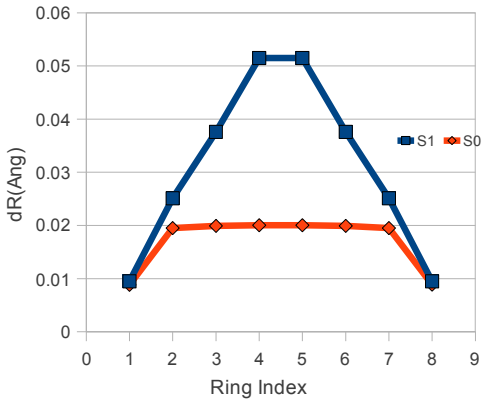
Collaboration with H. Lischka, F. Plasser (Vienna/Texas Tech/Tianjin University)

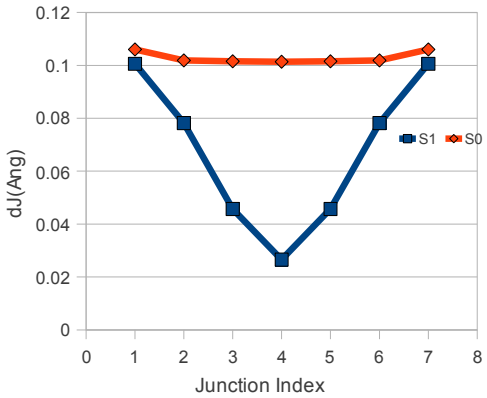
LUMO (105b)

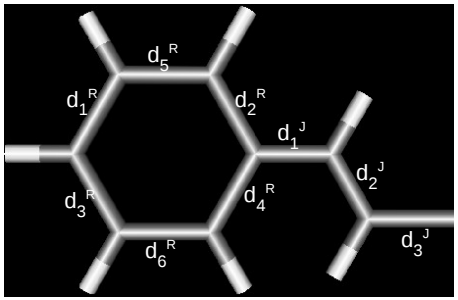


HOMO (106a)

- high-level electronic structure methods (ADC(2), CC2, MRCI)
- exciton trapping, due to BLA modes, described correctly





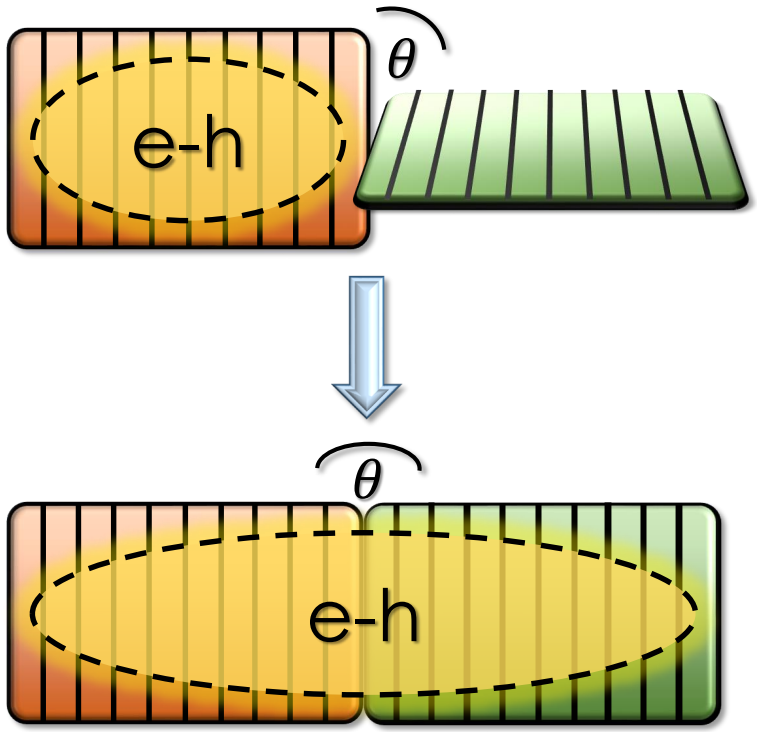


Panda, Plasser, Aquino, Burghardt, Lischka, JPCA, 117, 2181 (2013), see also: Sterpone, Rossky, JPCB 112, 4983 (2008), Nayyar et al., JPCL 2, 566 (2011)

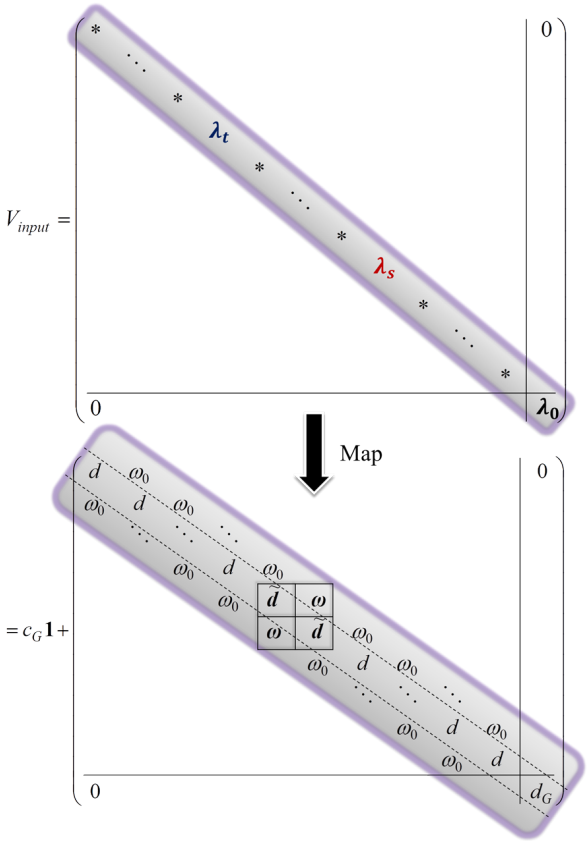
Dynamics: Test Case OT-20

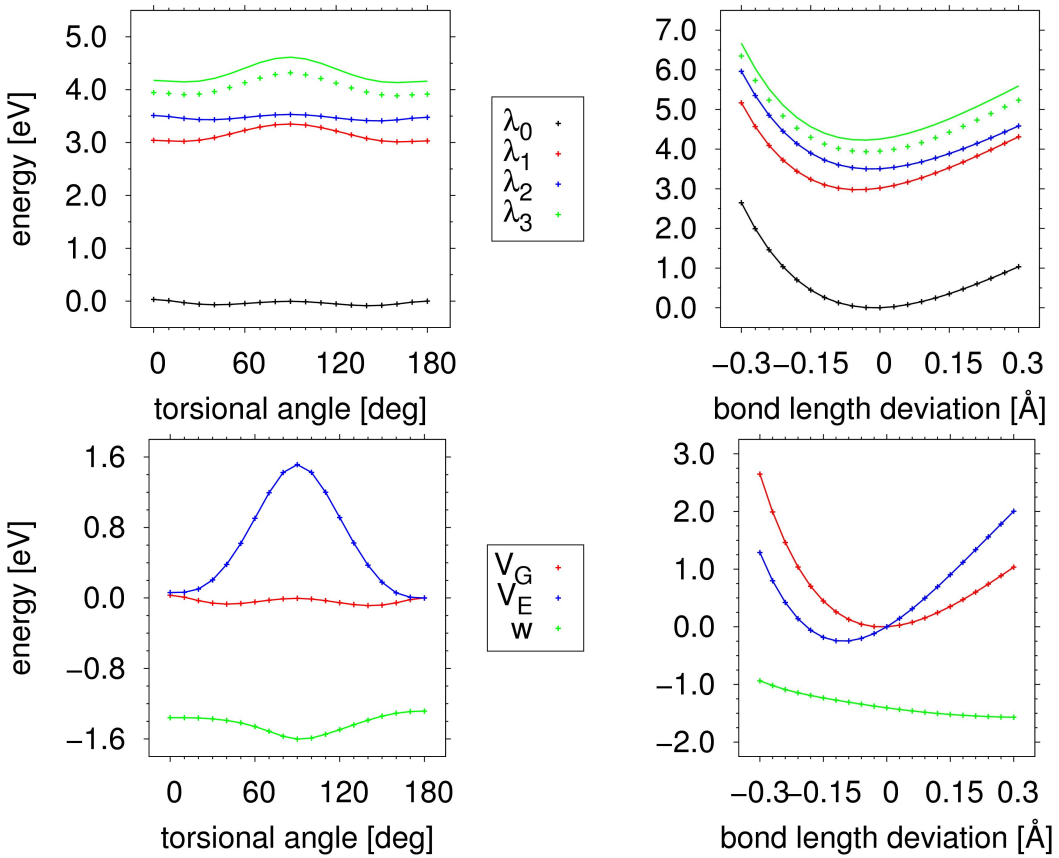
- Do we see trapped exciton-polarons in the dynamics?
- How exactly does the exciton migrate as the conjugation break "heals"?
- How does the spatial extension of the exciton change as a function of conformational (torsional) fluctuations?

Monomer representation:
most unbiased picture to answer these questions!



Relevant Coordinates: Torsions, CC Stretch, Ring Modes

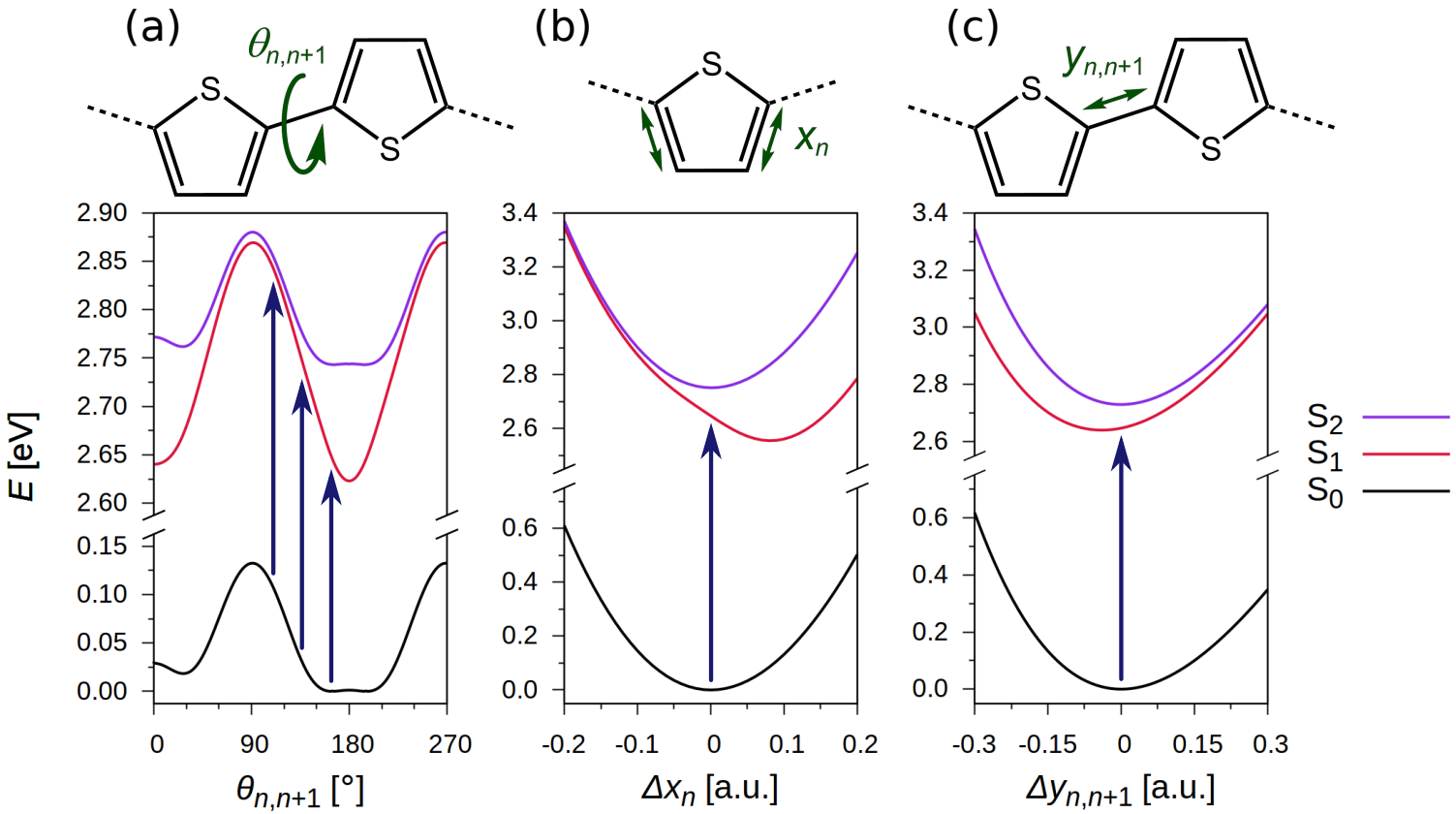




- analytical, pointwise mapping of oligomer PES's onto a Frenkel model
- diabatization in terms of solution to an inverse eigenvalue problem
- applicable to "extended Hückel systems" of J / H / HJ-aggregate type

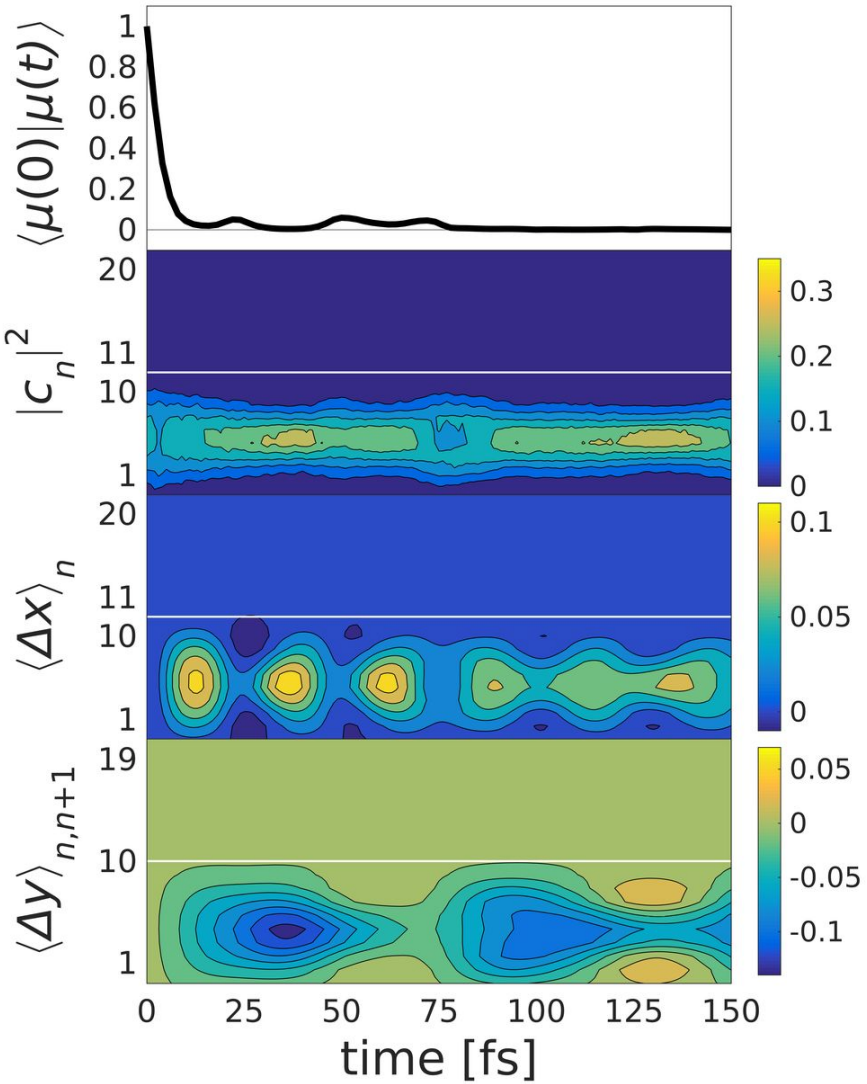
Binder, Römer, Wahl, Burghardt, J. Chem. Phys., 141, 014101 (2014), Binder, Polkehn, Ma, Burghardt, Chem. Phys. 482, 16 (2017)

Relevant Coordinates: Torsions, CC Stretch, Ring Modes



- high-dimensional PES as a function of site-local and site-correlated modes
- 20 monomer sites, 50 phonon modes

Quantum Dynamics: 20-Site J-Aggregate with Central Torsion



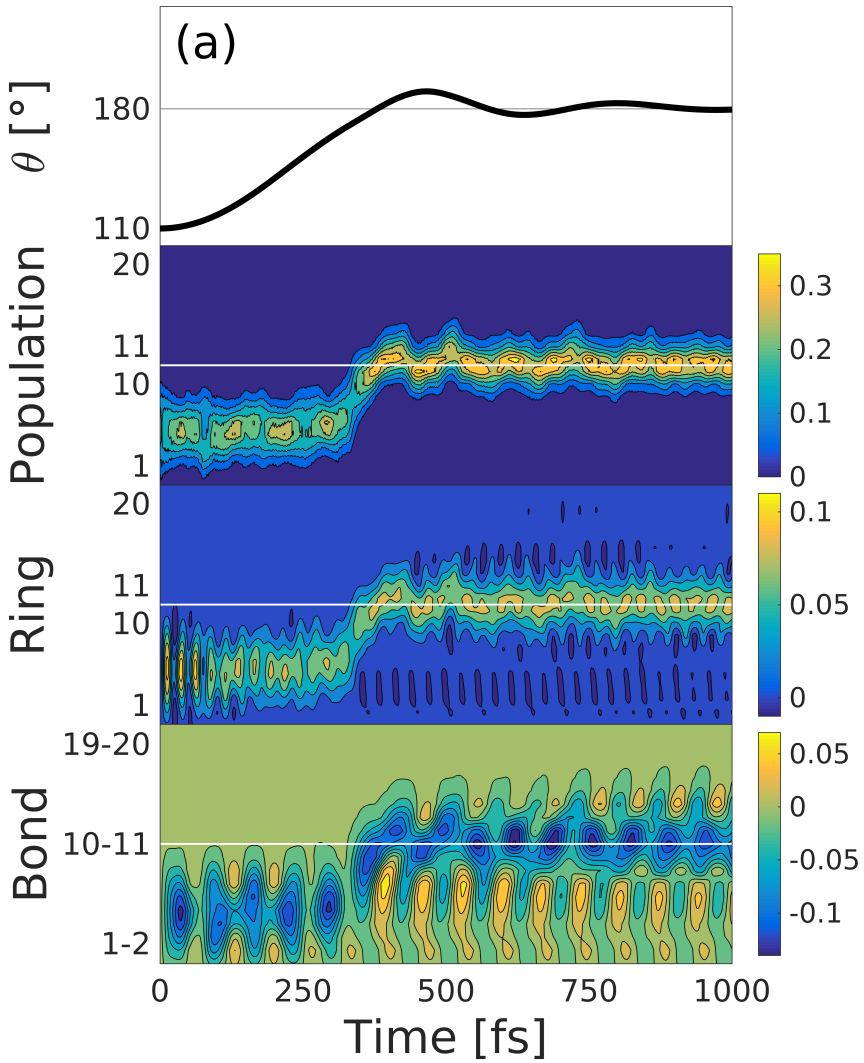
- earliest time scale: exciton trapping (contraction by ∼3 sites)
- high-frequency modes adapt to exciton distribution
- LEGS = local exciton ground state: nodeless left-localized exciton

  Tozer, Barford, JPCA 116:10310 (2012)
- ultrafast decay of transition dipole autocorrelation function (∼10 fs): $\langle\mu(0)\mu(t)\rangle = |\mu|^2\langle\psi_{\mathrm{exc}}(0)|\psi_{\mathrm{exc}}(t)\rangle$
- relates to anisotropy decay: ∼40 fs

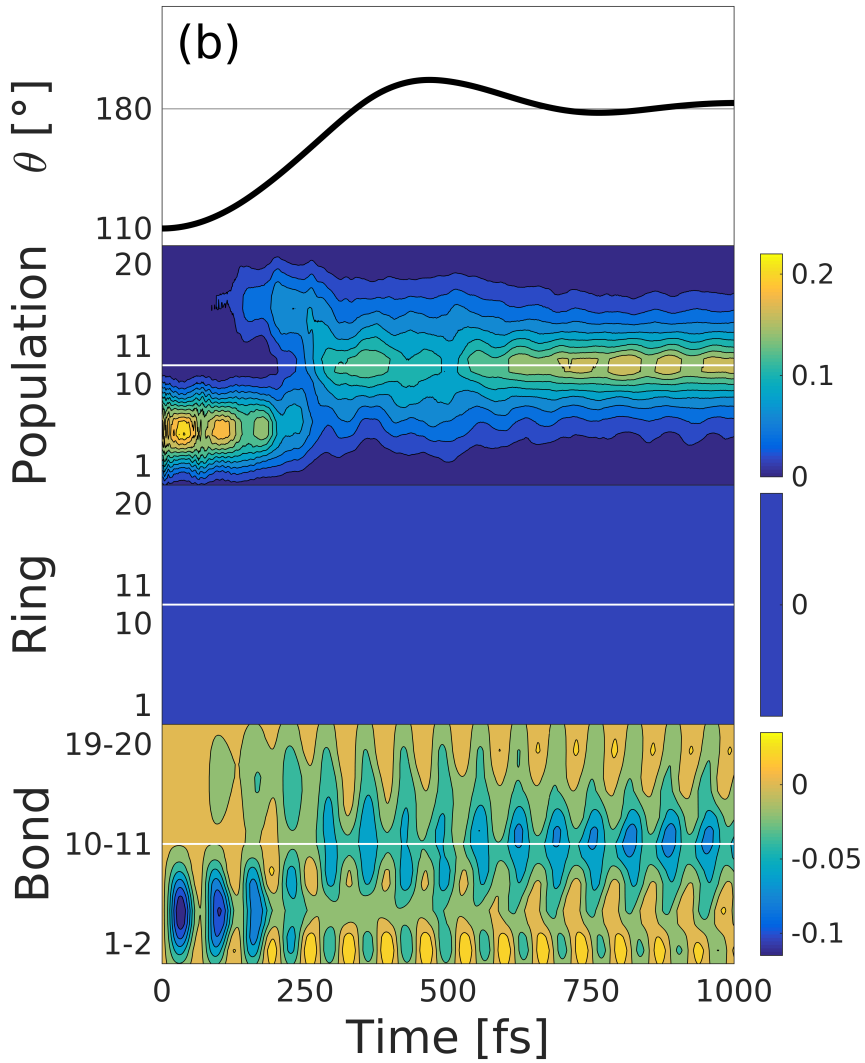
  Grage et al., Phys. Rev. B, 67, 205207 (2003)

Quantum Dynamics: 20-Site J-Aggregate with Central Torsion

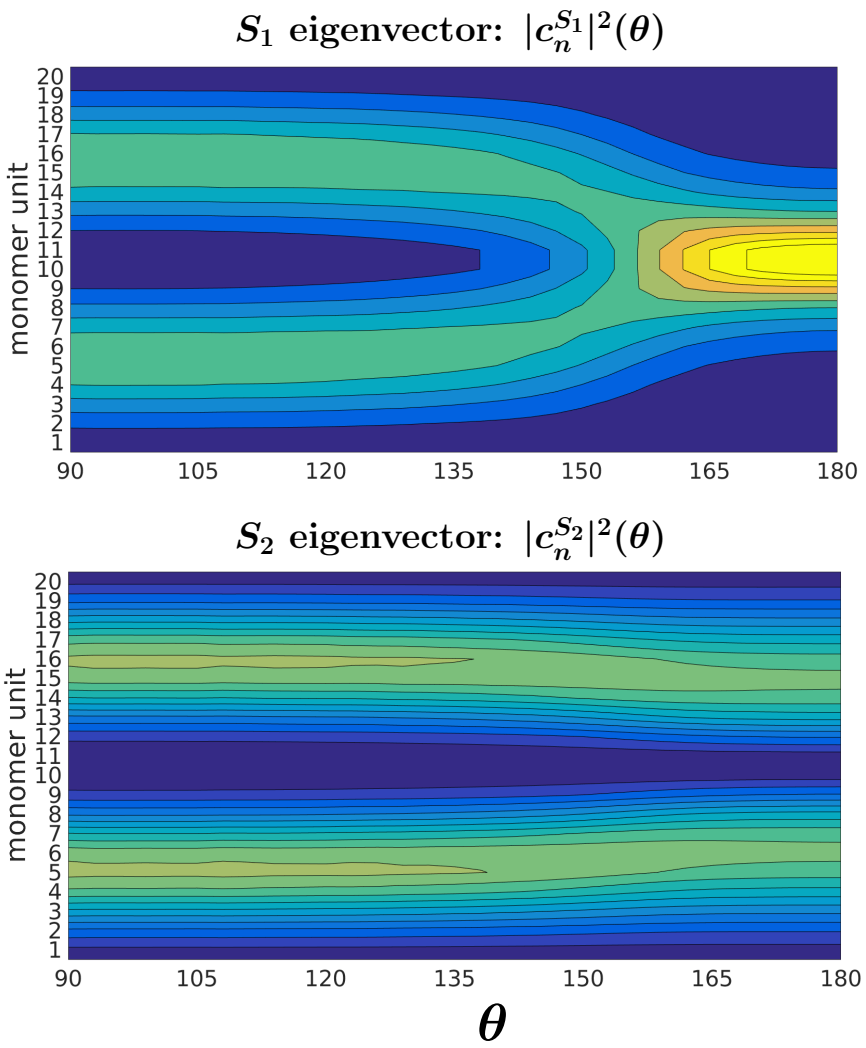
C-C inter-monomer mode + local C=C + torsion + bath



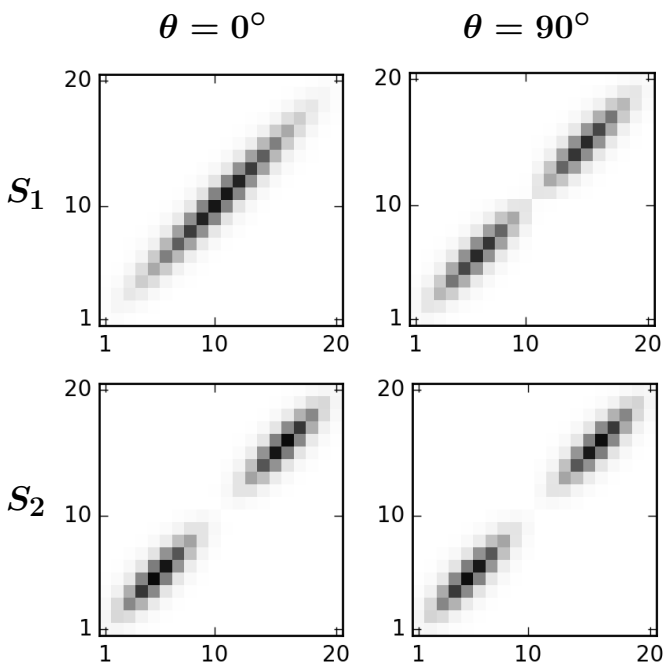
C-C inter-monomer + torsion + bath



Electronic Structure – Torsion Dependence

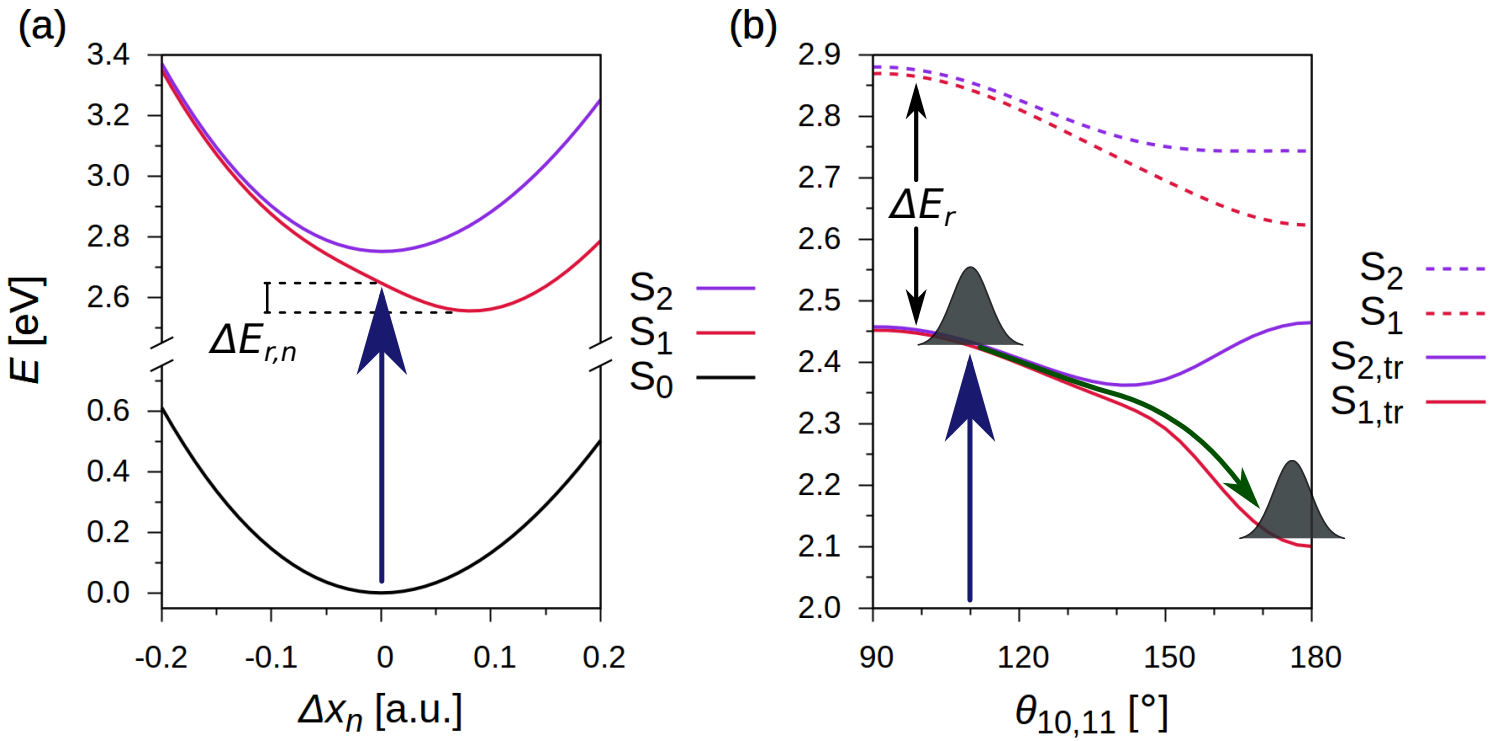


NB. polaronic (trapped) S_1/S_2 states



- transition density analysis
  Panda, Plasser, Aquino, Burghardt, Lischka, JPCA (2013)
- particle-in-the-box type e-h states
- marked dependence on torsion
- LEGS = local exciton ground state: nodeless S_1 exciton @180°
  Tozer, Barford, JPCA 116:10310 (2012)

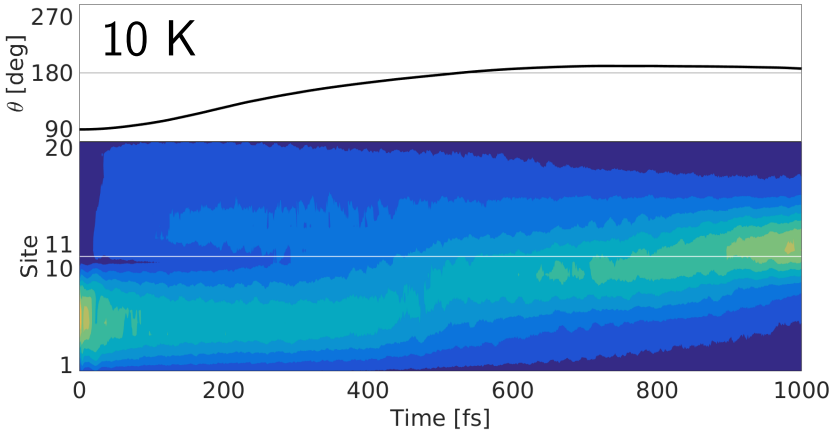
Exciton-Polaron Dynamics: Adiabatic Picture

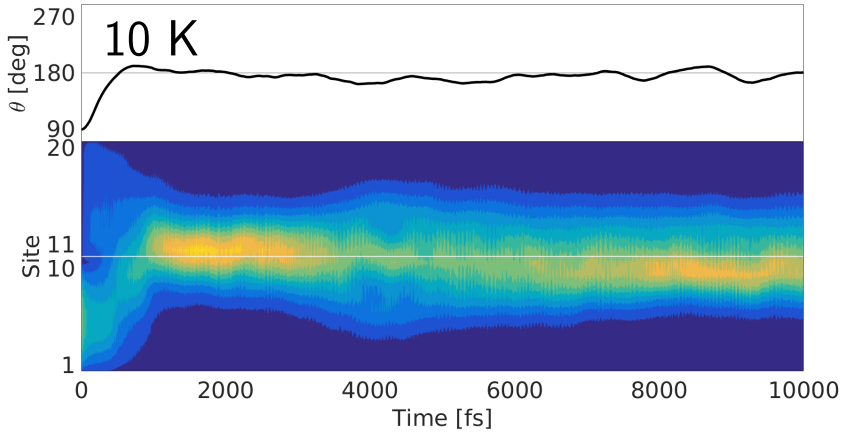


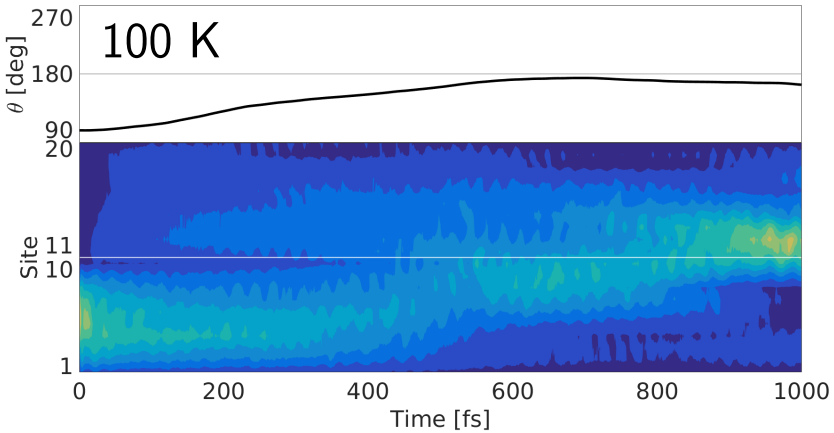
- dynamics is essentially happening on coupled S_1/S_2 surfaces
- effective torsion potentials including stabilization due to trapping $(S_{1,\mathrm{tr}}/S_{2,\mathrm{tr}})$[1]
- initial left/right localized state = superposition of S_1/S_2
- energy loss due to external bath acting on torsional mode
- exciton-polaron trapping persists at all stages of the dynamics

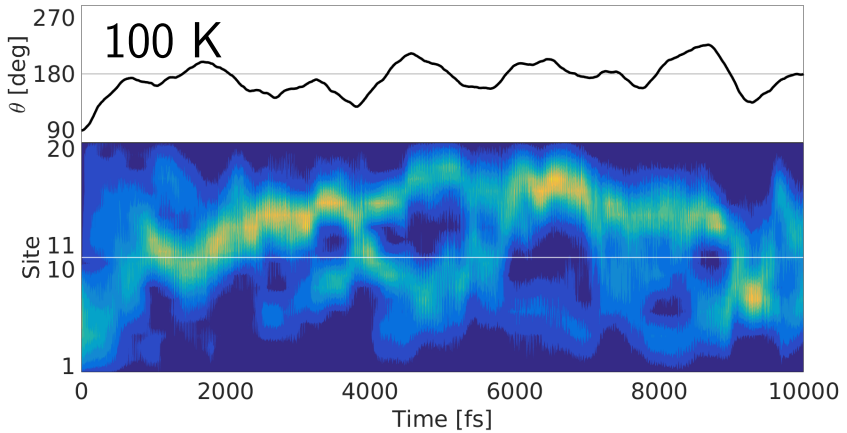
[1] i.e., "polaron transformed" potentials

Temperature Effects: Ehrenfest/Langevin dynamics









- ultrafast transients not correctly reproduced by Ehrenfest dynamics
- at increasing temperatures, fluctuations start driving exciton migration

Polarons in π-Conjugated Polymers: Anderson or Landau?

William Barford,[*,†] Max Marcus,[†,‡] and Oliver Robert Tozer[†,§]

"We show that the high-frequency C-C bond oscillation only causes Landau polarons for a very narrow parameter regime; generally we expect disorder to dominate and Anderson polarons to be a more applicable description."

J. Phys. Chem. A 120, 615 (2016)

Excitons in conjugated polymers:
Do we need a paradigma change?

Wichard J. D. Beenken

"The fact that we could not find partition of excitons by structural defects – except of rare gauche defects and accidental chemical defects – leads us to the conclusion that we have to search for new mechanisms."

Phys. Status Solidi A 206, 2750 (2009)

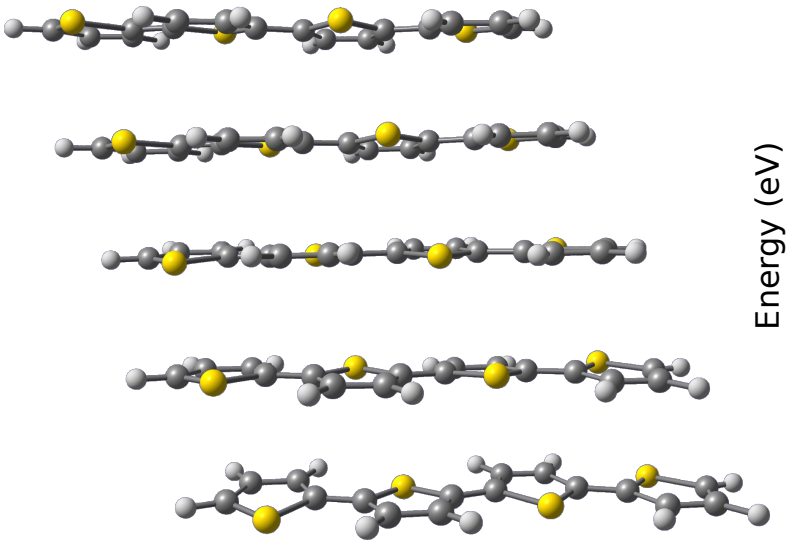
Our interpretation: Exciton-polarons driven by defects and fluctuations

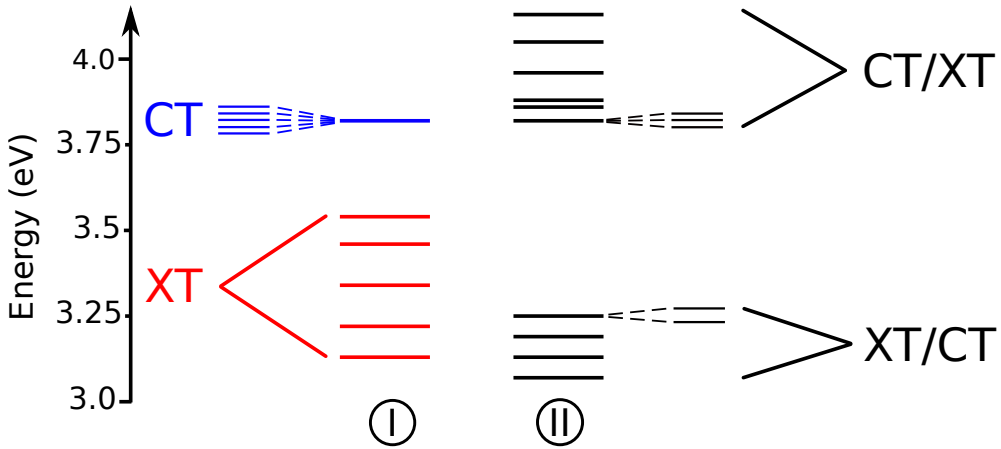
- exciton-polaron species: "exciton dressed by a cloud of local oscillators"
- typical delocalization length: 5-10 units (in line with experiment)
- Landau polaron (or Holstein "large" polaron) subject to disorder
- torsional defects confine excitons to sublattices ("spectroscopic units")
- hopping-type transition between exciton-polaron states induced by torsion
- elementary step is of "coherent hopping" type: highly correlated dynamics!

Topics

Charge Transfer Excitons in Neat Regioregular Polythiophene

experiment: Reid et al., Chem. Mater. 26, 561 (2014), De Sio et al., Nature Comm. 7, 13742 (2016)



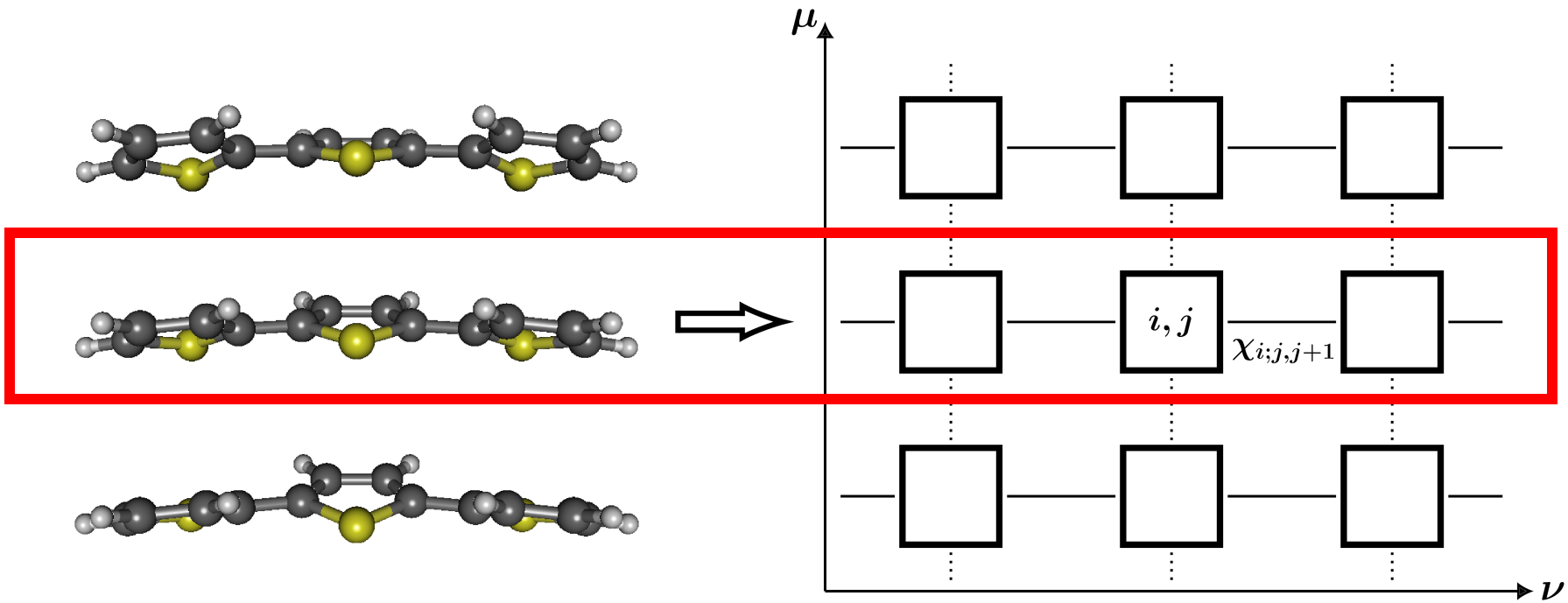


I: local adiabatic, II: full adiabatic

Popp, Polkehn, Tamura, Burghardt, to be submitted

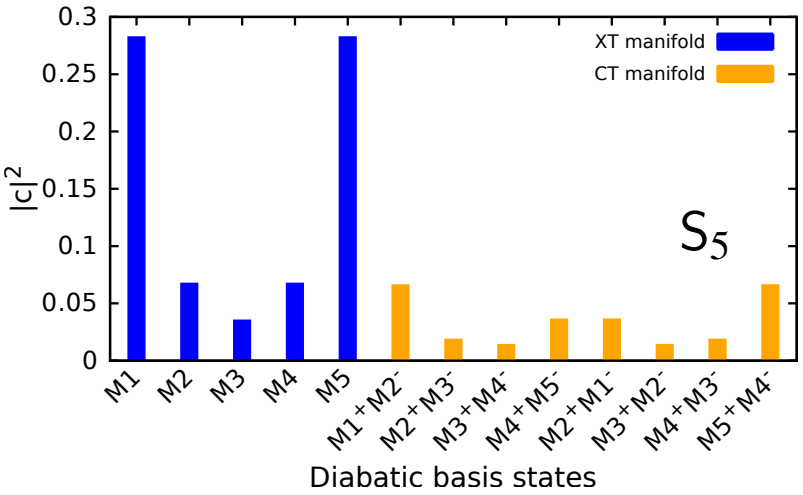
- inter-chain CTX states favored in PT (as compared with, e.g., PPV)
- electronic structure (ADC(2), TDDFT): low-energy inter-chain CT states
- representative quantum dynamics calculations for $(OT)_n$, $n=$ 3, 5
- diabatization + Linear Vibronic Coupling (LVC) model
- ML-MCTDH for up to 13 electronic states, 200 modes

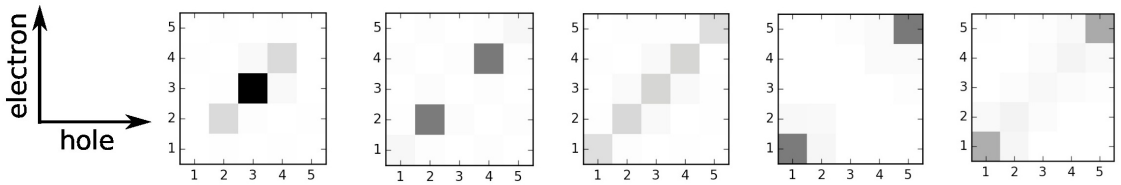
HJ Aggregates: Intra- & Inter-Chain Interactions



- partitioning either monomer-based or oligomer-based
- monomer-based partitioning: on-chain exciton dynamics
- oligomer-based partitioning: interchain exciton and charge transfer dynamics

Charge Transfer Excitons in Neat Regioregular Polythiophene



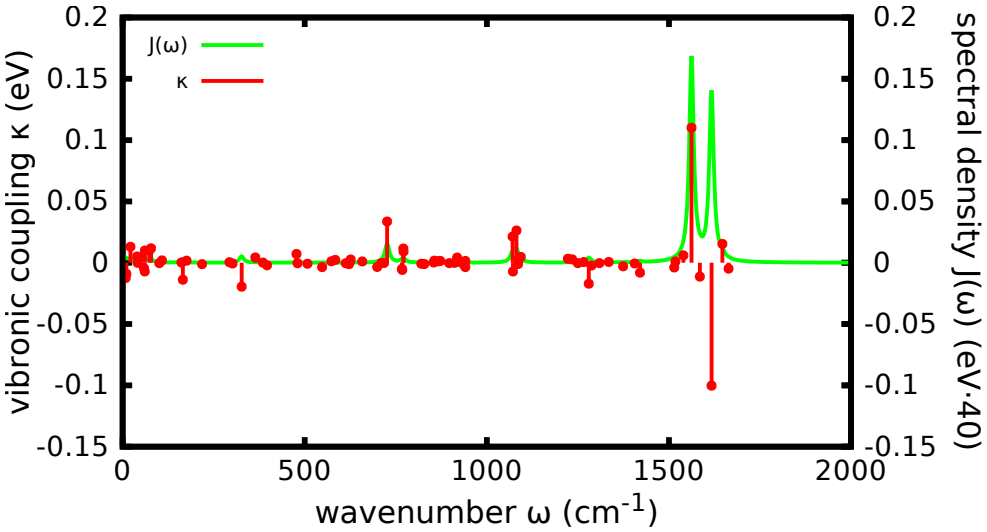


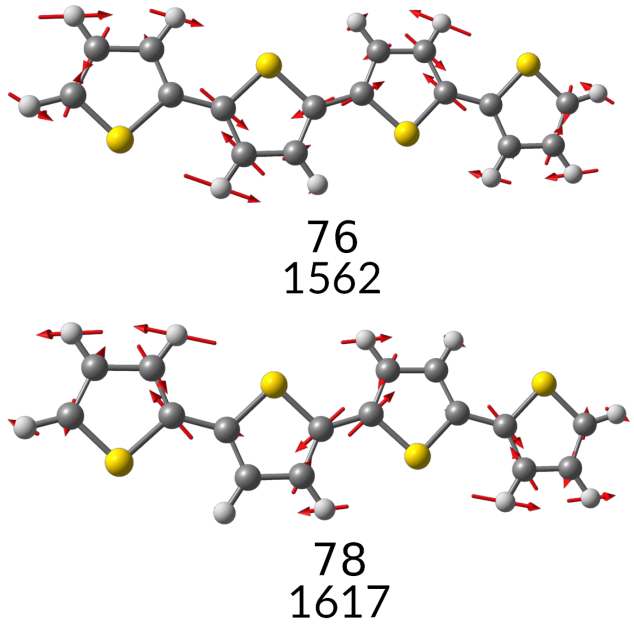
	S1	S2	S3	S4	S5
VEE [eV]	3.08	3.11	3.18	3.35	3.41
$f_{osc.}$	0.0006	0.0000	0.1370	0.0000	2.8247

Popp, Polkehn, Tamura, Burghardt, to be submitted

- $(OT)_5$ stack: significant mixing of XT and CT states
- bright state (S_5) looks distinctly different from typical H-aggregate (inverted curvature of nodeless exciton wavefunction) Hestand and Spano, J. Chem. Phys. 143, 244707 (2015)
- transition densities for H-type dimer *via* TheoDORE program (F. Plasser)
- very good agreement between ADC(2) and TDDFT/ωB97XD results
- in line with benchmark study by Lischka & collaborators JCTC 10, 3280 (2014)

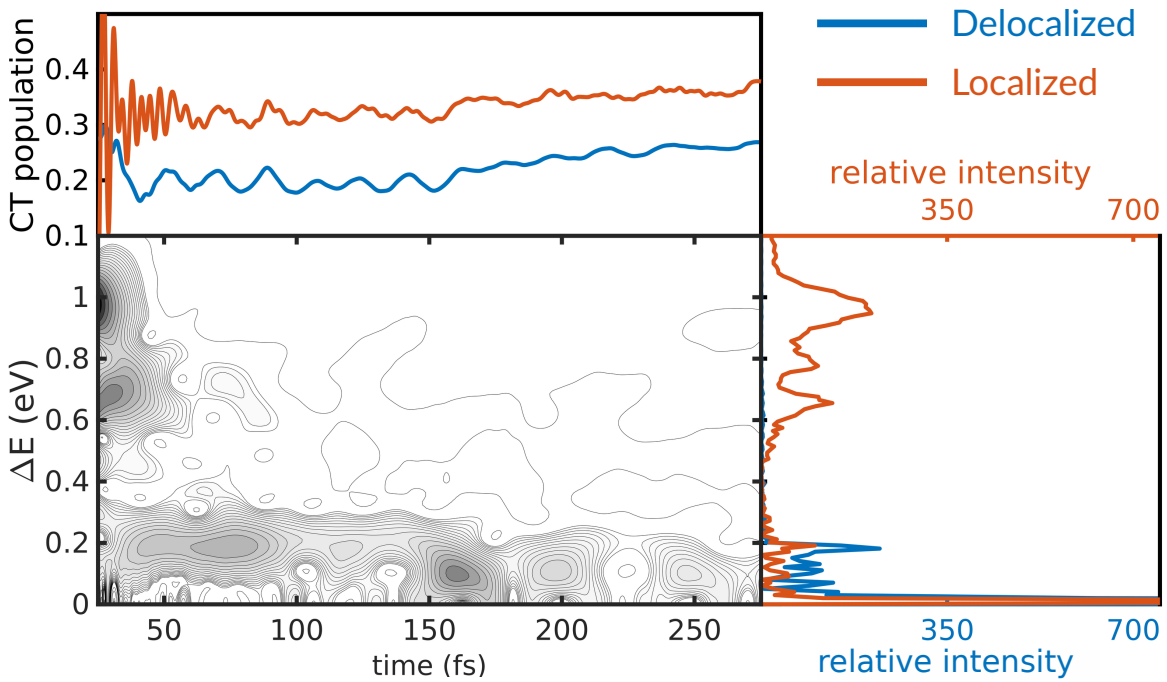
Spectral Densities (SD's)





- SD's calculated from state-specific Frank-Condon gradients
- SD's show large amplitude ($\sim$ Huang-Rhys factor) for CC stretch modes
- SD's similar for various electronic states
- ML-MCTDH: 13 states/195 modes (or 65 effective modes)

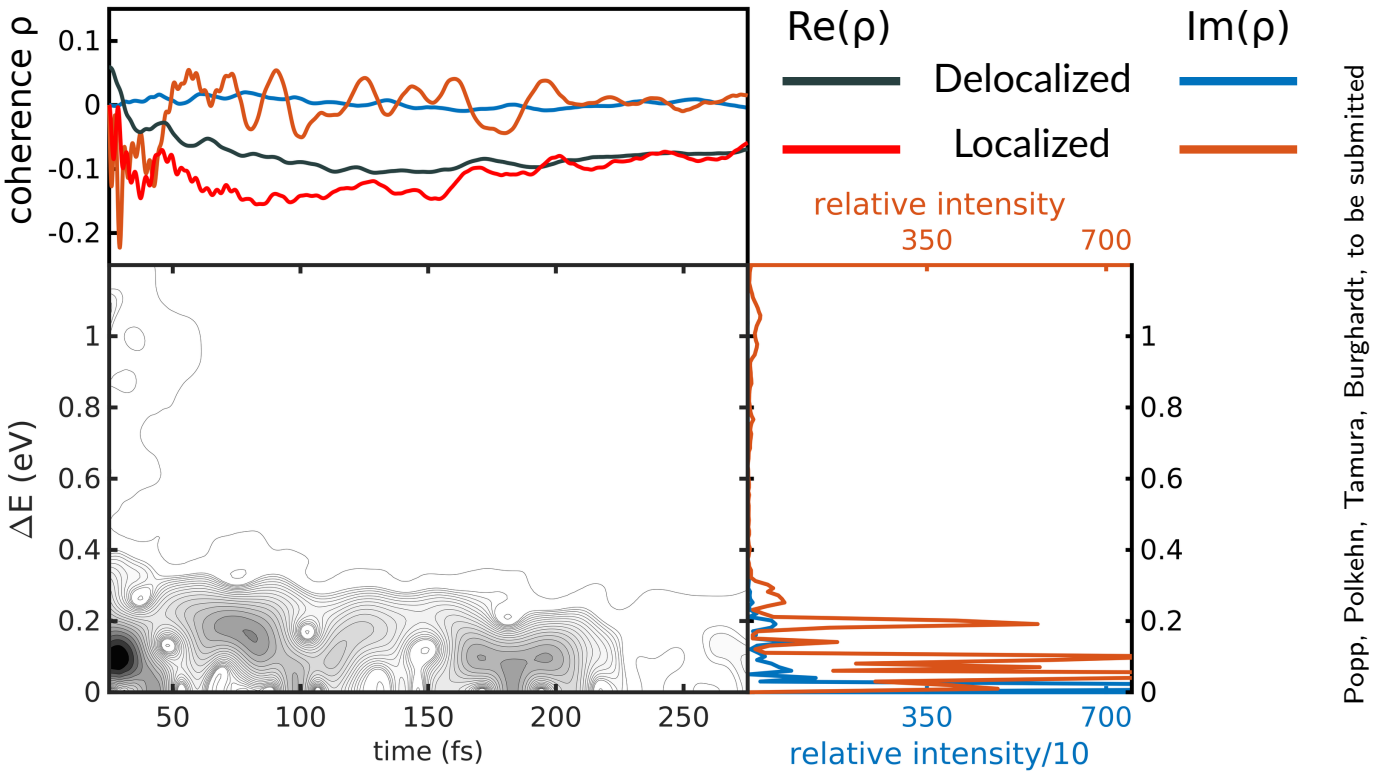
Full Quantum Dynamics (13 States, ∼200 modes)



Polkehn, Popp, Tamura, Burghardt, to be submitted

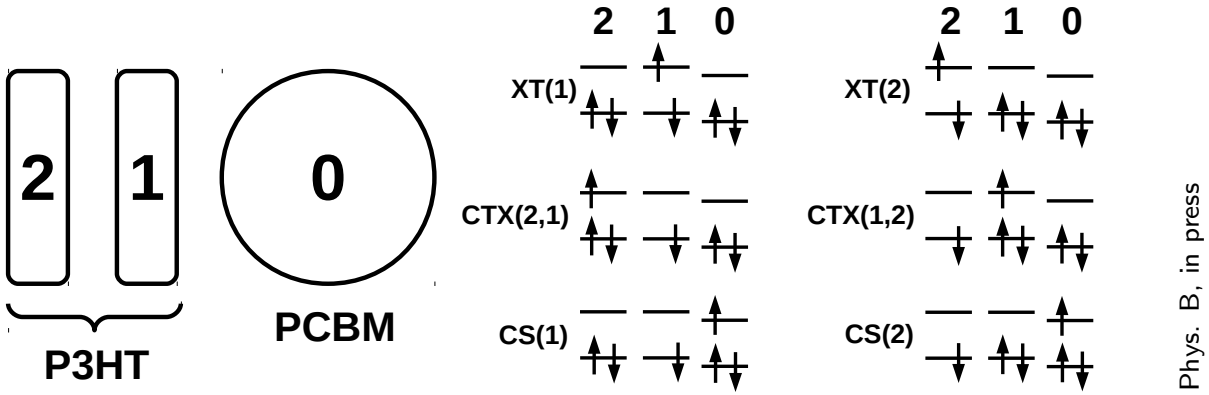
- CT population rises immediately
- early time (∼50 fs) depends strongly on state preparation
- delocalized bright-state (S_5) initial conditions yields smooth dynamics
- localized initial conditions yields marked initial XT/CT beatings
- windowed Fourier transform to separate frequency ranges
- time scale in good agreement with experiment [De Sio et al., Nature Comm. 7, 13742 (2016)]

Signatures of Excitonic Coherence



- windowed Fourier transform of time-dependent XT-XT electronic coherence
- localized initial condition produces beatings within excitonic manifold
- very similar frequency as dominant vibrations (∼0.1-0.2 eV)
- both vibrational and excitonic coherence could contribute

Do CTX States Affect Interfacial Charge Generation?

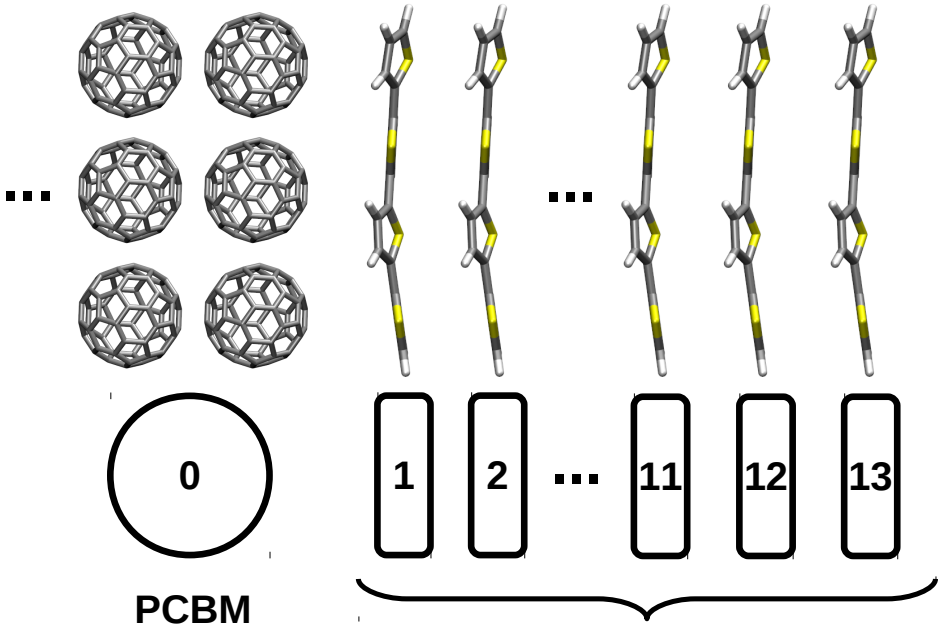


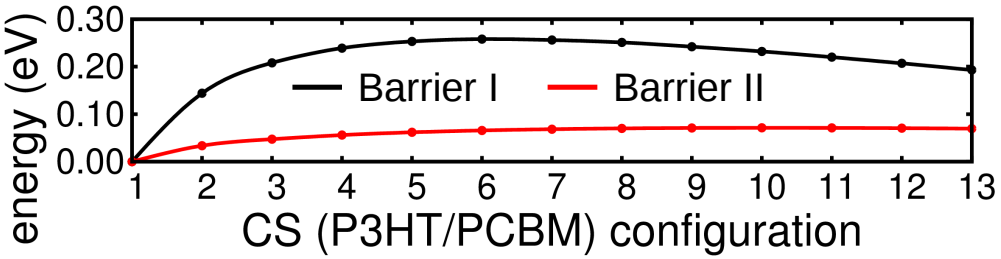
	XT(1)	XT(2)	CTX(2,1)	CTX(1,2)	CS(1)	CS(2)
XT(1)	0.100	0.100	0.357	0.139	0.200	0.007
XT(2)		0.100	0.139	0.357	0.014	0.013
CTX(2,1)			0.280	0.001	0.005	0.002
CTX(1,2)				0.230	0.019	0.165
CS(1)					0.000	0.102
CS(2)						0.140

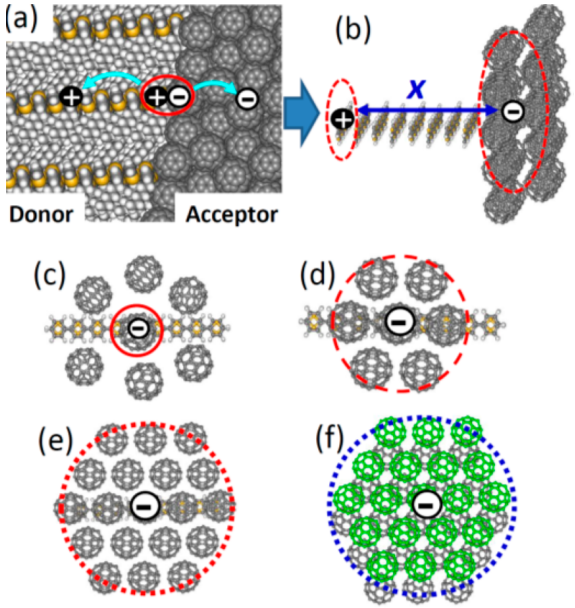
Polkehn, Tamura, Burghardt, J. Phys. B, in press

- CTX-to-CS transfer can circumvent interfacial XT-to-CS transfer step
- here: parameter determination via diabatization by projection onto reference wavefunctions Tamura, JPCA 120, 9341 2016

Interfacial Charge Generation in P3HT:PCBM Type Systems







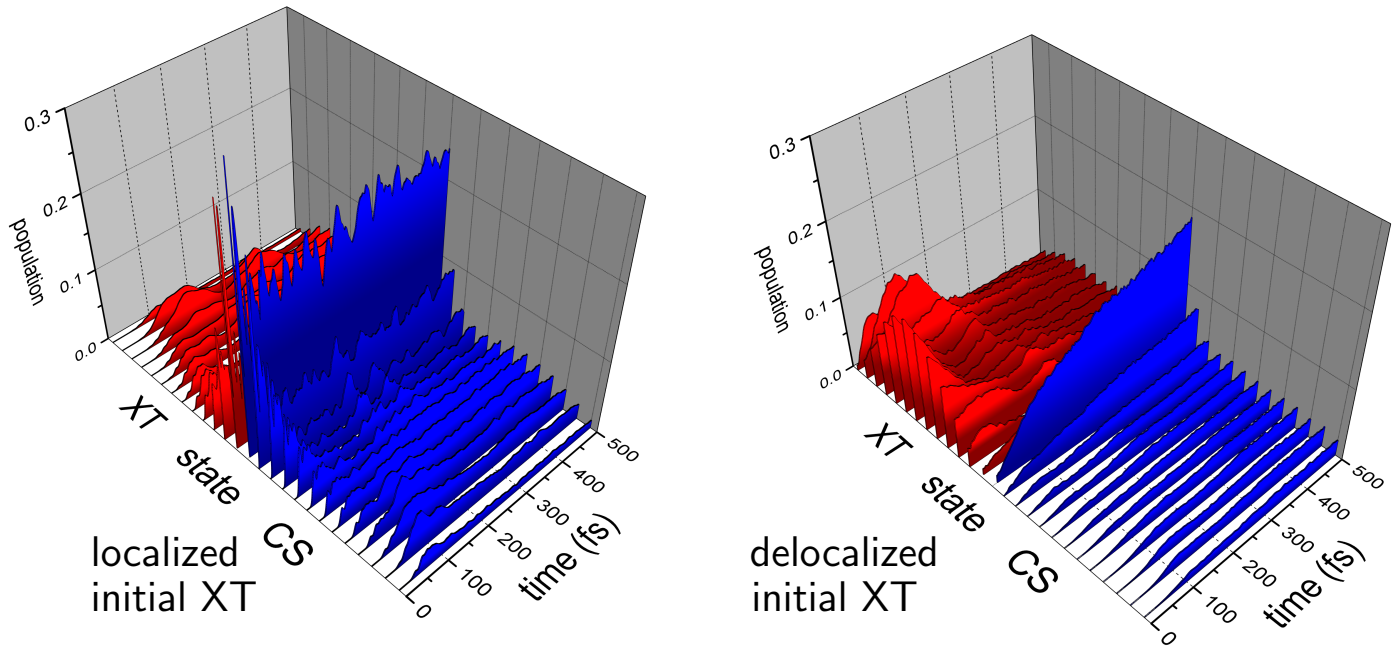
factors favoring ultrafast *e*-*h* separation:

- electron delocalization over fullerene aggregates: strong decrease of barrier
- hole delocalization on oligothiophenes
- XT delocalization in H-aggregate donor
- exciton (XT) excess energy: "Hot CT" mechanism

Tamura, Burghardt, JACS (Communication) 135, 16364 (2013)
Huix-Rotllant, Tamura, Burghardt, J. Phys. Chem. Lett., 6, 1702 (2015)

Interfacial Charge Separation in the Absence of CTX States

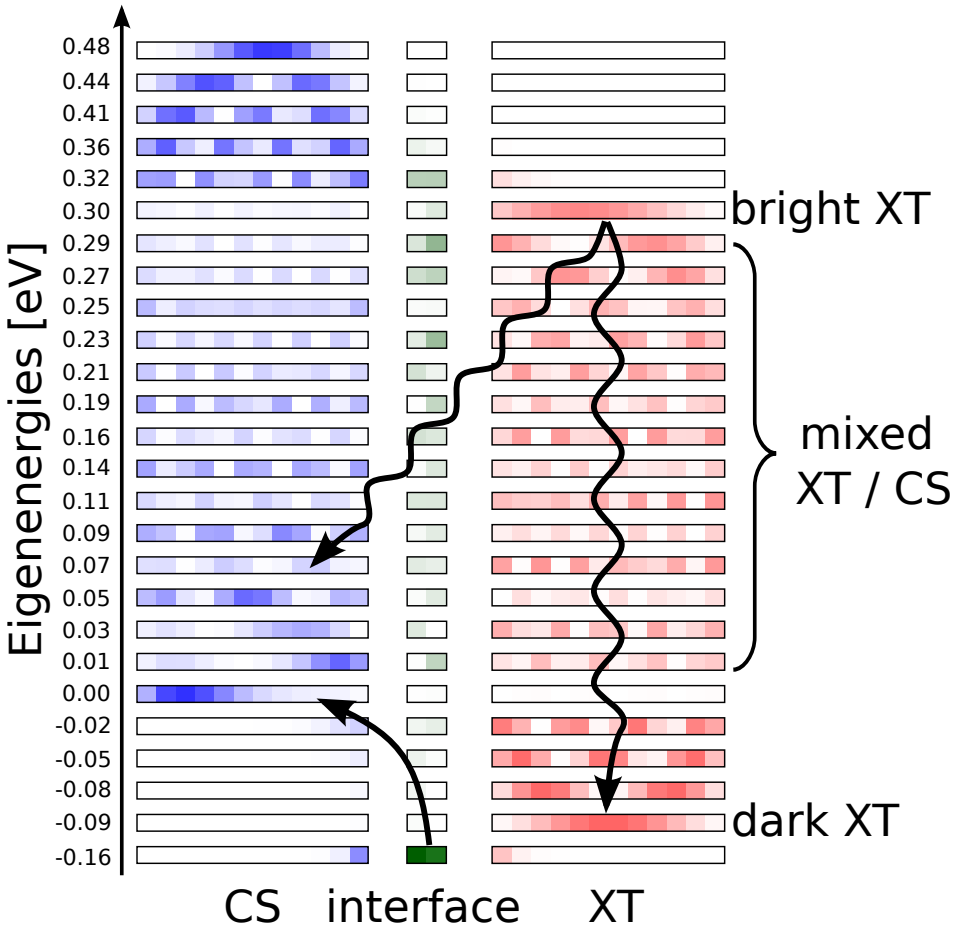
$$\hat{H} = \hat{H}_{\mathrm{XT_1\text{-}CT}}(\mathbf{x}) + \sum_n \hat{H}^{(n)}_{\mathrm{CS}}(\mathbf{x})|\mathrm{CS}_n\rangle\langle\mathrm{CS}_n| + t(\mathbf{x})(|\mathrm{CS}_1\rangle\langle\mathrm{CT}| + \sum_{nn'}|\mathrm{CS}_n\rangle\langle\mathrm{CS}_{n'}| + h.c.)$$
$$+ \sum_n \hat{H}^{(n)}_{\mathrm{XT}}(\mathbf{x})|\mathrm{XT}_n\rangle\langle\mathrm{XT}_n| + j(\mathbf{x})\sum_{nn'}(|\mathrm{XT}_n\rangle\langle\mathrm{XT}_{n'}| + h.c.)$$

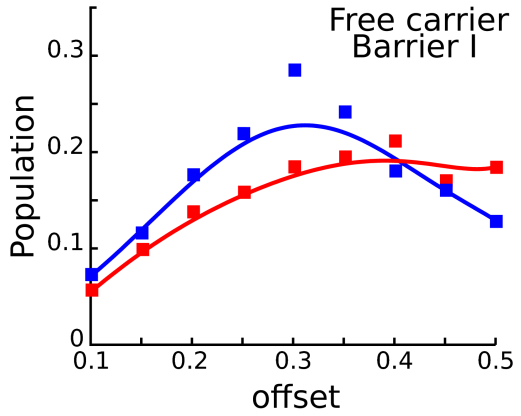


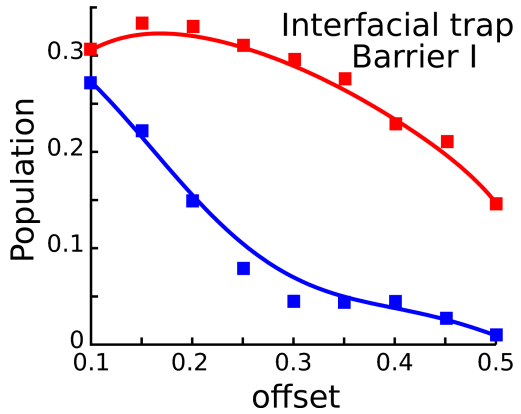
- CT/CS generation depends on exciton (de)localization
- ML-MCTDH calculations: 26 states/120 modes (barrier II)

Tamura, Burghardt, JACS (Communication) 135, 16364 (2013), Huix-Rotllant, Tamura, Burghardt, J. Phys. Chem. Lett. 6, 1702 (2015)

Electronic Eigenstate Picture



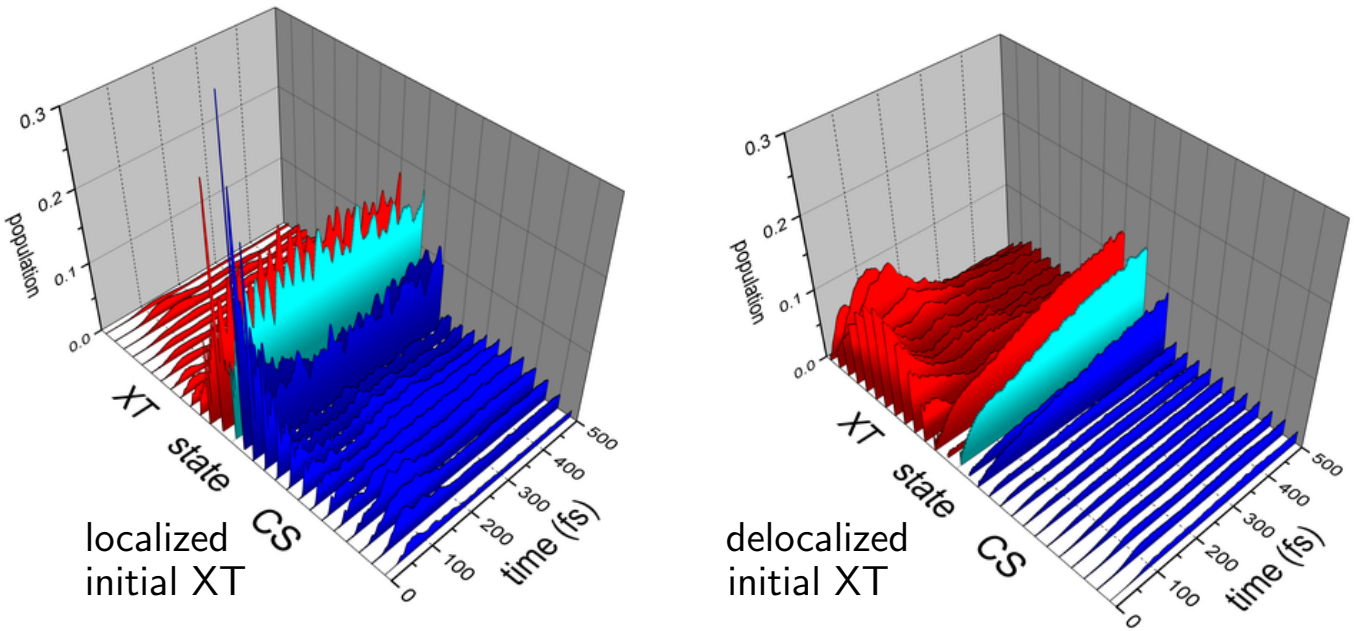




- interplay of delocalization, internal conversion, and charge transfer
- de/localized initial condition (blue/red) reduces/enhances interfacial trapping

Huix-Rotllant, Tamura, Burghardt, J. Phys. Chem. Lett., 6, 1702 (2015)

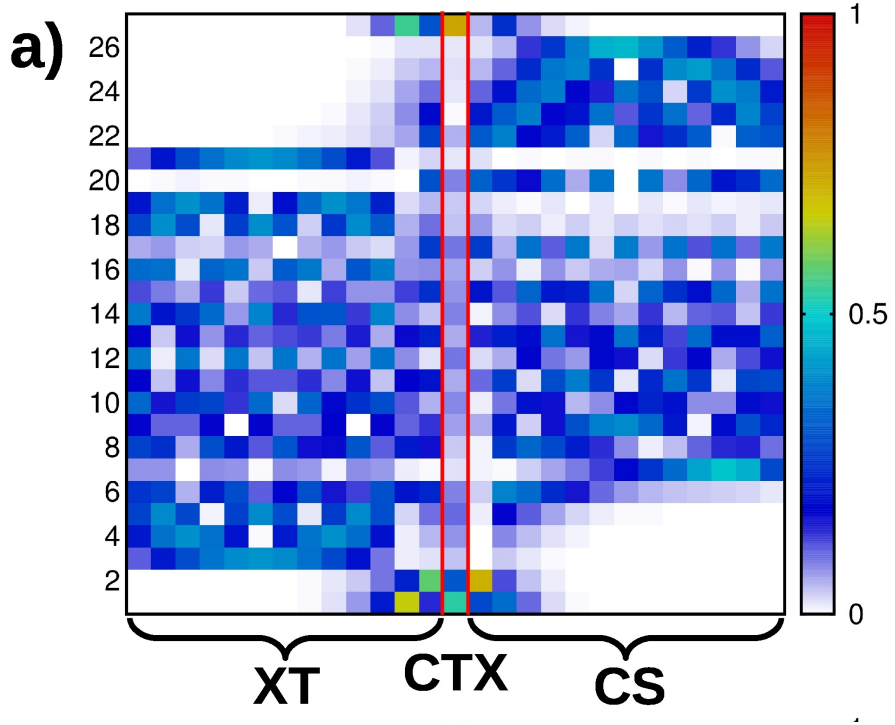
Interfacial Charge Separation in the Presence of CTX States

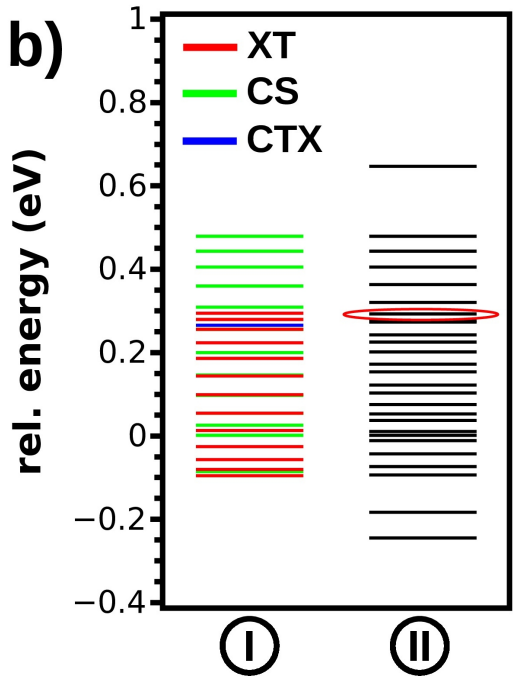


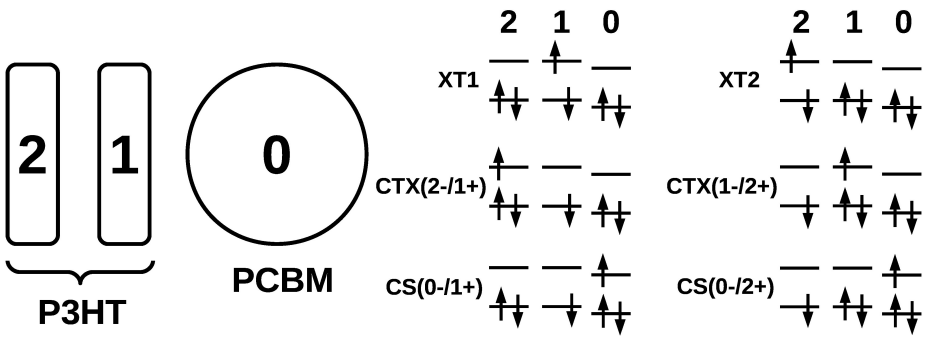
- CTX (turquoise) states emerge prominently as additional energetic traps
- ML-MCTDH calculations up to 182 states and 112 modes
- for a single CTX state: CS formation slightly reduced
- for larger models (50/182 states): reduction of CS yield is significant
- results depend in a sensitive fashion upon energetics and electronic couplings

Polkehn, Tamura, Burghardt, J. Phys. B, Special Issue "Light Energy Conversion, Light Harvesting", in press (2017)

P3HT/PCBM Model Including CTX States







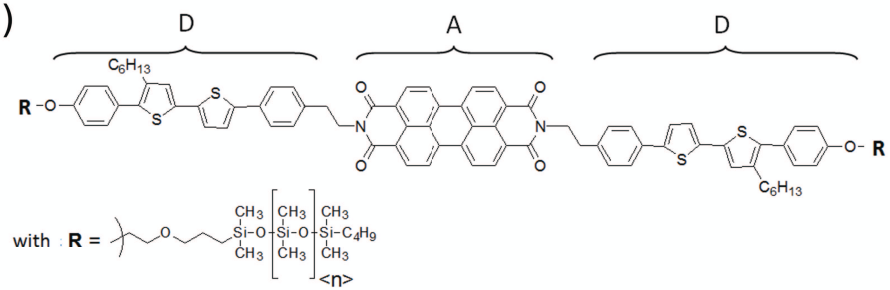
- 182 states/112 modes
- OT charge transfer excitons open new pathways for carrier formation
- but also act as energetic traps

Polkehn, Tamura, Burghardt, J. Phys. B, in press (2017)

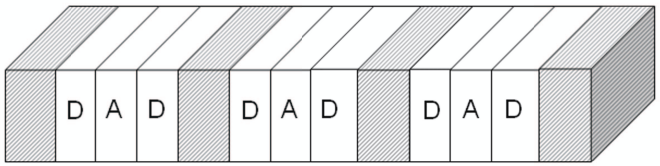
Highly Ordered DA Assemblies: Liquid Crystalline Material

collaboration with S. Haacke, S. Méry (Strasbourg)

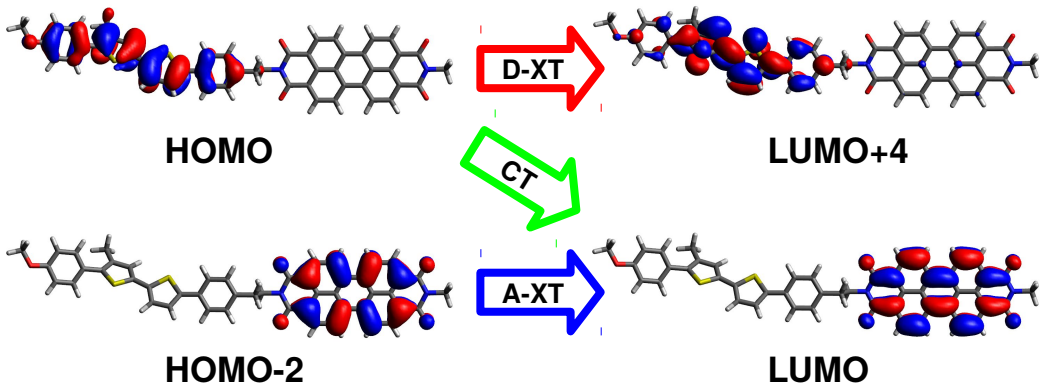
a)



b)



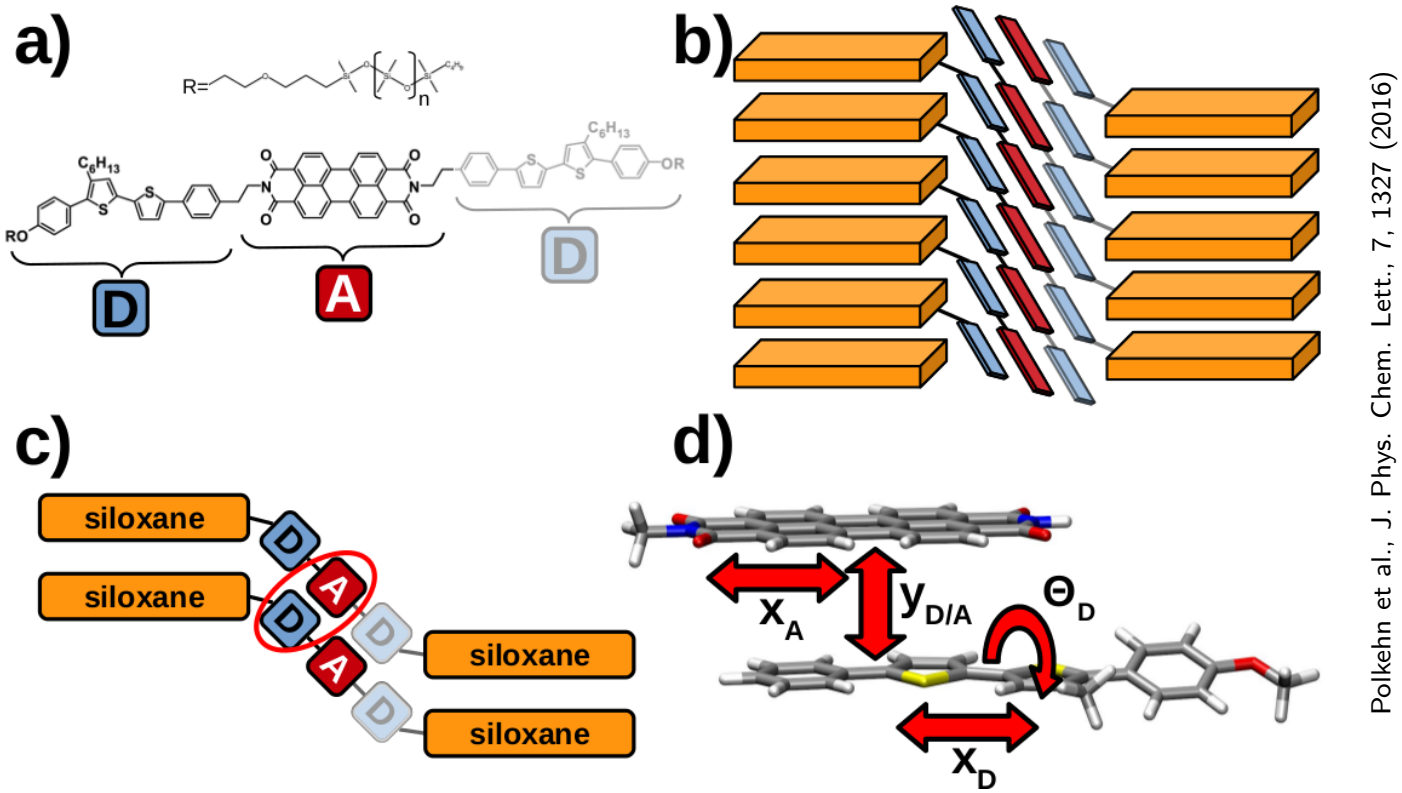
Roland, Ramirez, Léonard et al., PCCP, 14, 273 (2012)



Wenzel, Dreuw, Burghardt, PCCP, 15, 11704 (2013)

- competing ultrafast energy transfer (EET) and charge transfer (CT) processes
- in chloroform: EET in 130 fs, followed by CT in 2.7 ps
- in liquid crystalline phase: CT in 60 fs!
- relatively fast recombination (50 ps) – material doesn't really work well ...

What is Happening in the First-Generation Material?



Polkehn et al., J. Phys. Chem. Lett., 7, 1327 (2016)

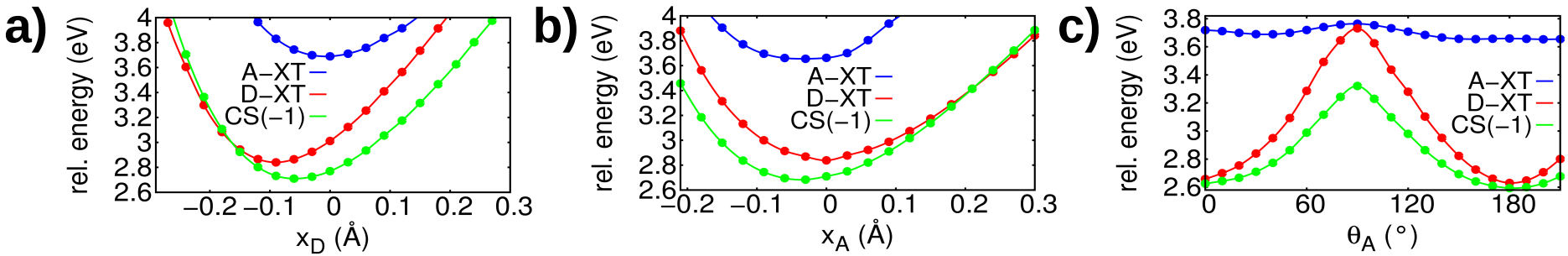
- first-generation material: liquid crystalline smectic mesophase
- idea: D/A stacks serve as "quantum wells" for carrier transport
- much faster charge transfer in film than solution (∼50 fs vs. ∼3 ps)
- calculations suggest unexpected inter-chain D-A interactions

$$\hat{H} = \hat{H}_{\text{on-site}} + \hat{H}_{\text{coupl}} + \hat{H}_{\text{e-ph}}$$

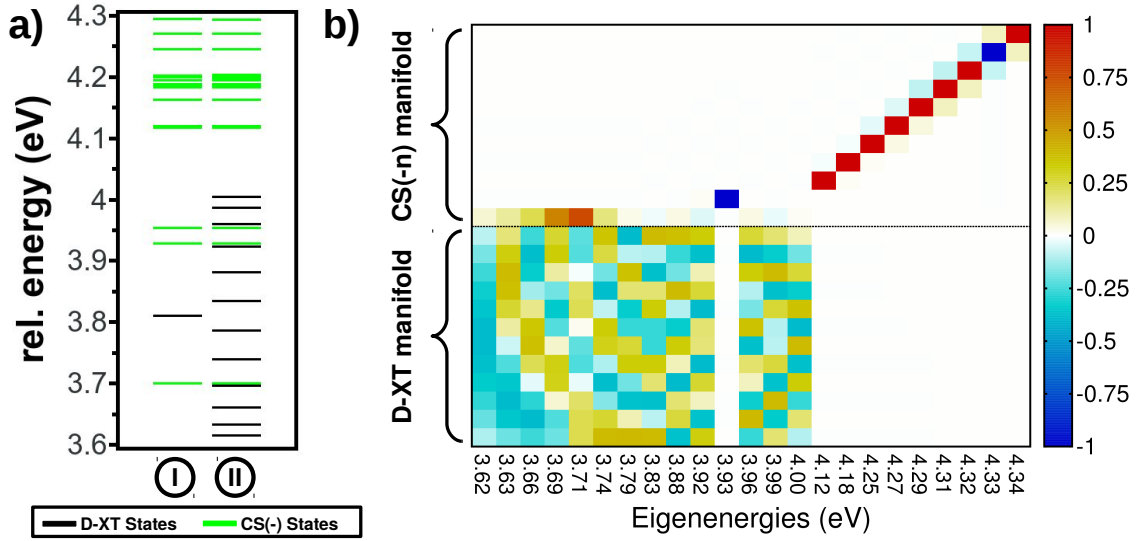
$$\hat{H}_{\text{on-site}} = \varepsilon_D \sum_{i=1}^{N_D} |D_i^{XT}\rangle\langle D_i^{XT}| + \varepsilon_A \sum_{i=1}^{N_A} |A_i^{XT}\rangle\langle A_i^{XT}| + \sum_{i=1}^{N_D}\sum_{j=1}^{N_A} \varepsilon_{D_i^+A_j^-} |D_i^+A_j^-\rangle\langle D_i^+A_j^-|$$

$$\begin{aligned}\hat{H}_{\text{coupl}} &= J_D \sum_{i=1}^{N_D}\sum_{j=1}^{N_D}(|D_i^{XT}\rangle\langle D_j^{XT}| + \text{h.c.}) + J_A \sum_{i=1}^{N_A}\sum_{j=1}^{N_A}(|A_i^{XT}\rangle\langle A_j^{XT}| + \text{h.c.}) + J_{DA} \sum_{i=1}^{N_D}\sum_{j=1}^{N_A}(|D_i^{XT}\rangle\langle A_j^{XT}| + \text{h.c.}) \\ &+ \kappa_D \sum_{i=1}^{N_D}\sum_{j=1}^{N_A}(|D_i^{XT}\rangle\langle D_i^+A_j^-| + \text{h.c.}) + \kappa_A \sum_{i=1}^{N_A}\sum_{j=1}^{N_A}(|A_i^{XT}\rangle\langle D_j^+A_i^-| + \text{h.c.}) \\ &+ t_e \sum_{i=1}^{N_D}\sum_{j=2}^{N_A-1}(|D_i^+A_j^-\rangle\langle D_i^+A_{j\pm1}^-| + \text{h.c.}) + t_h \sum_{i=2}^{N_D-1}\sum_{j=1}^{N_A}(|D_i^+A_j^-\rangle\langle D_{i\pm1}^+A_j^-| + \text{h.c.})\end{aligned}$$

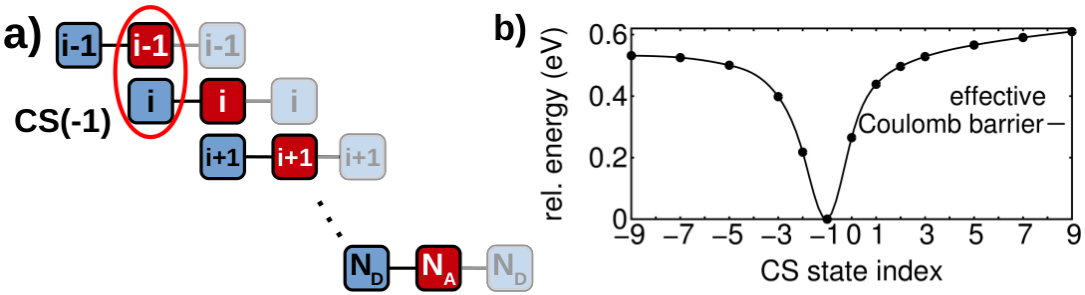
$$\begin{aligned}\hat{H}^{\text{e-ph}} &= \hat{T}_{\text{ph}}(\{\zeta^D\},\{\zeta^A\},\{\zeta^{DA}\}) + \sum_i \hat{V}_D^{XT}(\{\zeta_i^D\},\{\zeta_i^{DA}\})|D_i^{XT}\rangle\langle D_i^{XT}| + \sum_i \hat{V}_A^{XT}(\{\zeta_i^A\},\{\zeta_i^{DA}\})|A_i^{XT}\rangle\langle A_i^{XT}| \\ &+ \sum_i\sum_j \hat{V}_{DA}(\{\zeta_i^D\},\{\zeta_j^A\},\{\zeta_{ij}^{DA}\})|D_i^+A_j^-\rangle\langle D_i^+A_j^-|\end{aligned}$$



Liquid Crystalline Phase – Energetics



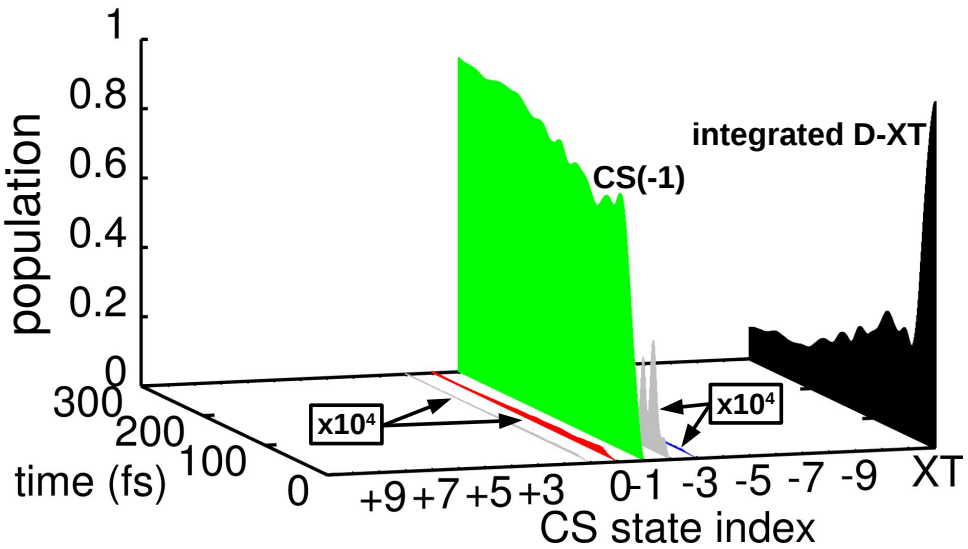
- energetics at Franck-Condon geometry
- state mixing: excitonic manifold and CS(-1) state
- but higher charge separated states barely accessible



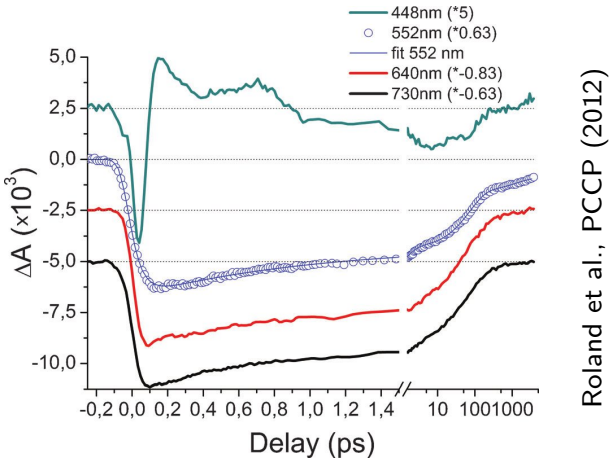
- on-site energies computed from ADC(2) and TDDFT
- internal field: 20 V/μm
- CS(-1) state strongly stabilized

Polkehn, Tamura, Eisenbrandt, Haacke, Méry, Burghardt, J. Phys. Chem. Lett., 7, 1327 (2016)

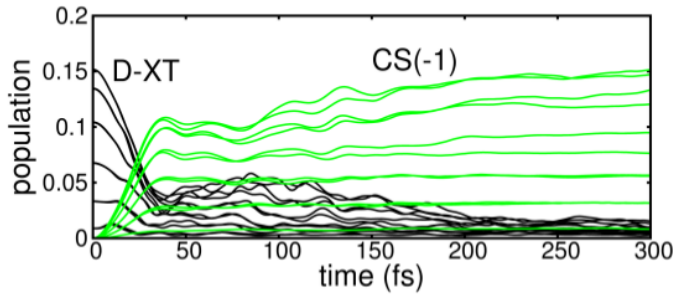
Liquid Crystalline Phase – Dynamics

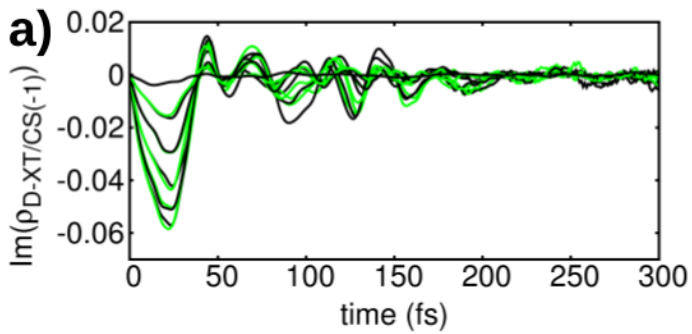


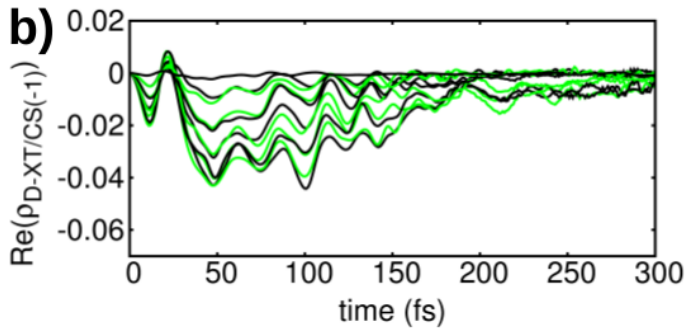
Polkehn et al., JPCL (2016)



Roland et al., PCCP (2012)

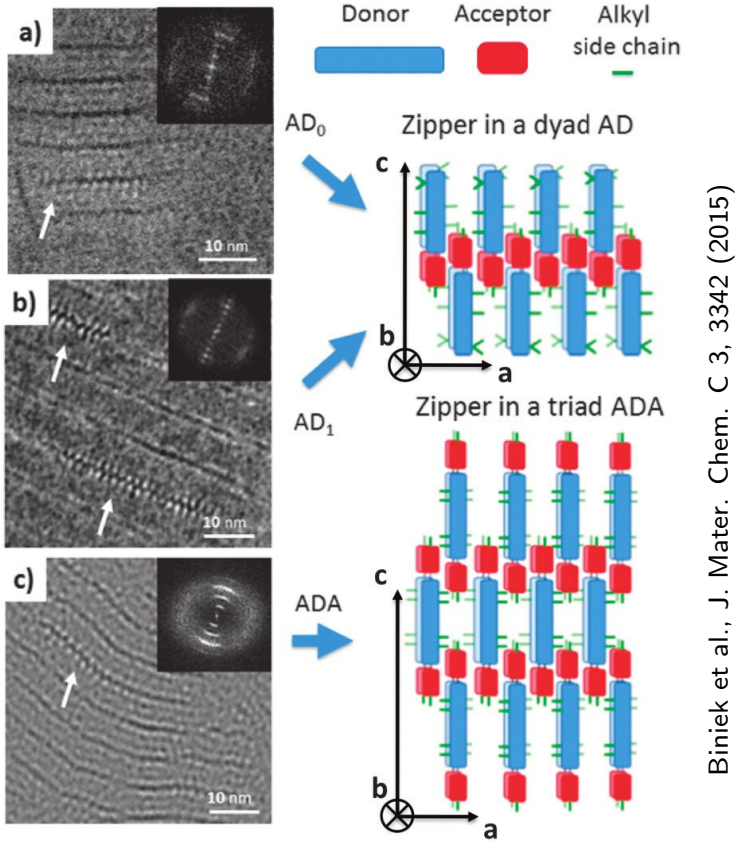




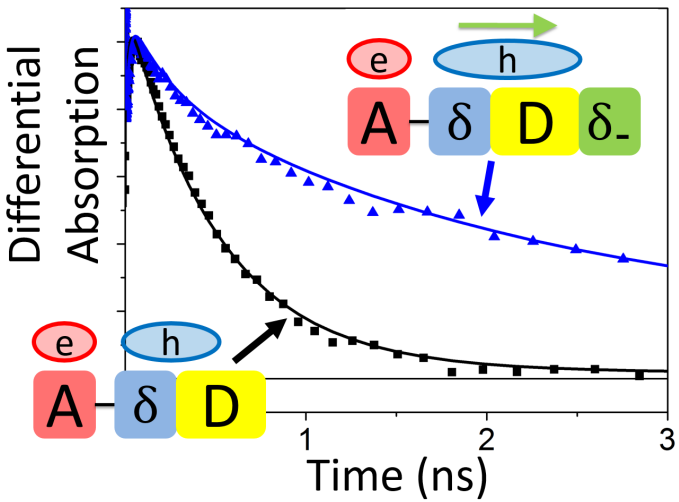


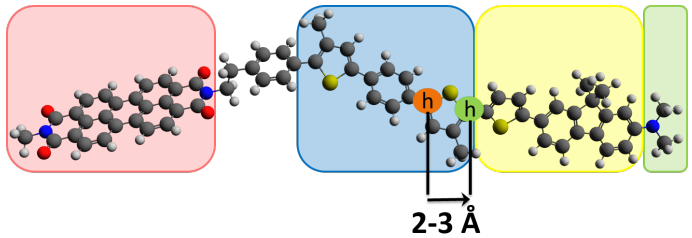
- transition to CS(-1) states (∼50 fs) explains transient absorption experiments (Haacke)
- ML-MCTDH simulations for 156 states/48 modes

Second Generation Material: Zipper-like Molecular Packing



Biniek et al., J. Mater. Chem. C 3, 3342 (2015)

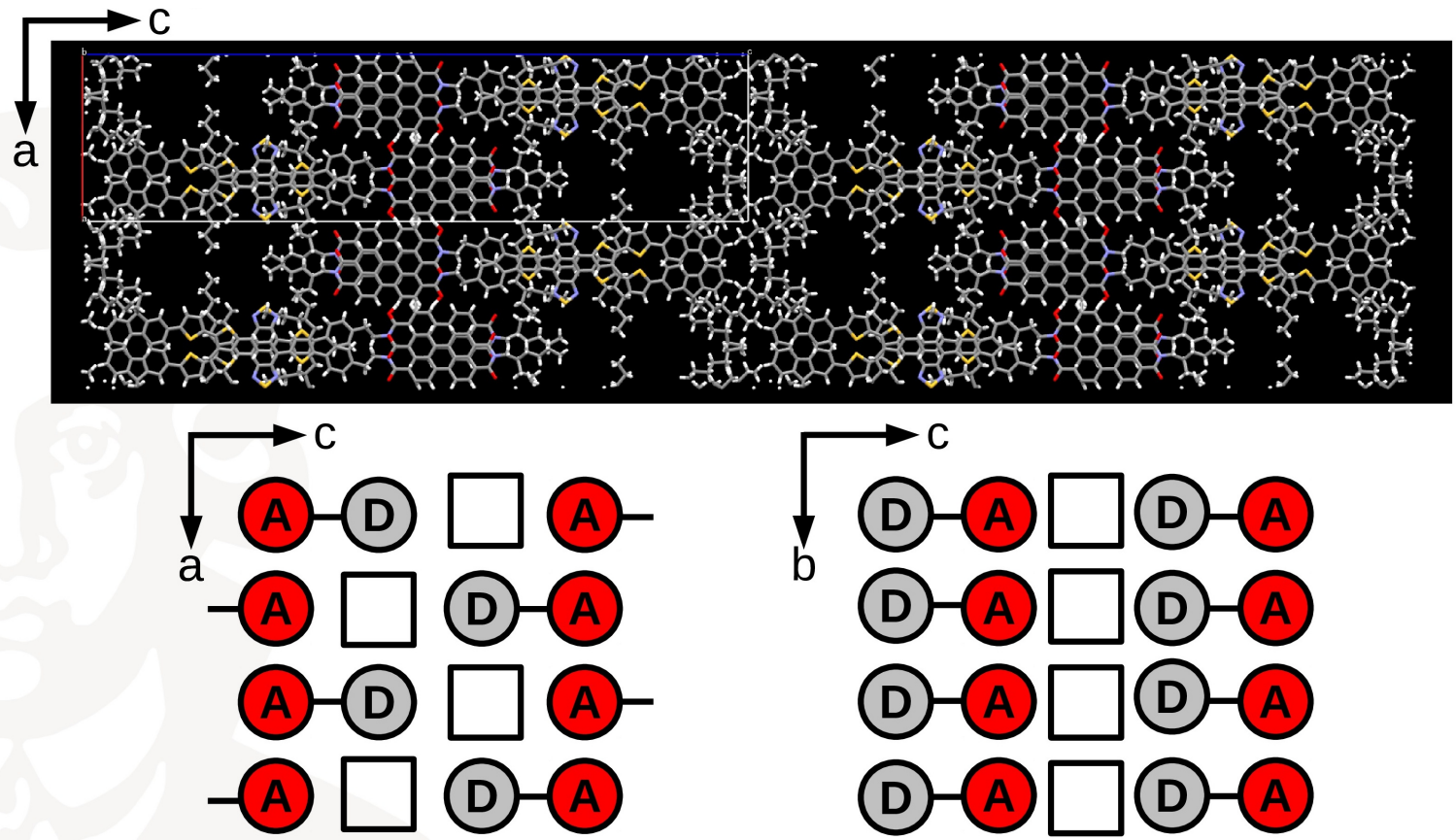




Liu, Eisenbrandt et al., PCCP 18, 18536 (2016)

- tunable donor species: alternating thiophene/fluorene/benzothiadiazole units; electrodeficient bridge to the perylene acceptor – chemical design!
- organization in lamellae (both DA and ADA – but not DAD)
- comparatively slow CT formation (tens of ps) - and less recombination

Second Generation Material: In Progress . . .



- coarse-grained model for Kinetic Monte Carlo (KMC) simulations
- microelectrostatics calculations (collaboration with G. d'Avino, Grenoble)
- multi-scale modeling needed!

Summary

1. Molecular-Level Approach to Organic Photovoltaics
   - combine electronic structure & high-dimensional quantum dynamics
   - e-h lattice model: highlights fragment properties + molecular packing
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   - charge-transfer excitons in regioregular oligothiophene phases
   - coherent formation of charge transfer excitons
   - impact on charge separation at donor-acceptor interface

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- R. Binder
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- T. Ma
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- M. Bonfanti
- K. Schwinn

Former members:

- J. Wahl
- M. Huix-Rotllant

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- D. Beljonne, Y. Olivier (Mons, Belgium)

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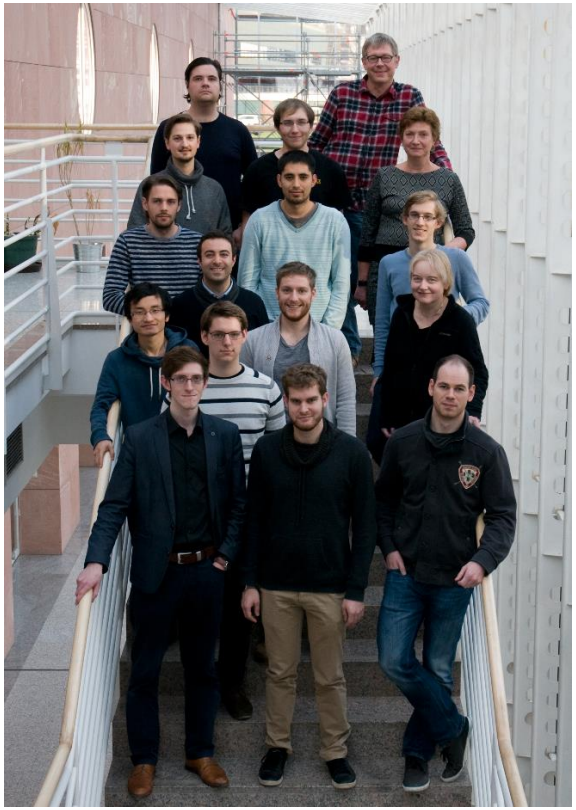


Theoretical Chemistry
of Complex Systems

AK Burghardt

Quantum Coherence Plays a Non-Negligible Role!

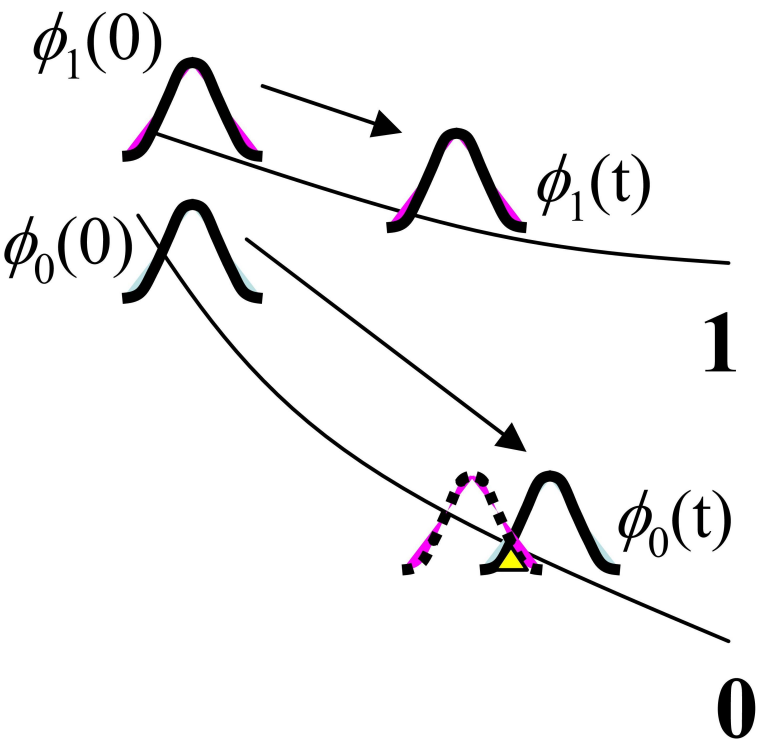
$$|\psi(t)\rangle = c_0(t)|0\rangle|\phi_0(t)\rangle + c_1(t)|1\rangle|\phi_1(t)\rangle$$

electronic coherence:

$$\rho_{01}(t) = \mathrm{Tr}[|0\rangle\langle 1|\hat{\rho}(t)]$$
$$= \langle 1|\hat{\rho}(t)|0\rangle = c_1^*(t)c_0(t)\langle\phi_1(t)|\phi_0(t)\rangle$$

- coherence $\propto$ overlap of nuclear wavefunctions
- typical decoherence times: tens to hundreds of fs or more (estimate from $\tau_{\mathrm{dec}} \sim \tau_g(6k_BT/\lambda)^{1/2}$ or $\tau_{\mathrm{dec}} \sim \gamma^{-1}(\lambda_T/\Delta x)^2)$

  Prezdho, Rossky, PRL 81, 5294 (1998)
- loss of coherence not captured by classical trajectory picture



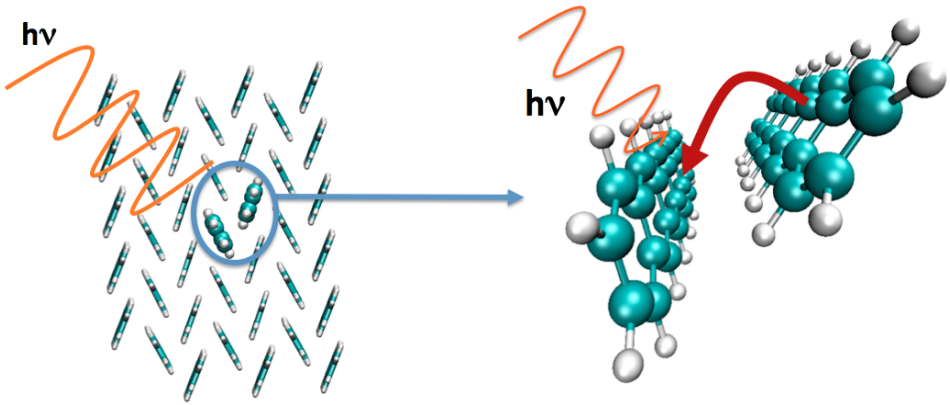
picture: P. Rossky et al.

Singlet Fission: Route To Carrier Multiplication

(collaboration with H. Tamura (Sendai/Tokyo), D. Beljonne (Mons))

$$\mathrm{XT} \longrightarrow {}^1(\mathrm{TT}) \longrightarrow \mathrm{T}_1 + \mathrm{T}_2 \text{ (spin conserving)}$$

possibly overcome Shockley-Queisser limit

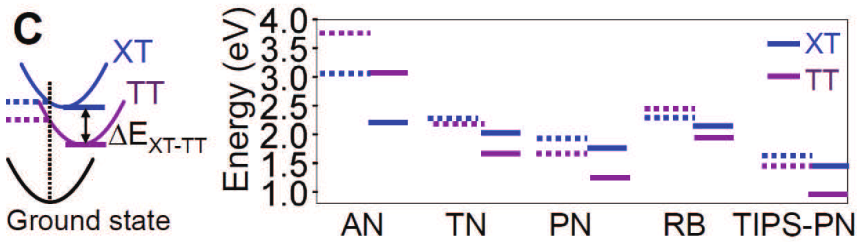


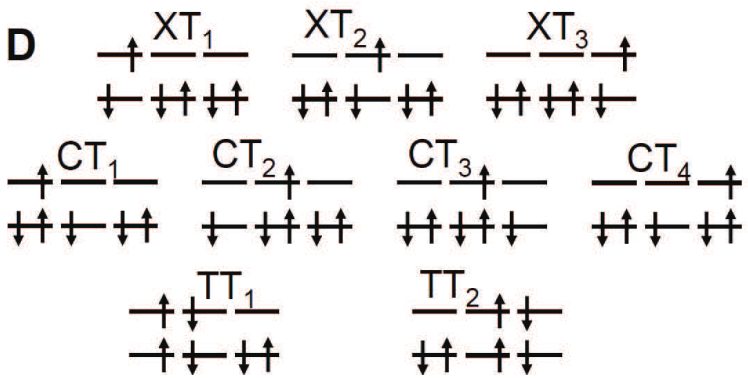
http://sites.lsa.umich.edu/zimmerman-lab/wp-content/uploads/sites/52/2014/03

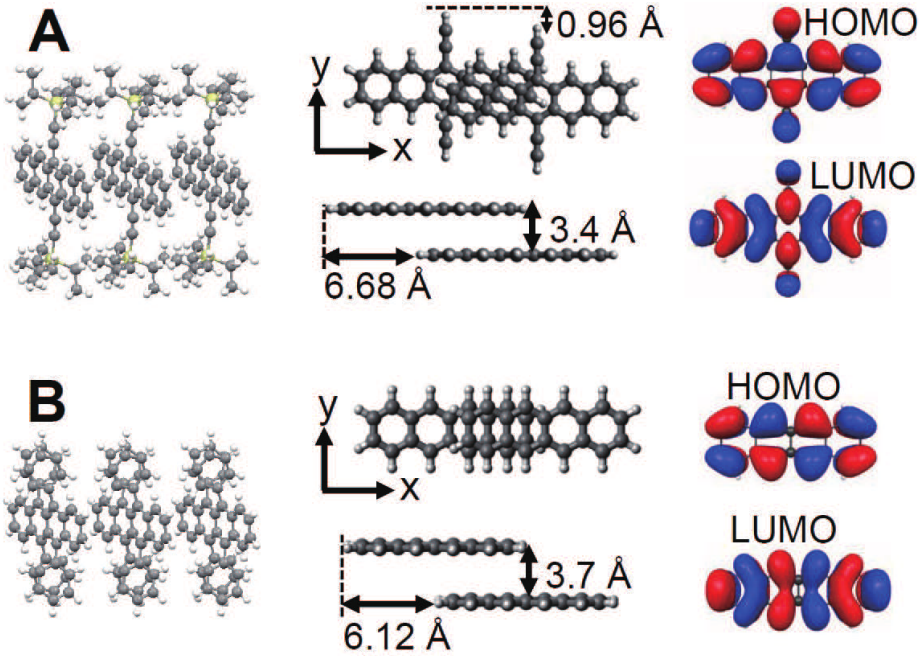
- driving force $\Delta E_{\mathrm{XT-TT}} < 0$ doesn't explain the whole picture
- possible involvement of intermediate CT states (superexchange)
- vastly different time scales for different materials

- discovered in 1965: anthracene
- reviews by Smith & Michl, Annu. Rev. Phys. Chem. 2013, 64, 361, Chem. Rev. 110, 6891 (2010)

Molecular Packing: Energetics & Electronic Couplings







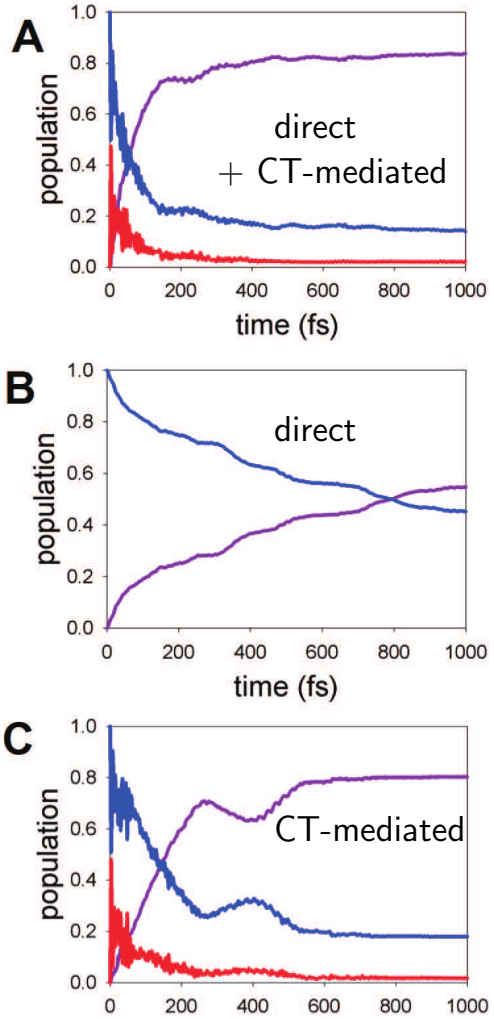
- energetics of acene series (C)
- trimer model: 9 states (D)

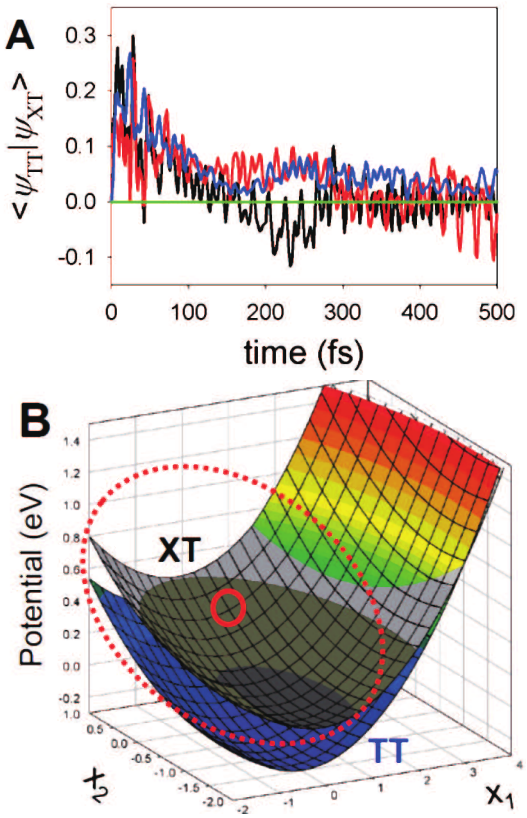
- TIPS-pentacene (A): slip-stacked
- rubrene (B): C_{2h} symmetric

Electronic coupling @ equilib. non-zero for TIPS-pentacene but vanishing for rubrene!
(MRMP2 calculations for dimers, el. couplings via diabatization protocol)

Tamura, Huix-Rotllant, Burghardt, Olivier, Beljonne, Phys. Rev. Lett., 115, 107401 (2015)

TIPS-Pentacene: Ultrafast Singlet Fission



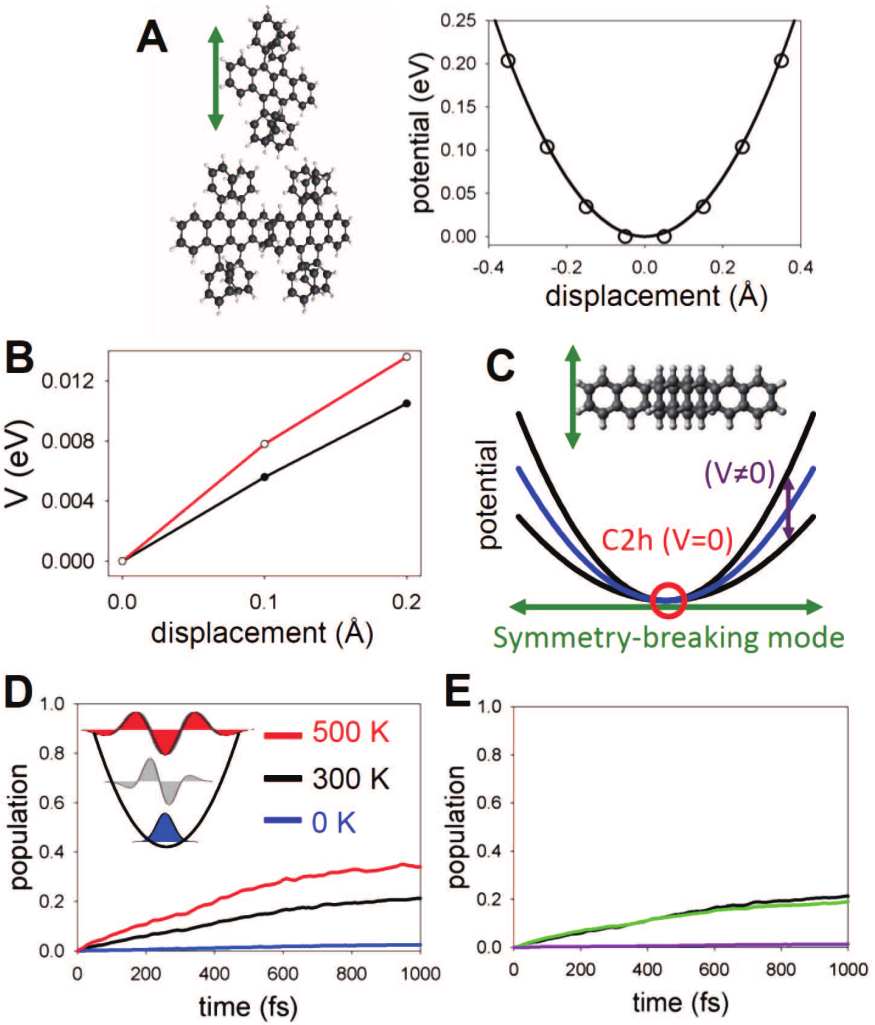


- ultrafast, coherent SF
- slip-stacked geometry: avoided crossing
- interfering direct and CT-mediated pathways (electronic coupling via CT's dominates)
- vibrational coherence effectively transferred between XT and TT states (see $\langle\psi_{TT}|\psi_{XT}\rangle$)

  Musser et al., Nature Phys. 11, 352 (2015)
- MRMP2 calculations + diabatization

Tamura, Huix-Rotllant, Burghardt, Olivier, Beljonne, Phys. Rev. Lett., 115, 107401 (2015)

Rubrene: Thermally Activated Singlet Fission

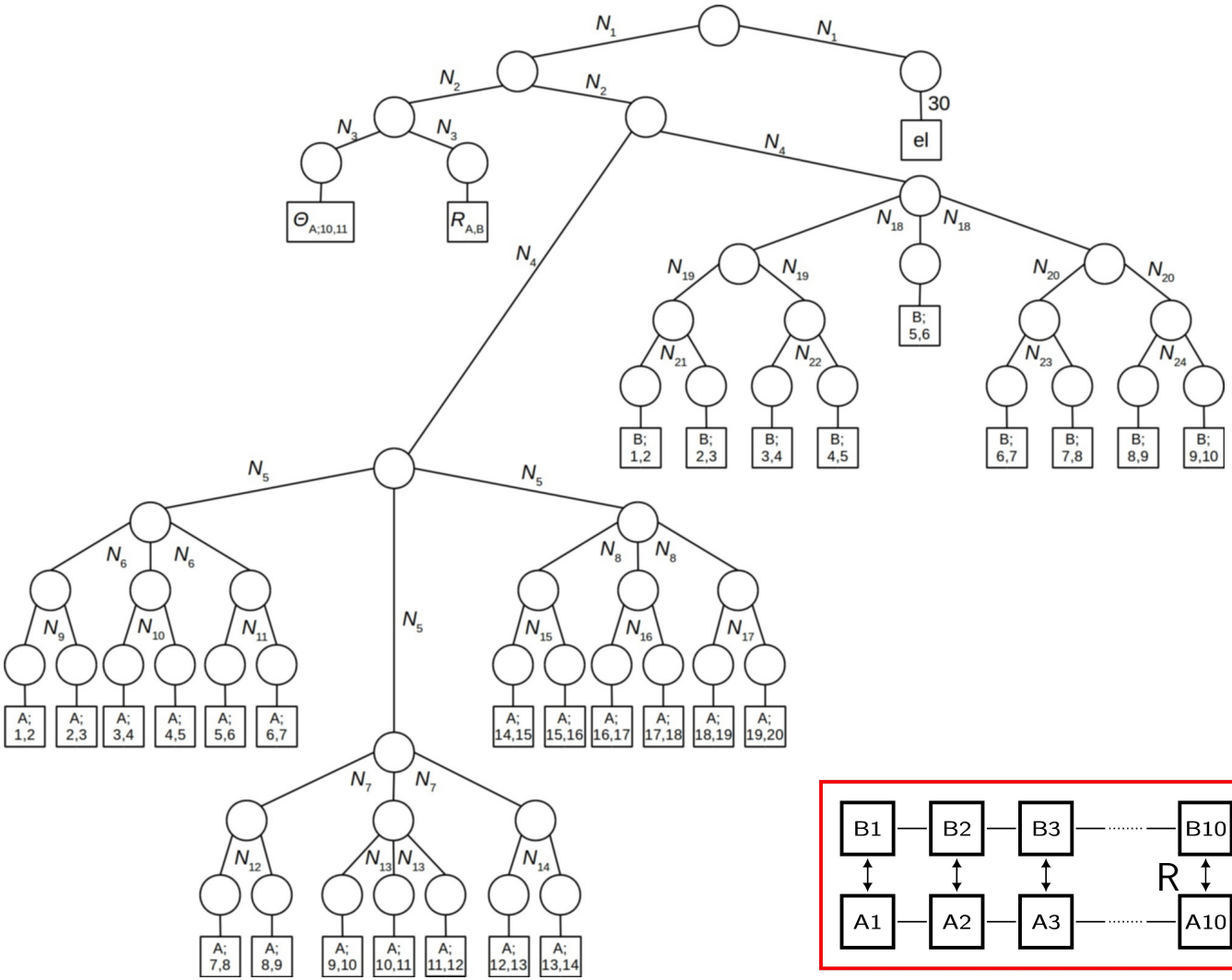


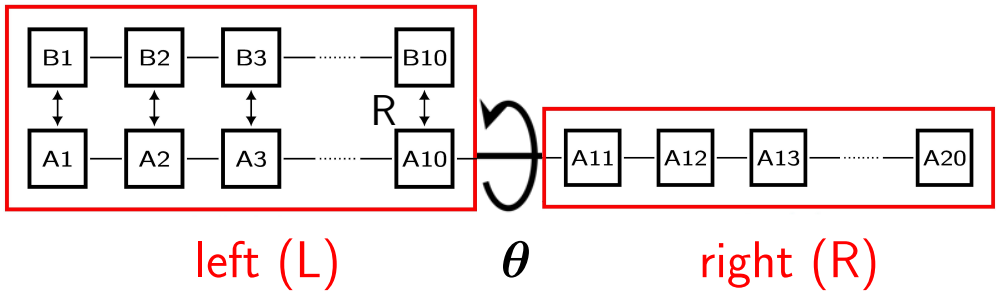
- driving force slightly exergonic (like tetracene), but thermally activated SF (picosecond scale)
- C_{2h} crystal geometry: electronic coupling vanishes – conical intersection
- electronic couplings depend on symmetry-breaking coordinate: $V(X) = \lambda X$, $\lambda \sim 10^{-3}$ eV
- slow, incoherent dynamics
- key influence of molecular packing

Tamura, Huix-Rotllant, Burghardt, Olivier, Beljonne, Phys. Rev. Lett., 115, 107401 (2015)

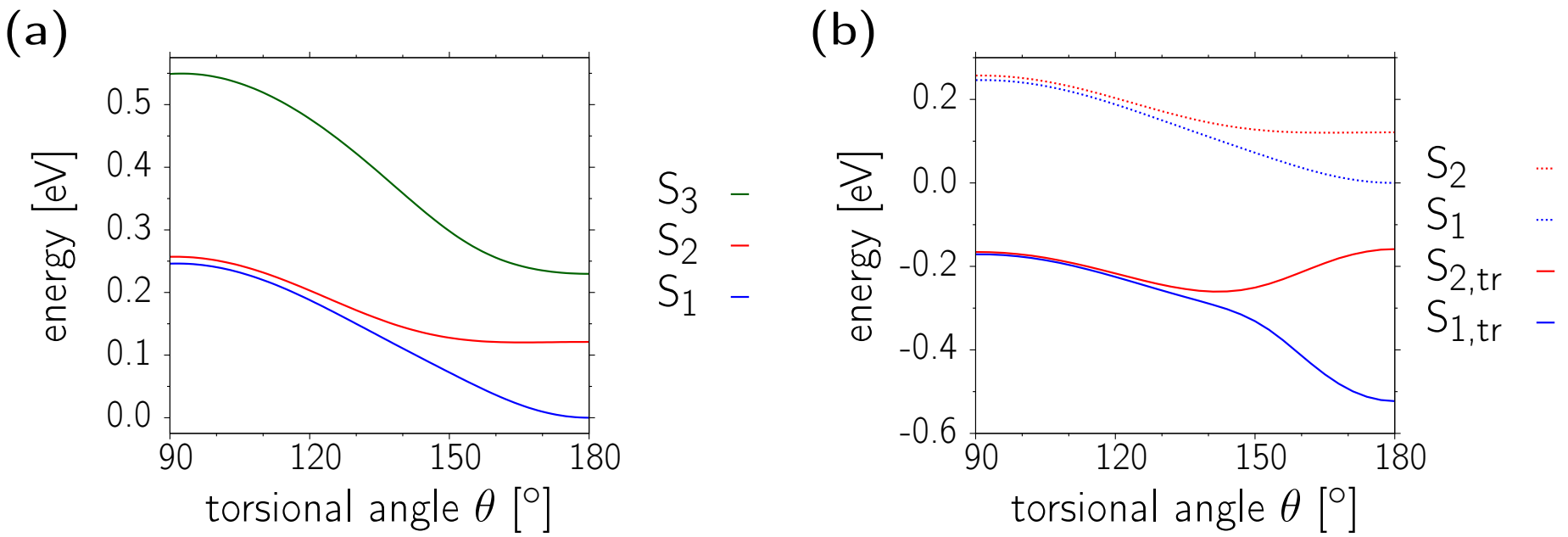
ML-MCTDH: Example

Binder, Polkehn, Ma, Burghardt, Chem. Phys. 482, 16 (2017)





Exciton-Polaron Dynamics: Adiabatic Picture

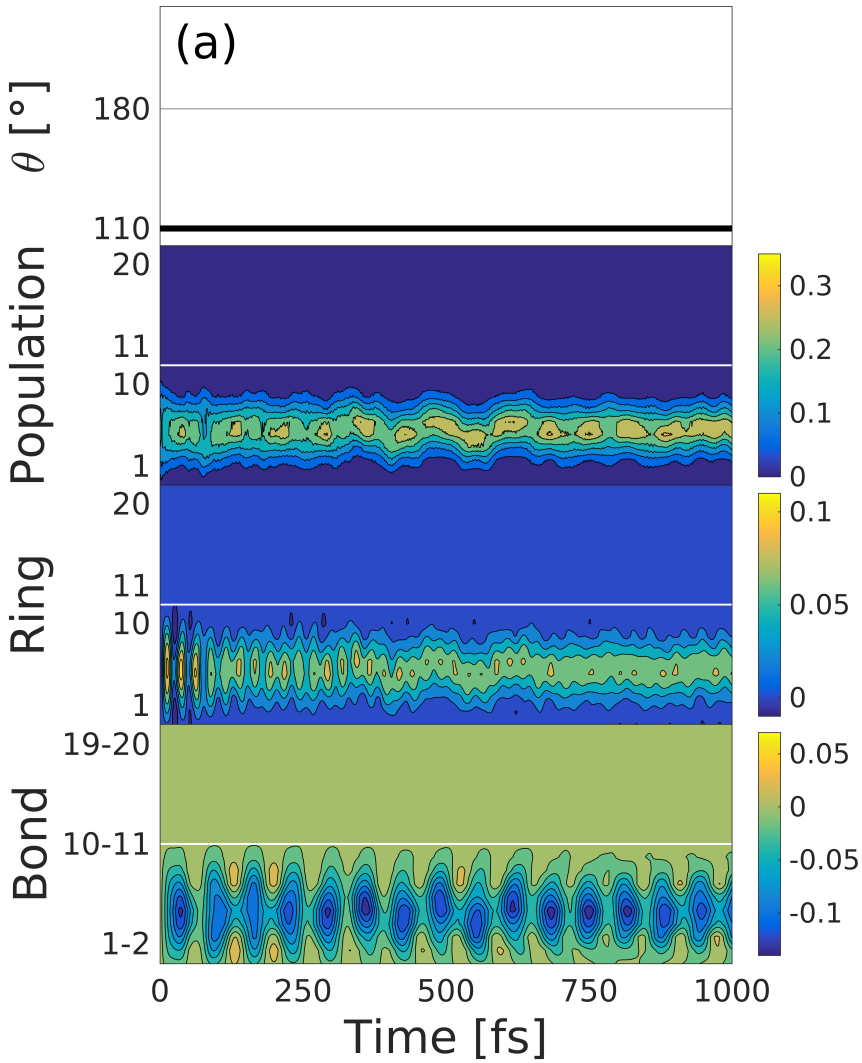


- dynamics is essentially happening on coupled S_1/S_2 surfaces
- effective torsion potentials including stabilization due to trapping $(S_{1,\mathrm{tr}}/S_{2,\mathrm{tr}})$[1]
- initial left/right localized state = superposition of S_1/S_2
- energy loss due to external bath acting on torsional mode
- exciton-polaron trapping persists at all stages of the dynamics

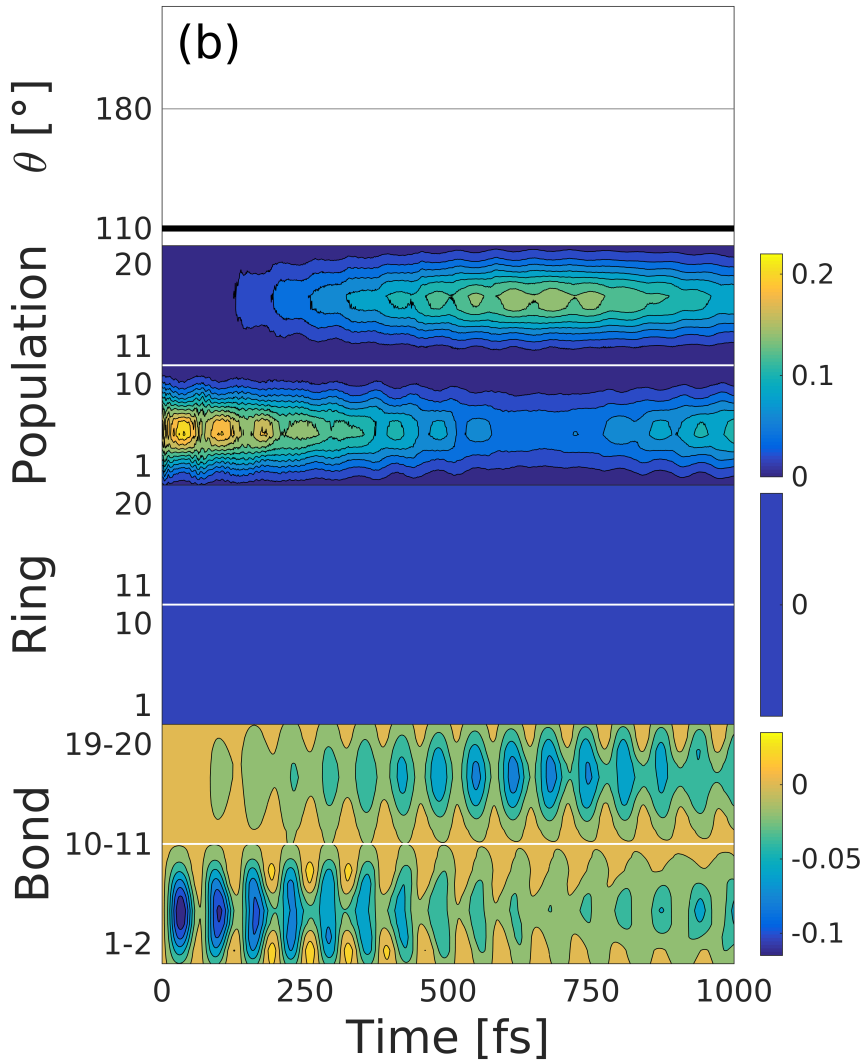
[1] i.e., "polaron transformed" potentials

Quantum Dynamics: 20-Site J-Aggregate with Central Torsion

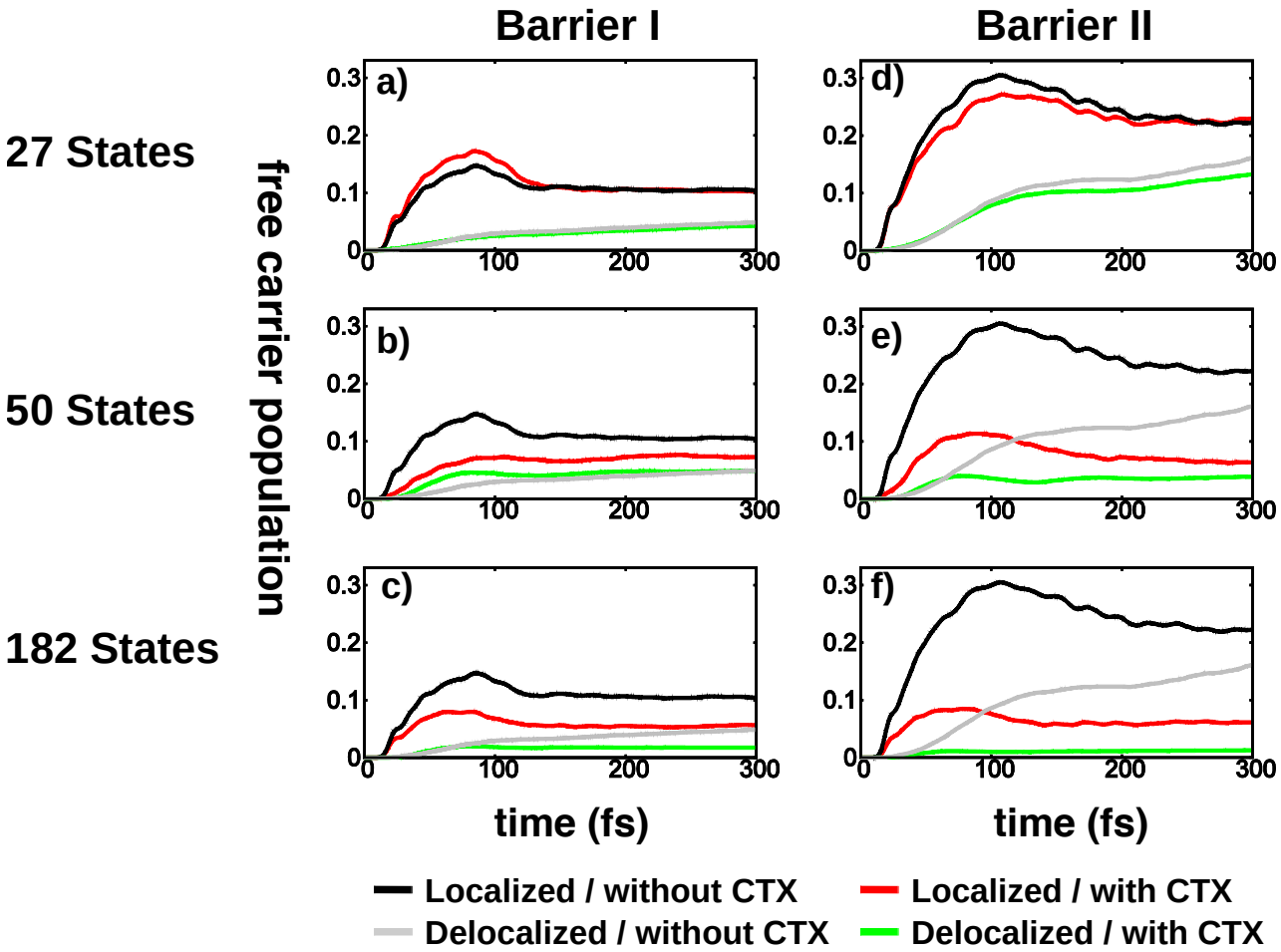
C-C inter-monomer mode + local C=C + torsion + bath



C-C inter-monomer + torsion + bath



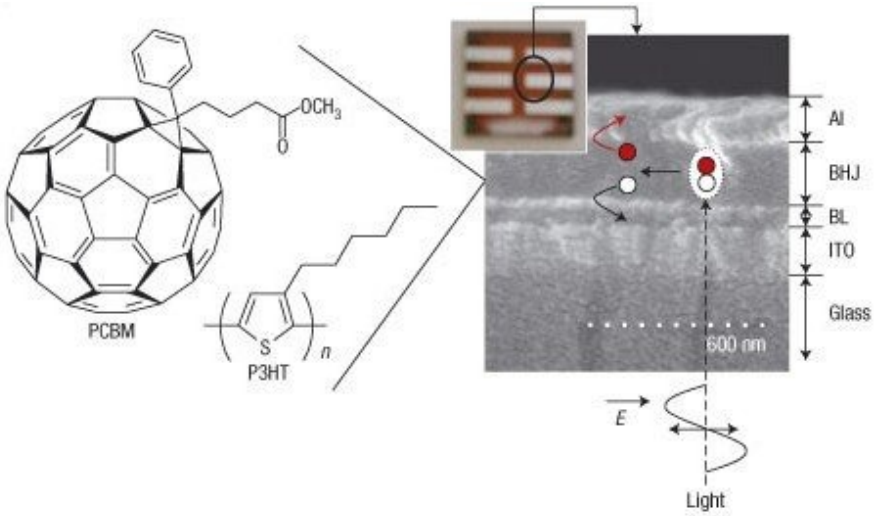
Interfacial Charge Separation in the Presence of CTX States

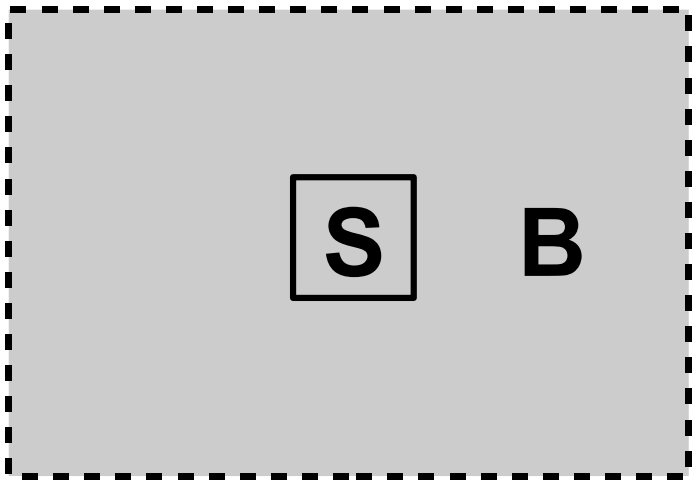


- time-dependent free carrier populations

Polkehn, Tamura, Burghardt, J. Phys. B, Special Issue "Light Energy Conversion, Light Harvesting", submitted (2017)

System-Bath Models





S region: e.g., electronic degrees of freedom (electron-hole states)

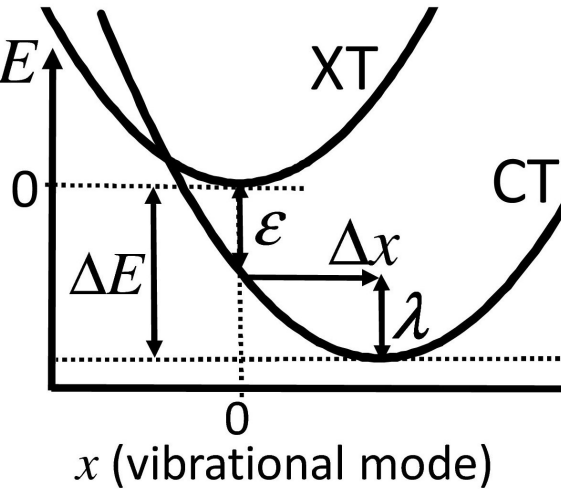
B region: all vibrations (phonons) mapped to harmonic oscillator model

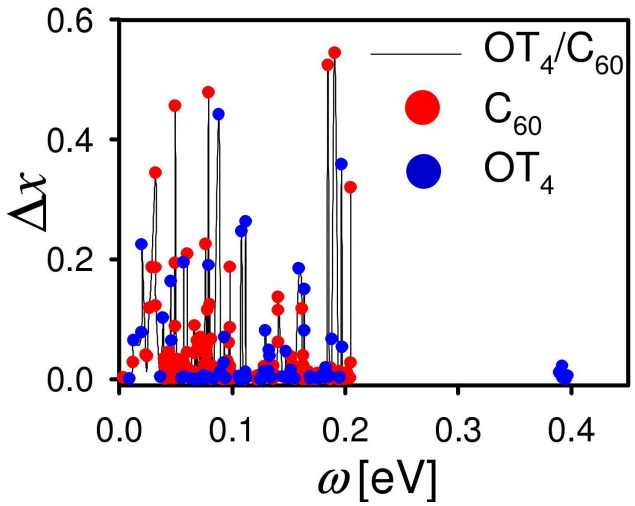
$$\hat{H}_B + \hat{H}_{SB} = \sum_n \tfrac{1}{2}(\hat{p}_n^2 + \tfrac{1}{2}\omega_n^2 \hat{x}_n^2) + \hat{s}\sum_n c_n \hat{x}_n$$

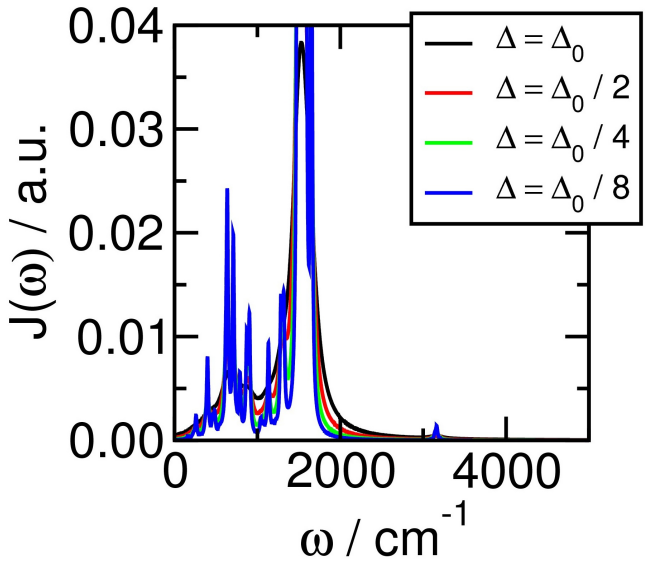
$$J(\omega) = \pi/2 \sum_n c_n^2/\omega_n \delta(\omega - \omega_n)$$

spectral density

Spectral Densities from Electronic Structure Calculations(*)







$$J(\omega) = \frac{\pi}{2} \sum_n^N \frac{c_n^2}{\omega_n} \delta(\omega - \omega_n) \simeq \frac{\pi}{2} \sum_n^N \frac{c_n^2}{\pi} \frac{\Delta}{(\omega - \omega_n)^2 + \Delta^2}$$

Tamura, Martinazzo, Ruckenbauer, Burghardt, J. Chem. Phys., 137, 22A540 (2012)

(*)NB. Alternatively: obtain SD's from correlation functions (MD, CPMD, ...)