Advanced Materials Modeling

Lecture on
Modeling of organic semiconductors

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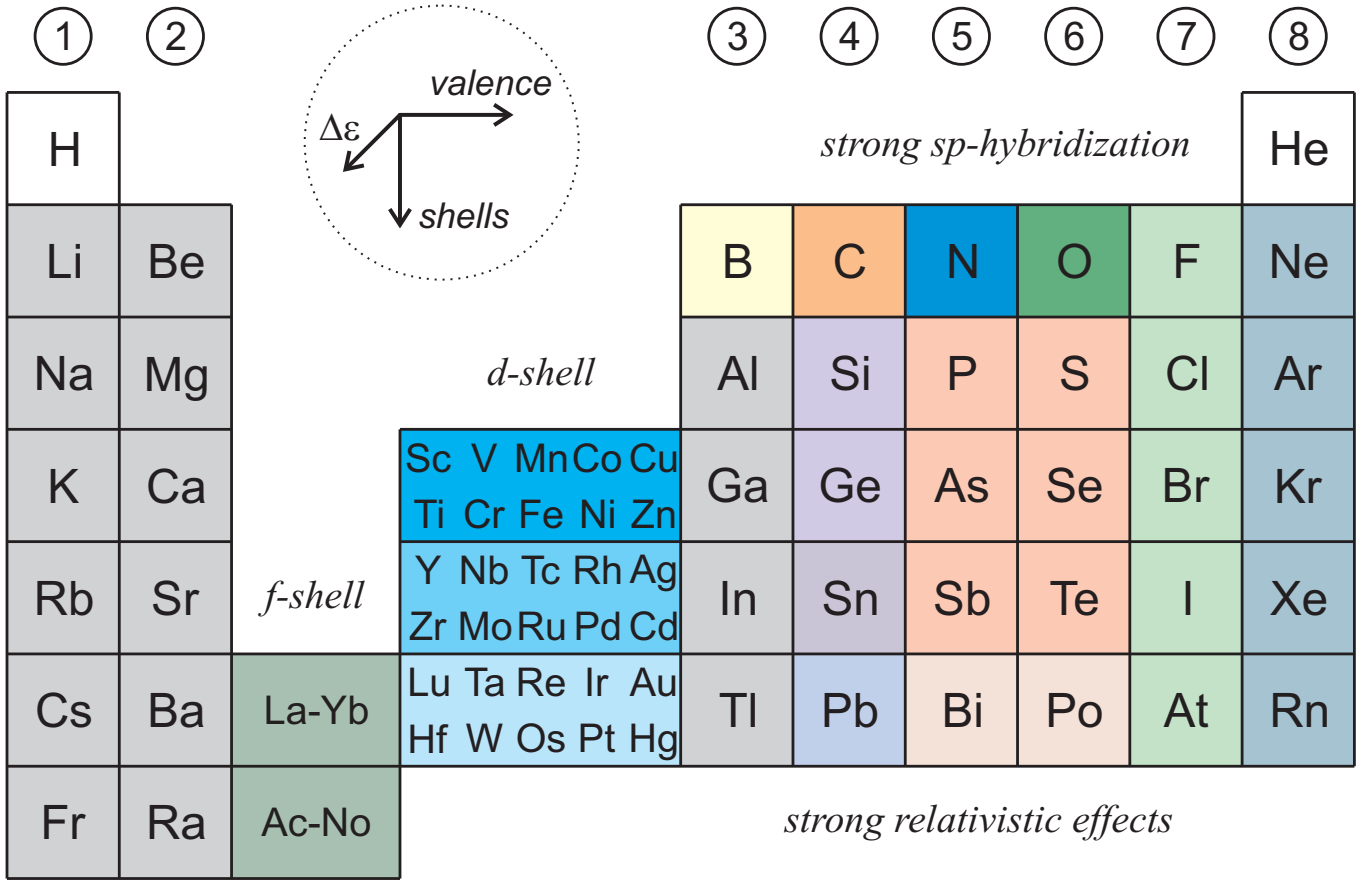
April 23, 2021

Outline

- Introduction
- Scale gap problem
- Structural studies
- Electronic properties
- Spectroscopy (vibronic couplings, UV-Vis and Raman spectra)
- Energy and charge transport
- Electronic coarse-graining

Different classes of materials require different approaches



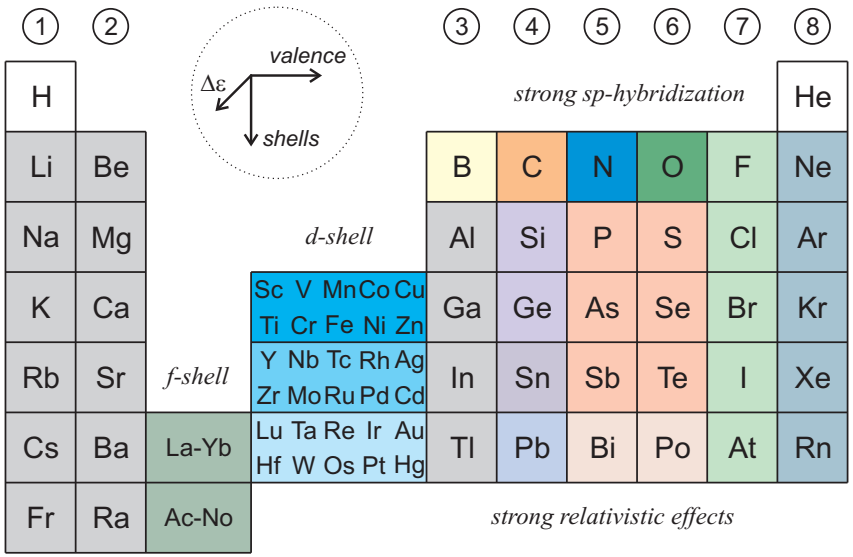
Depends on type of chemical bonding and phenomena of interest

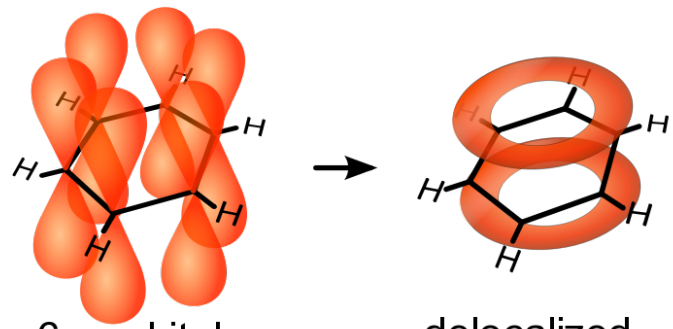
Different classes of materials require different approaches

- Rare gas elements – LJ
- Simple metals – LDA, EAM, ML (but not superconductivity)
- Ionic insulators – EIM, DFT
- Small molecules – CCSD(T), ML
- Small molecule solids/liquids – FF, EFP
- Organic insulators – OPLS, PM7, DFT-D
- Biopolymers – FF, PM7 (but not charge transport)
- Tetrahedrally coordinated semiconductors – TB, DFTB, GW
- Pnictide/chalcogenide semiconductors – DFT
- Organic semiconductors – will be discussed here
- Simple oxides – COMB, DFT
- Transition metal oxides – GGA+U
- Actinides – ???

What is organic semiconductor

1. **Organic** – built from C with terminal H, possibly with isovalent substitutions (N for CH, O/S for CH_2, F/Cl for H)
2. π-**conjugated** – only π-electrons on frontier orbitals





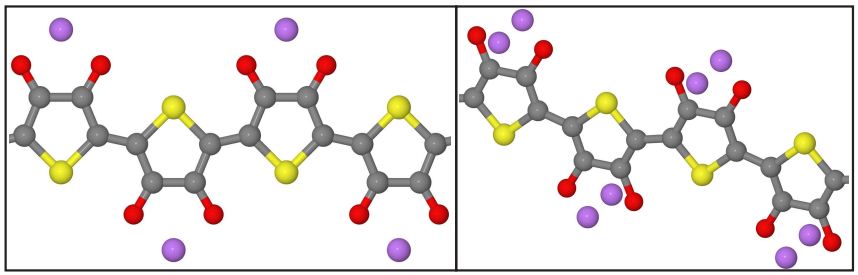
$$t_{sp2} = 3.26\frac{\hbar^2}{md^2} \gg t_{pp\pi} = 0.63\frac{\hbar^2}{md^2}$$
(Harrison's parameterization)

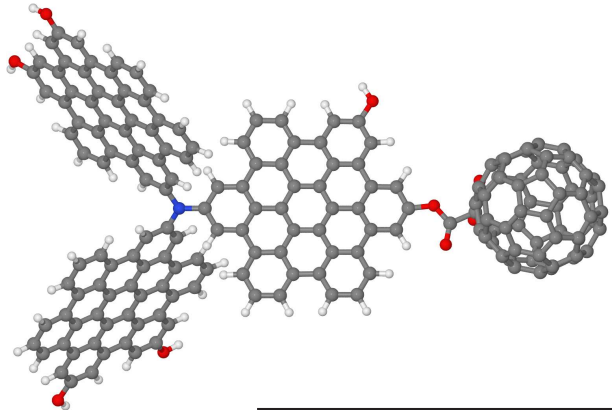
- Also **metal-organic** – include *d*-elements via $pd\pi$
- Also **hybrid** – include any electronic system in resonance

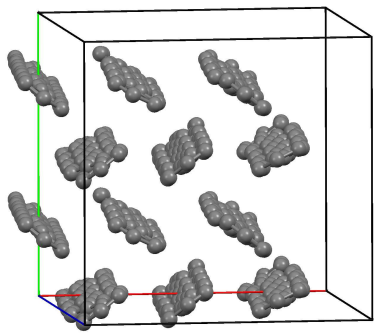
Number of organic semiconductors is comparable to number of inorganic ones
Display is an example of a competitive application

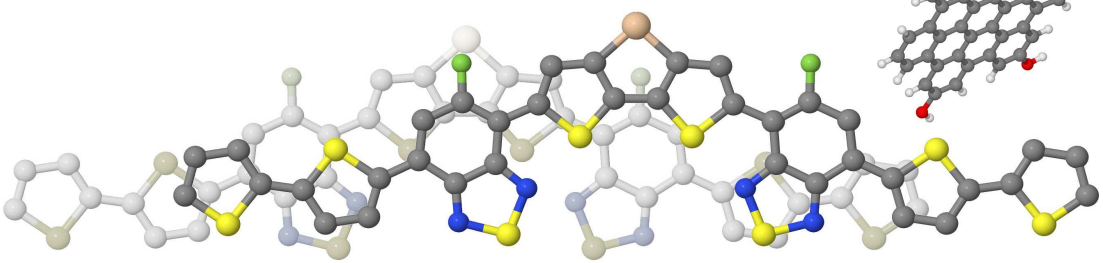
Structural diversity

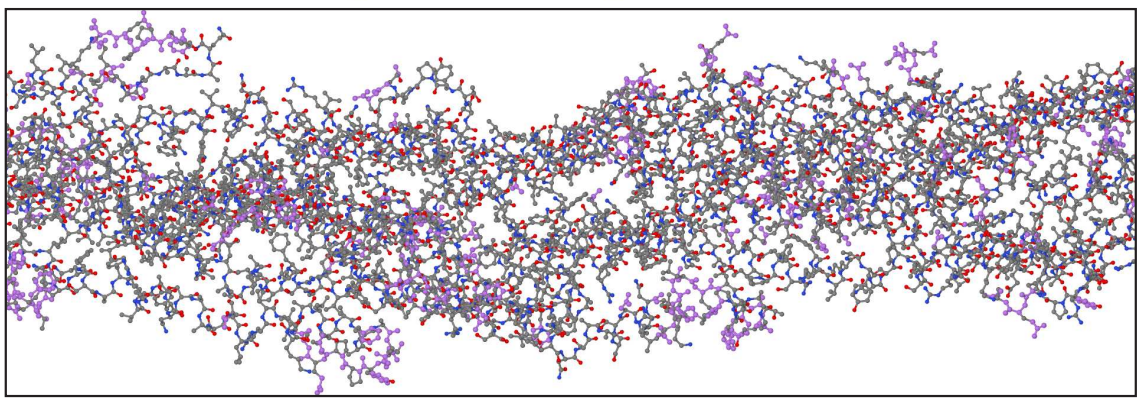
From 0D to 3D, from rigid to soft, often heterogeneous with multiscale structuring

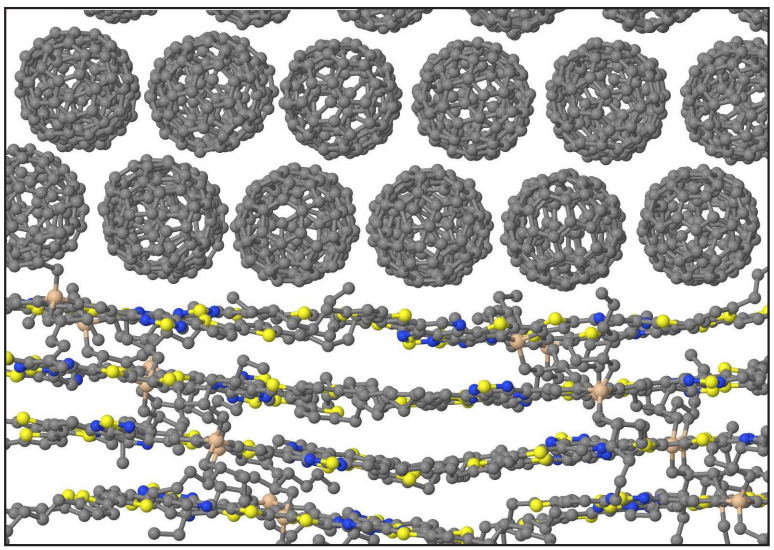












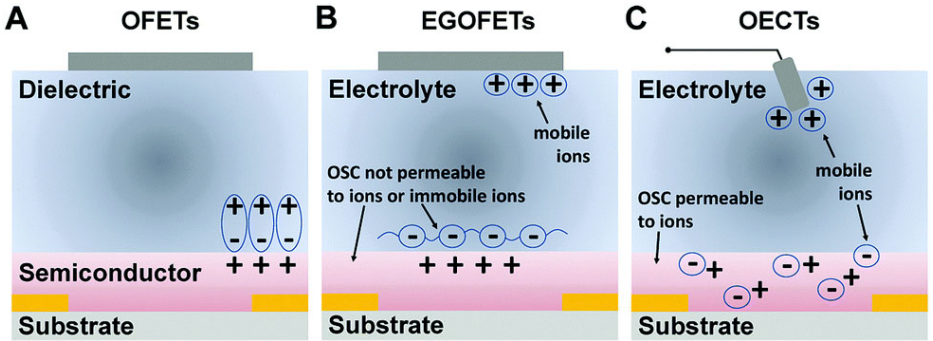
Some applications of organic semiconductors

Any electronic device can be made all-organic

Light emitters (most successful)

Adv Mater 33, 2005630 (2021)

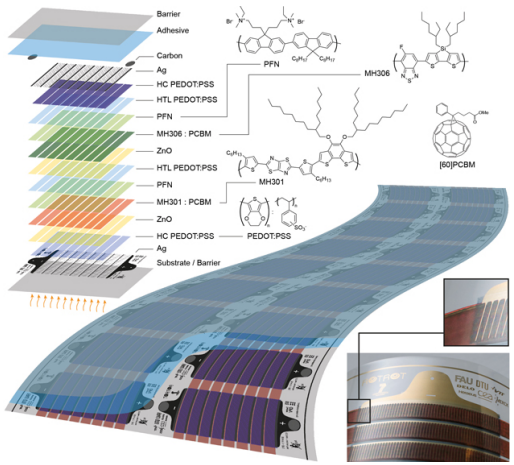
Transistors (most ubiquitous)



J Mater Chem C 6, 11778 (2018)

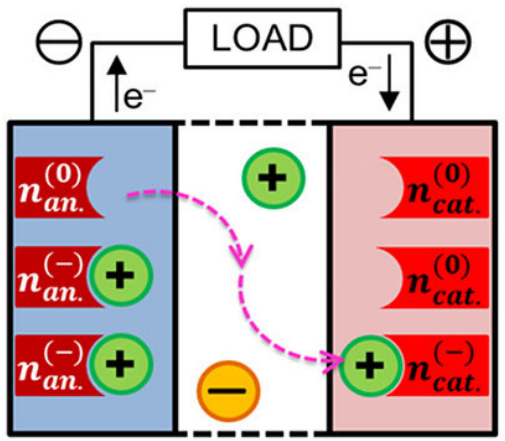
Solar cells (approaching 20% PCE)

Adv Energy Mater 11, 2002653 (2021)



Energy Environ Sci 7, 2925 (2014)

Batteries (early research)



Chem Rev 120, 6490 (2020)

Modeling of organic semiconductors

Challenges vs. opportunities

Main challenges:

- Small band gap – GGA is inaccurate and unreliable
- Soft structure – no harmonic approximation to nuclei dynamics
- Strong electron-phonon coupling[†] – consider nonadiabatic processes
- Complex multiscale morphology (up to 100 nm) – scale gap[††]
- Complex device structure – multiscale multi-material modeling
- Large repeating unit (10s-100s of atoms) – no high level methods

$\Longrightarrow$ *Brute force (material-nonspecific) approach is rarely used*

To model them efficiently one has to take advantage of

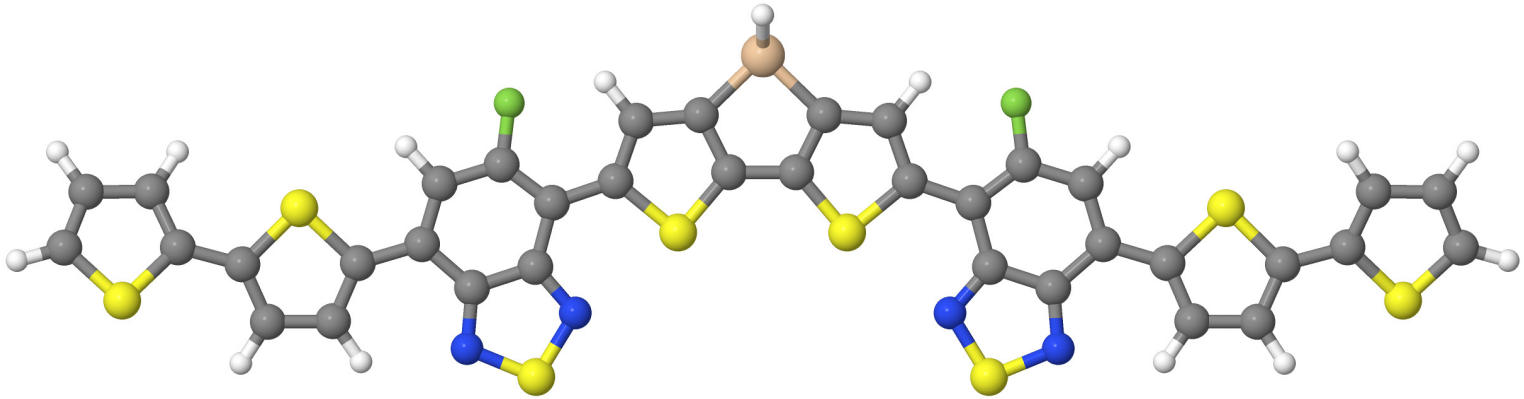
- Only one π-orbital per π-conjugated atom
- Consist of small rigid closed-π-shell blocks
- Light elements – small number of electrons, no SOC
- Heavily benchmarked with multitude of methods
- Fault-free scalable methods exist: CAM-B3LYP-D3/6-31G*

[†] Compared to electronic bandwidth

[††] What is measured is not what is modeled

Example: molecular solids and polymers

(quasi-1D π-conjugated systems – majority of materials used in organic electronics)



- Have block structure with few interconnections per block
- Each block is rigid, limited number of local structural patterns

$\Longrightarrow$ *Success of simple force fields*

- The π-conjugated system of each block is closed-shell
- Inter-block couplings ~ 1 eV $\ll$ band gap of blocks
- Intermolecular couplings ~ 0.1 eV $\ll$ band gap of molecules

$\Longrightarrow$ *There must be a set of methods well-tuned for accurate prediction of electronic properties of this class of materials*

Commonly used high-level methods (up to 1000 atoms)

- CCSD(T) – only fragments, be careful with approximations
- MP2 – no, only for CBS extrapolation of CCSD
- DFT+D – for intermolecular structure, D3 is safe choice
- LDA – no
- PBE – only for crystal structure
  - PBE-D3 – fastest available
  - PBE-MBD – most accurate available
  - vdW-DF2 – analytic gradients
- B3LYP – underestimates band gap, dihedrals, ep-couplings
- APFD – might be best hybrid (needs more benchmarking)
- Range separated hybrids are the most accurate
  - CAM-B3LYP – safe choice for organic semiconductors
  - ωB97XD – another good functional
  - HSE06 – best available for plain waves
- Basis set
  - 6-31G* – safe choice for organic semiconductors
  - Def2-TZVP – for high accuracy

Electronic structure methods are well-benchmarked

Some low-level methods (thousands of atoms)

- Semiempirical – no accurate parameterization yet
  - AM1 – bad geometry
  - PM7 – best available but still inaccurate
  - PM7+D – is also inaccurate
- DFTB – very promising but needs to be well parameterized
- TB – yes but always requires parameterization
- QM+MM – naturally the best (for conjugated systems)
  - MM3 – most transferable for conjugated molecules
- Force fields – no accurate parameterization
  - OPLS – good starting point
  - CHARMM, AMBER – no atom types
  - ML – let's see

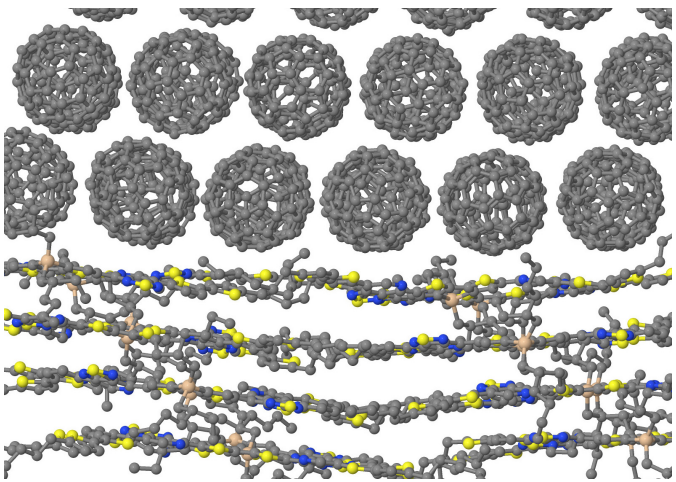
Parameterization is the main problem

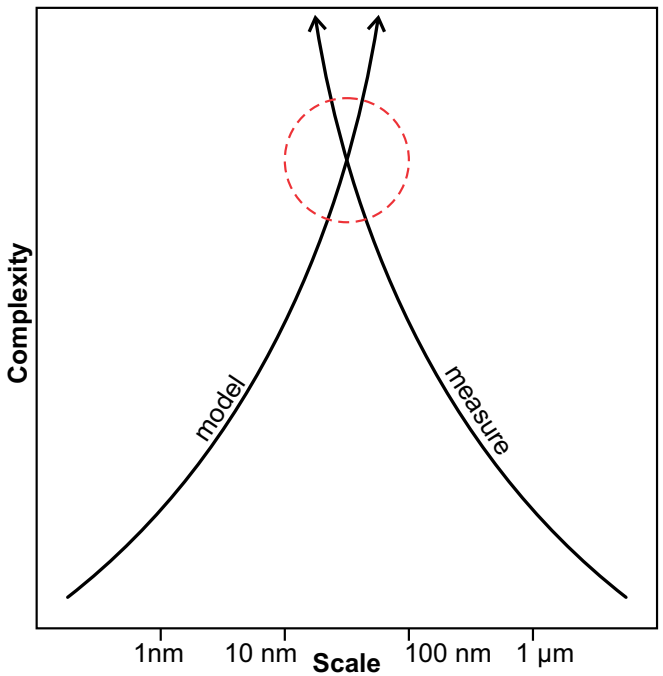
Questions

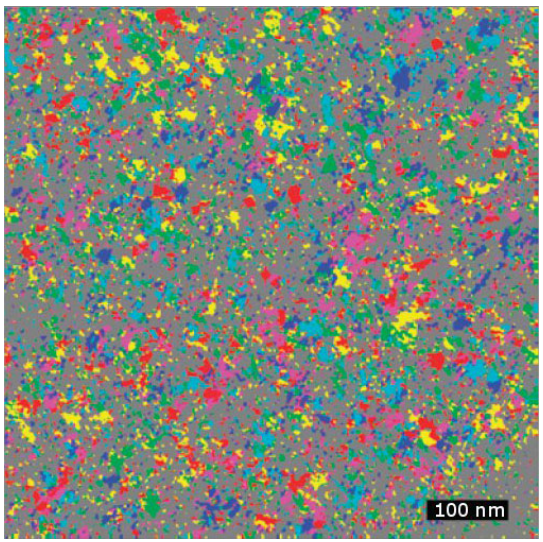
1. How many π-orbitals are there per transition metal atom?
2. Do you know other applications of organic semiconductors?
3. What if we replace some C atoms by Si and N by P – will we get π-conjugated system?

Scale gap problem

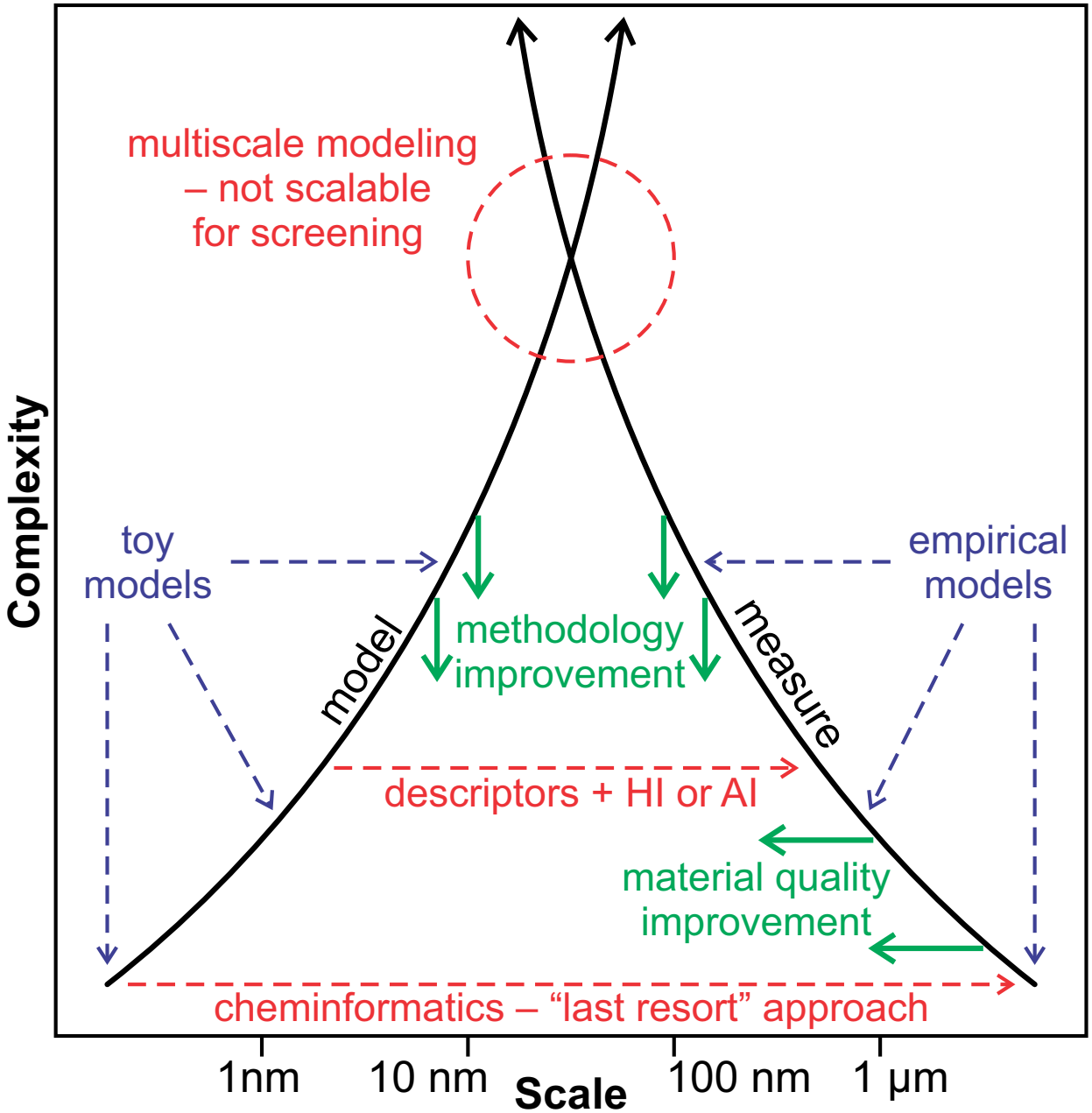
What is modeled is not what is measured



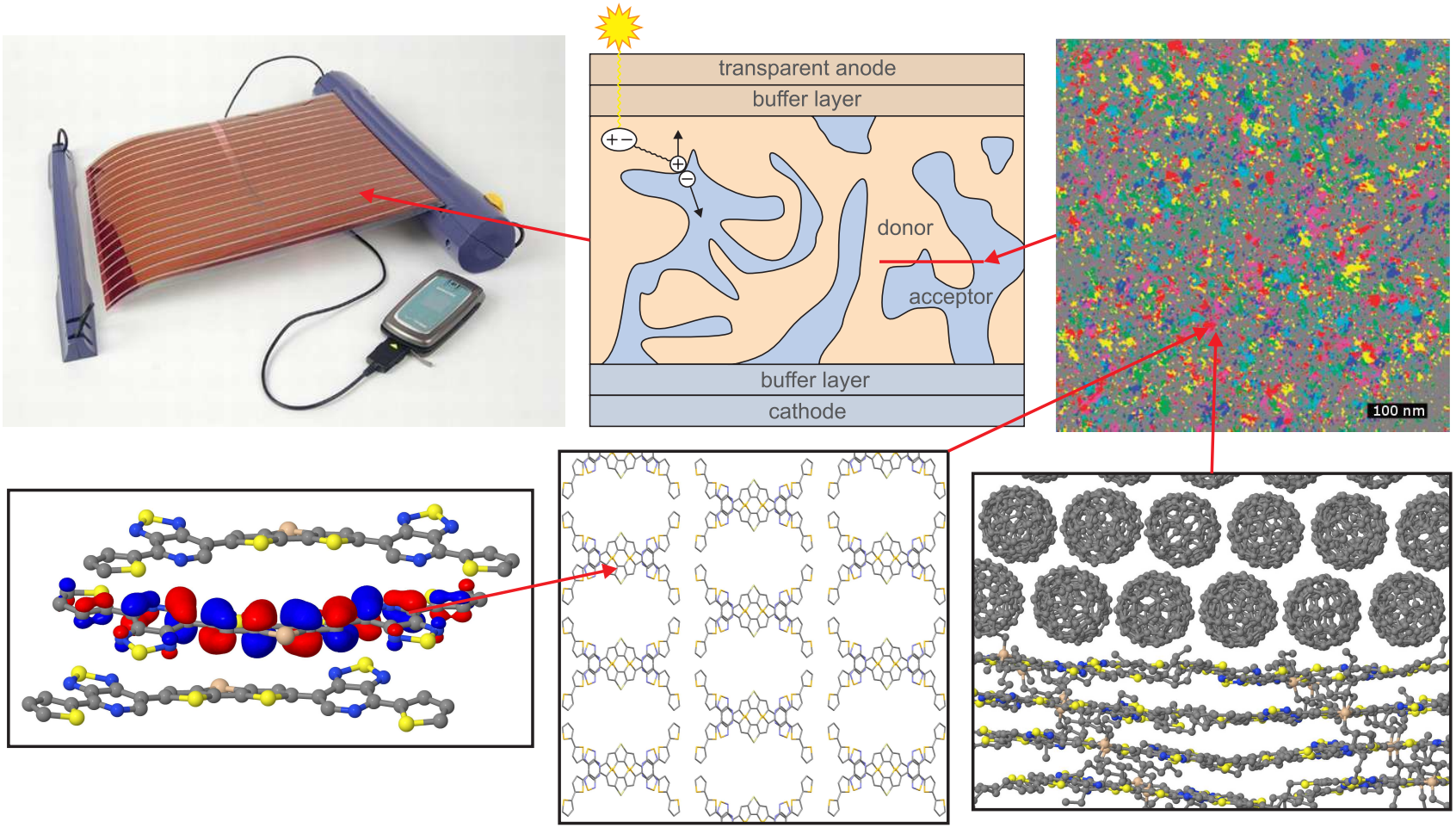




Bridging the scale gap



Challenges: multiple scales – solar cell example



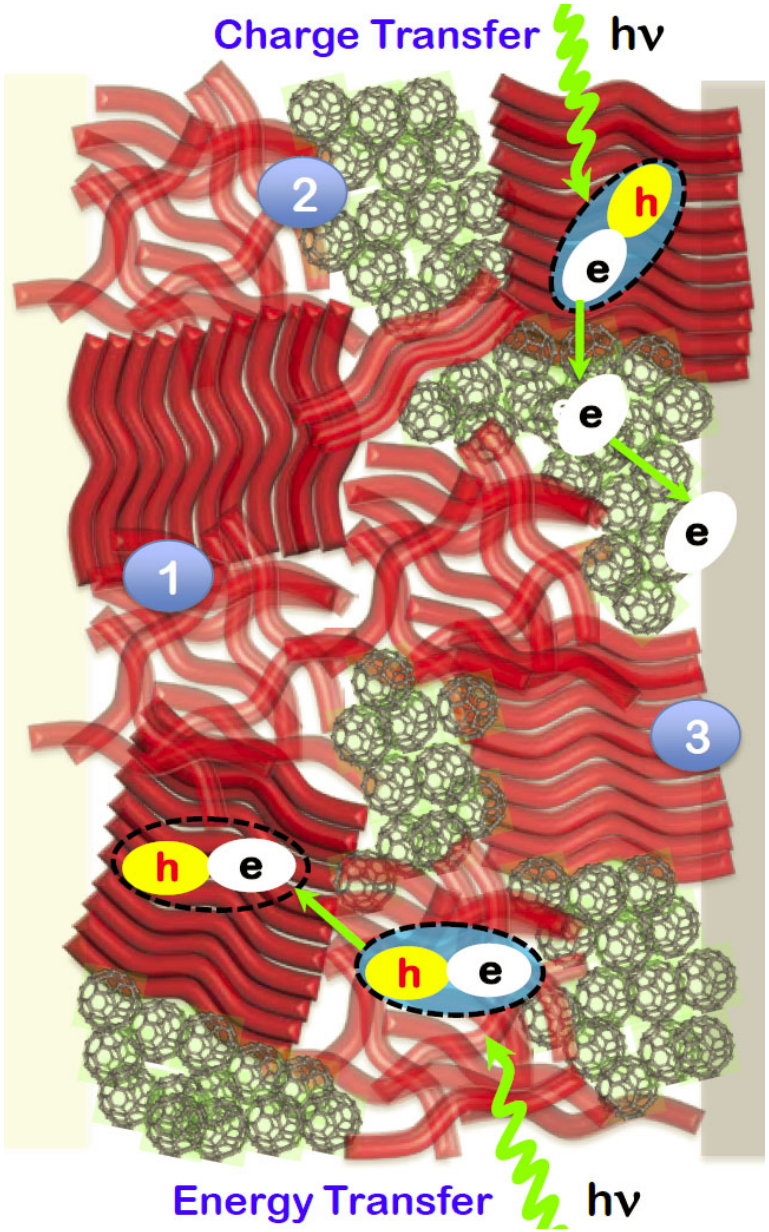
Multiple scales: broad range of scales – solar cell example

Spatial scales:

- molecule ($\lesssim 1$ nm)
- single phase (~ 10 nm)
- interfaces (intra and inter)
- functional layer ($\gtrsim 100$ nm)

Time scales:

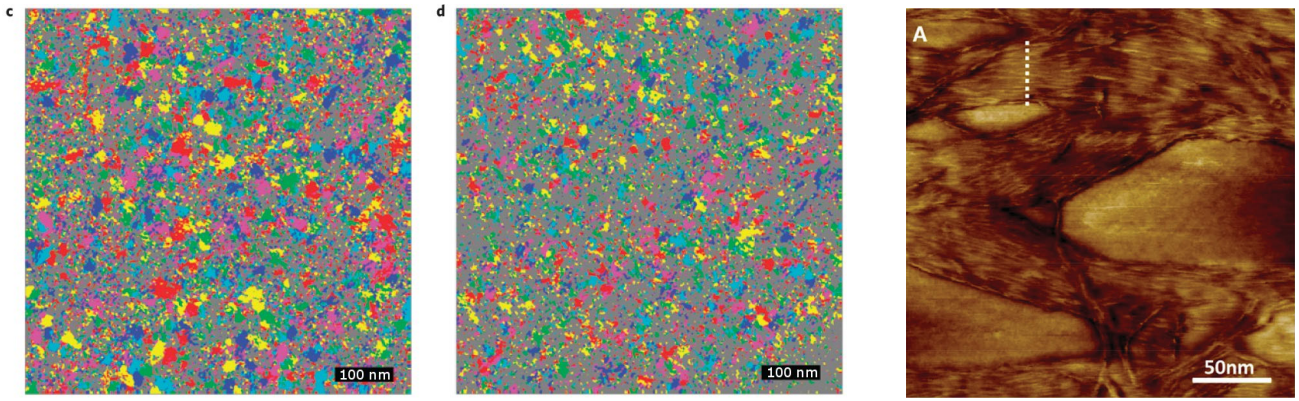
- ultrafast intramolecular (fs)
- intermolecular transfer (ps)
- electronic transport (ns)
- transients, degradation (>ns)



Understanding scales

Functional properties of organic semiconductors are often determined by structure on scales up to tens of nm

$\Longrightarrow$ atomistic description is needed for up to 10^6 atoms



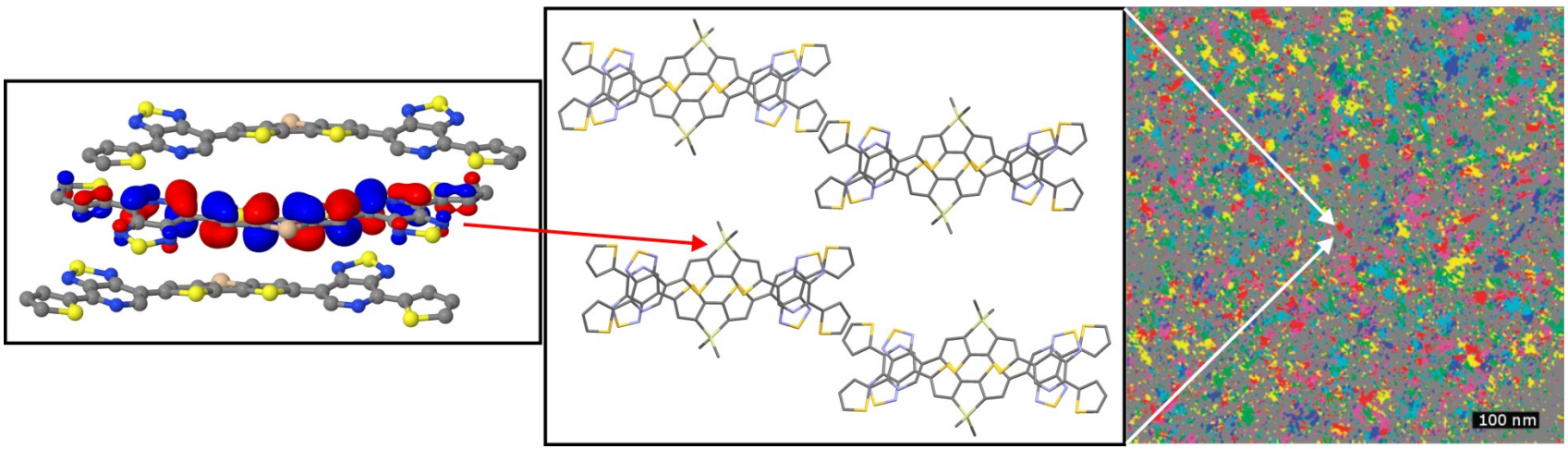
Challenges

- realistic mesoscale structure (coarse-grained MD)
- accurate intermolecular geometry (best DFT-D)
- accurate electronic structure (best range-separated hybrids)
- accurate charge dynamics (best NAMD)

No direct simulation – only multiscale modeling and "machine learning"

First-principles multiscale modeling: bird's eye view

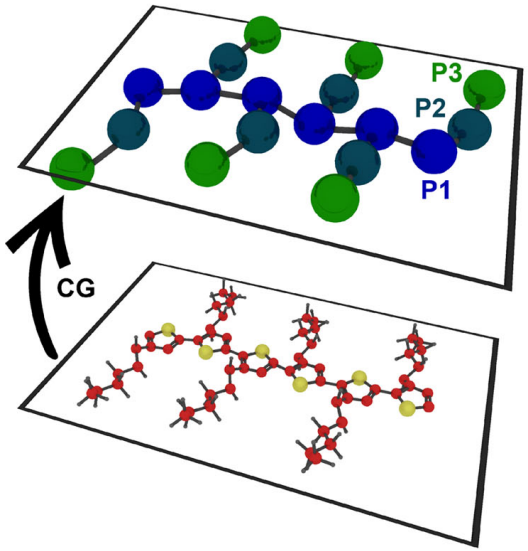
- Combine different approaches on different scales
- Control the accuracy (errors accumulate through the scales)

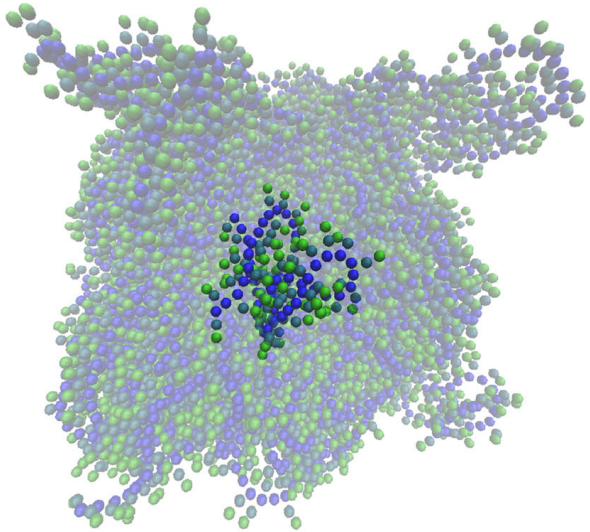


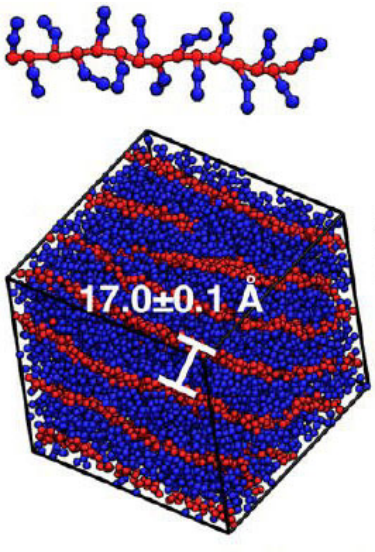
- Density functional theory on few-molecules scale
- Model Hamiltonian on intermolecular scale
- Molecular mechanics + kinetic equation on mesoscale
- Continuum models on larger scales (diffusion + electrostatics)

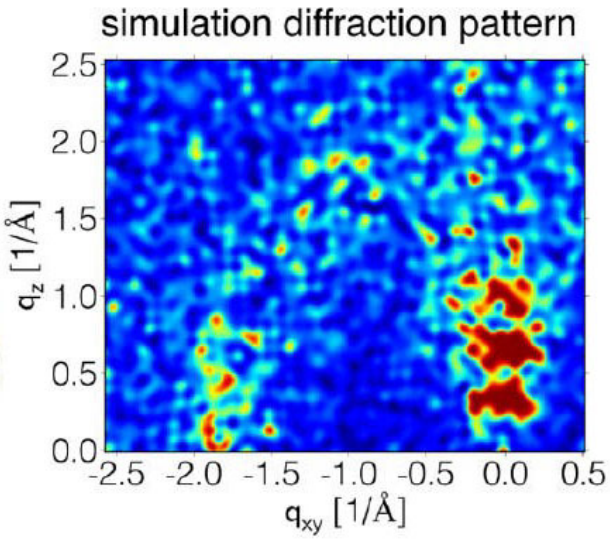
Example: coarse-graining molecular degrees of freedom

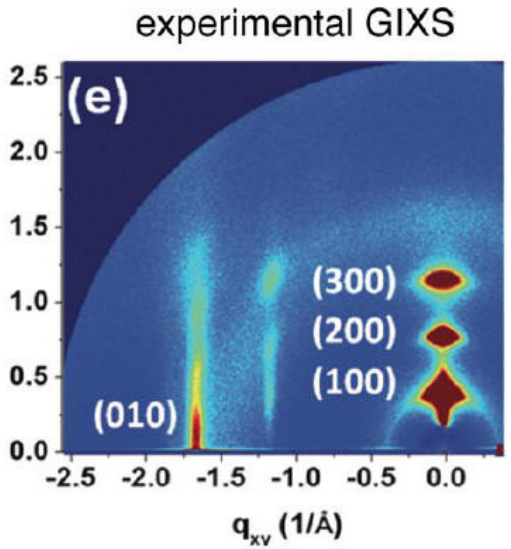
M L Jones, E Jankowski, Molec Simul 43, 756 (2017)





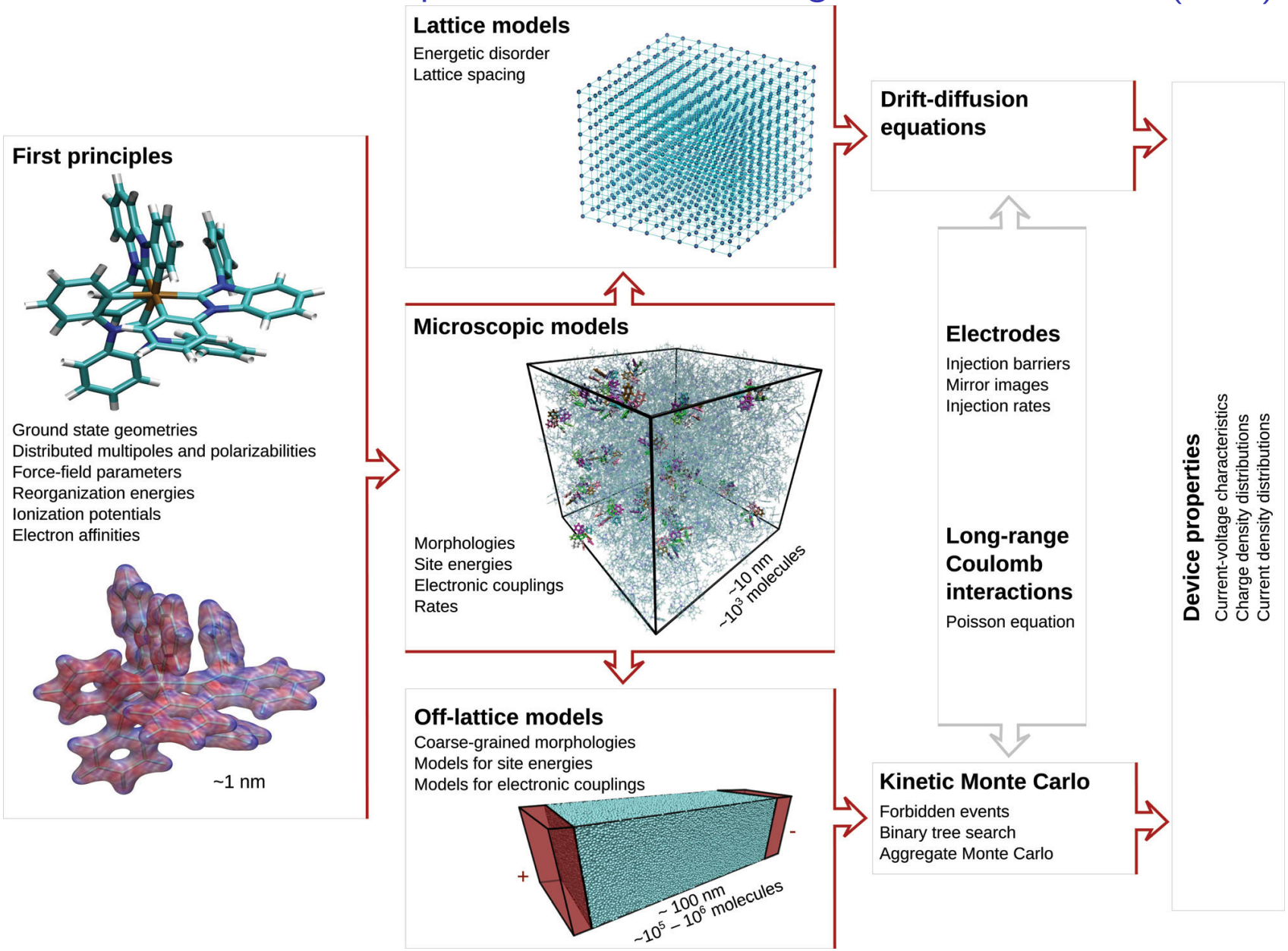






Example: fitting statistical models

D Andrienko, Multiscale Concepts in Simulations of Organic Semiconductors (2018)



Another approach: Use descriptors

- Materials stiffness correlates with Young's modulus
- Charge carrier mobility correlates with effective mass
- Ionic conductivity correlates with diffusion barrier
- Battery capacity correlates with metal-ion intercalation energy
- Solar power conversion efficiency correlates with band gap
- Luminescence color correlates with relative dipole moment

  Chem Phys 481, 133 (2016)

If many descriptors – use machine learning approaches. The main challenge is to get enough quantity and quality of experimental data. See review *Japan J Appl Phys 59, SD0801 (2020)*

Questions

1. Suggest descriptors for bulk-heterojunction solar cells.
2. Which processes determine charge carrier mobility in real-world organic materials?
3. Give examples of π-conjugated systems without scale gap problem.

Structural studies

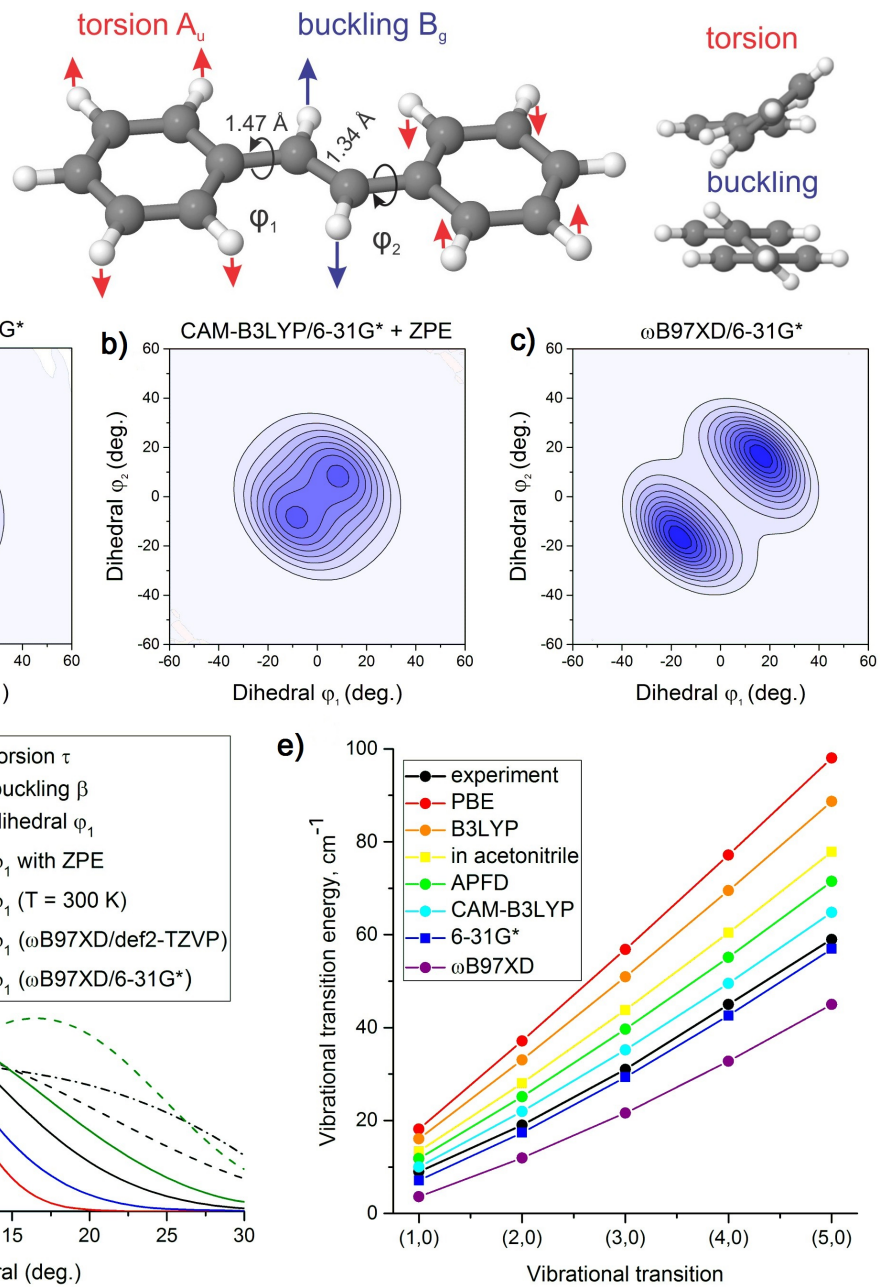
- Refine guessed or measured structure
- Study dependence of structure on parameters
- Establish structure-property relationships
- Predict structure
- Determine or sample conformations and polymorphs

Structural properties sensitive to the method

- Bond Length Alternation (BLA) and dihedrals
- Conformations
- Intermolecular geometry
- Polymorphism

BLA and dihedrals

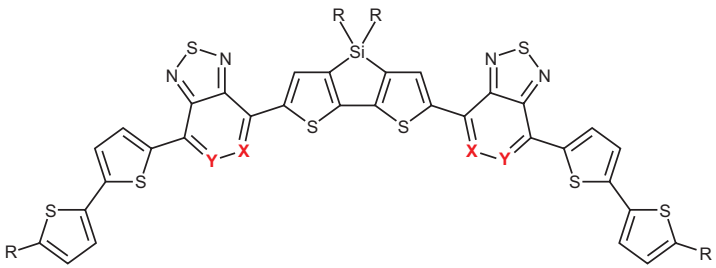
J Phys Chem Lett 10, 3232 (2019)

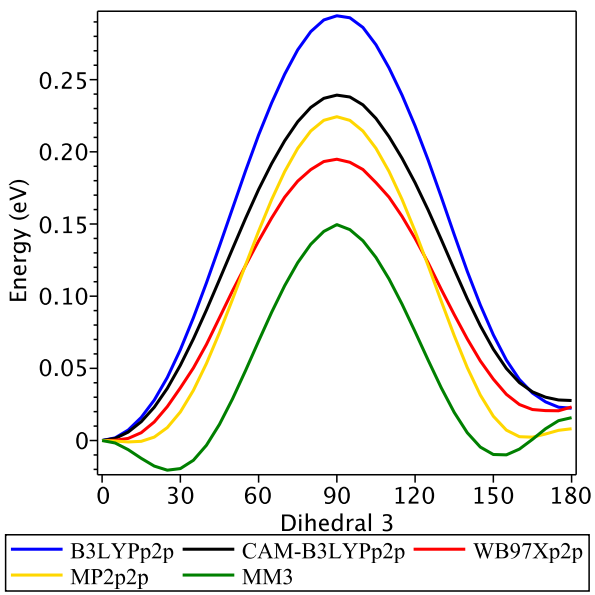


Highly sensitive to method, multidimensional non-harmonic PES

Conformations: conjugated backbone

J Phys Chem Lett 5, 2700 (2014) Cryst Growth Des 20, 4875 (2020)



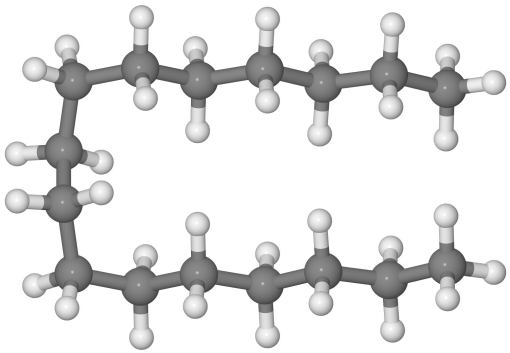


method	solv.	1a		3a	
		bb	mol.	bb	mol.
		planarized conjugated base			
B3LYP		2		2	
CAM-B3LYP		9		9	
ωB97X		17		17	
MP2		96		...	
MM3		130		251	
		dihedrals #3,4 are flipped			
ωB97X		119		38	
MP2		123		...	
CAM-B3LYP		129	128	46	32
B3LYP		132		34	
MM3		132		21	
ωB97X	clf	119		22	
CAM-B3LYP	clf	128	130	33	14
B3LYP	clf	128		19	
		dihedrals #1,3,4 are flipped			
ωB97X		147		65	
CAM-B3LYP		159	105	75	98
B3LYP		165		67	
ωB97X	clf	142	242	43	141
CAM-B3LYP	clf	155	102	59	77
B3LYP	clf	158	64	49	-47
		saddle point for dihedral #3			
ωB97X		377		169	
CAM-B3LYP		407		209	
B3LYP		468		253	

Table S4. Energies (in meV) of different conformations relative to the energy of the lowest energy conformation: dependence on method. The geometry is fully relaxed from crystalline geometry to local extremum. The default basis set is 6-31g*. Note that conformations with C_2 symmetry is slightly lower in energy than that with σ_h symmetry (typically less than 1 meV difference). Here "bb" means conjugated backbone, "mol." means the whole molecule. Entries are ordered by the third column ("1a bb").

Conformations: aliphatic chains

J Phys Chem C 122, 9141 (2018)



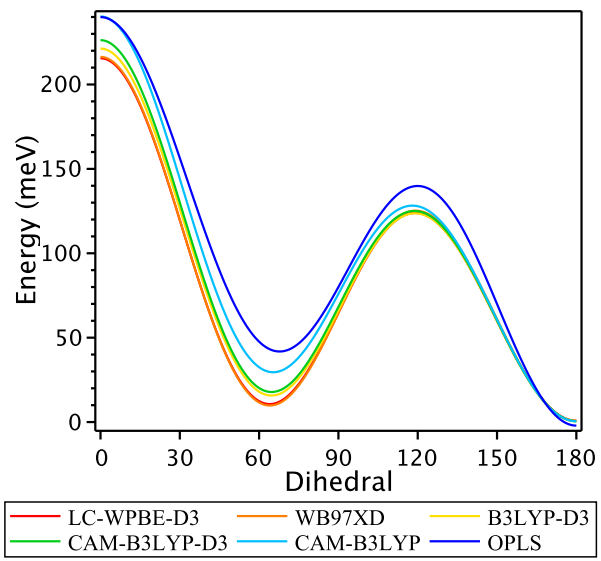


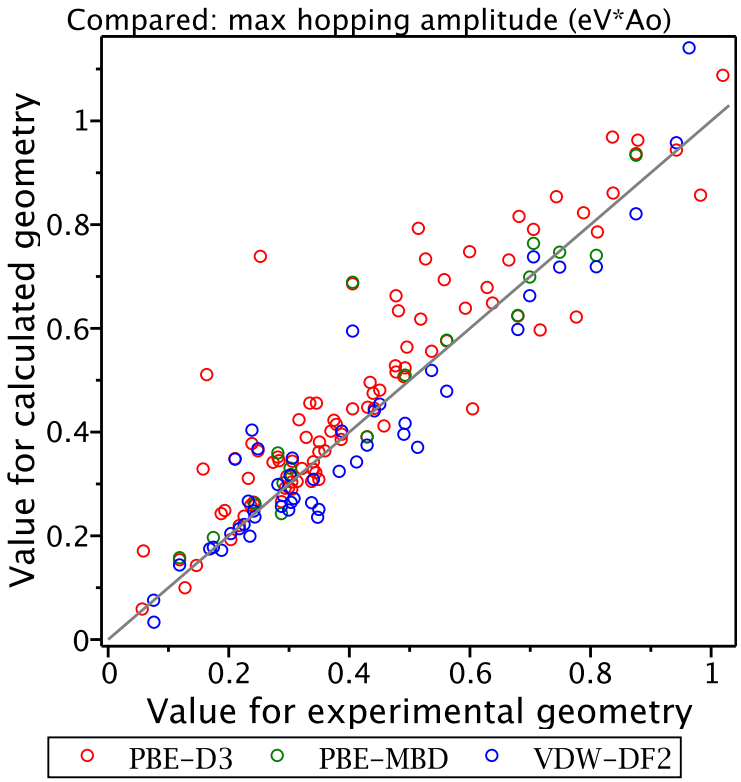
Table S4: Comparison of different methods estimating the relative, hairpin minus trans, energy for a set of polyethylene oligomers (8 to 18 carbons). The geometry is fixed at MP2/cc-pvTZ geometry obtained in Ref.,[2] except for the last block in the table. The entries correspond to energies in meV. Here σ is RMSD with respect to the reference method which is CCSD(T)/cc-pVTZ.[2] "Optimized OPLS" means optimized C-C-C-C dihedral. The supercell size for plane waves is $40 \times 20 \times 20$ Å. See also graphical representation in Fig. S5.

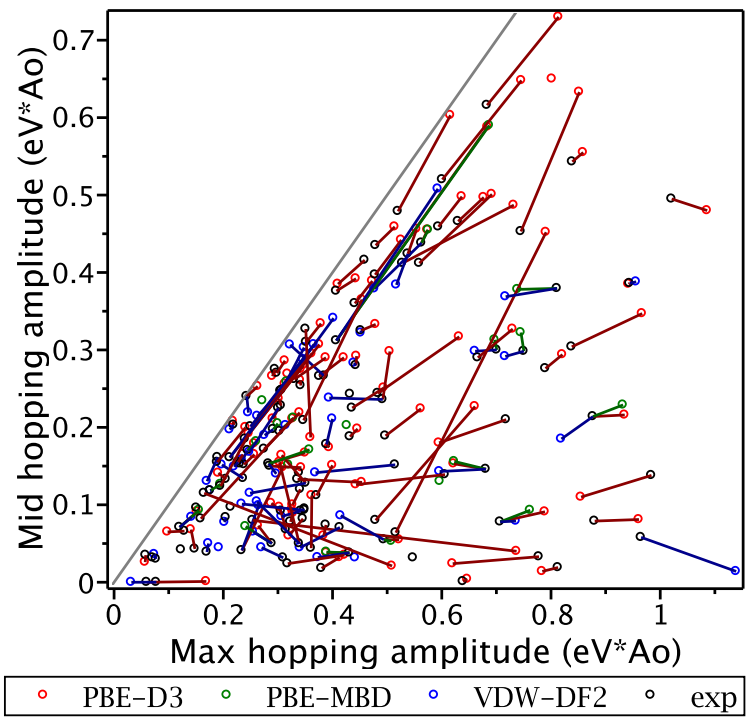
	σ	8	10	12	14	16	18
Reference data							
CCSD-T/cc-pVTZ	0	65	52	37	5	-30	-73
6-311G*							
CAM-B3LYP-D3	5	71	61	42	10	-30	-72
B3LYP-D3	16	60	50	31	-12	-53	-98
vdW-DF2	19	90	83	62	14	-31	-71
PBE-MBD	22	66	55	34	-21	-62	-108
LC-wPBE-D3	50	29	15	-5	-47	-88	-140
wB97XD	90	24	11	-10	-95	-145	-215
CAM-B3LYP	195	138	143	148	227	222	227
6-311+G(3df,2p)							
CAM-B3LYP-D3	10	78	67	49	7	-33	-75
B3LYP-D3	21	65	54	36	-20	-61	-106
LC-wPBE-D3	39	41	29	10	-39	-77	-127
wB97XD	84	33	20	1	-90	-138	-207
CAM-B3LYP-D3							
6-311G*	5	71	61	42	10	-30	-72
6-311G**	8	68	57	38	-2	-43	-86
6-311+G(3df,2p)	10	78	67	49	7	-33	-75
6-311G(2d,p)	10	78	68	49	9	-30	-72
6-311+G(2d,p)	14	82	72	54	16	-23	-65
6-31G(2d,p)	18	73	61	37	-11	-56	-103
6-31G*	19	66	56	33	-12	-58	-104
6-31G**	20	67	57	34	-14	-59	-106
6-31+G(2d,p)	29	94	84	67	34	-4	-45
Geometry relaxed with the same method							
CAM-B3LYP-D3	4	67	57	38	4	-36	-79
optimized OPLS	8	54	41	27	3	-34	-72
B3LYP-D3	18	56	45	25	-14	-55	-100
LC-wPBE-D3	51	28	15	-6	-49	-88	-141
wB97XD	96	21	8	-13	-103	-154	-223
OPLS	118	160	161	149	135	97	58
CAM-B3LYPp3p	128	127	129	128	128	128	128

Intermolecular geometry

Tested here is product of electronic coupling and hopping distance

Test set: $>$ 50 crystals, including all high-μ from Chem Soc Rev 47, 422 (2018)

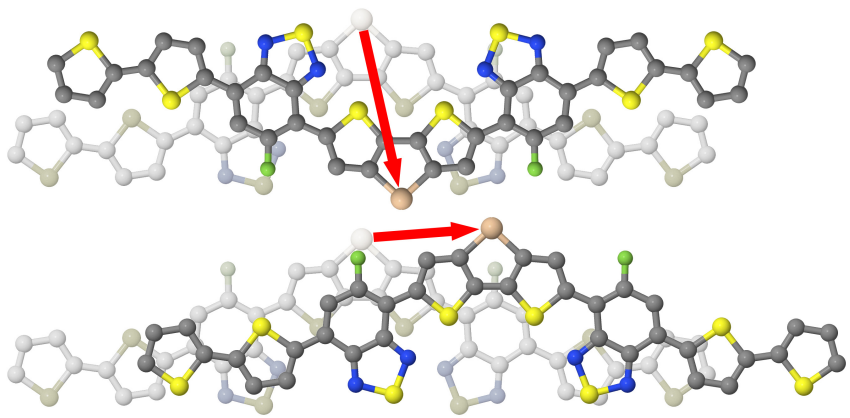




Polymorphism of molecular crystals

Sci Adv 5, eaau3338 (2019)

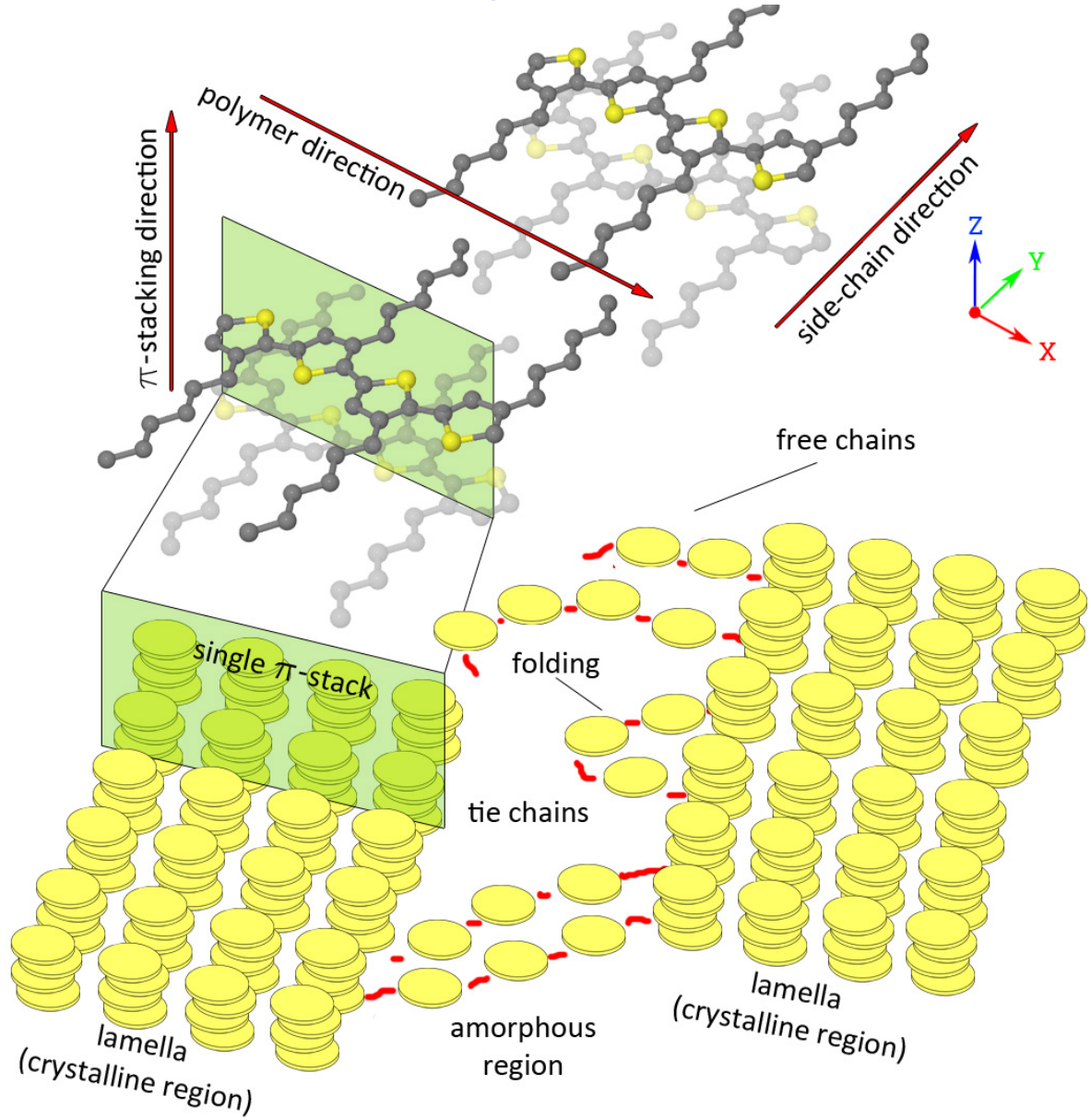
- DFT-D correctly predicts relative energy of polymorphs for small-molecule crystals (TCNQ, indigo, rubrene)
- Force fields can be used for prescreening (MM3 in J Phys Chem Lett 5, 2700 (2014), OPLS in J Phys Chem C 122, 9141 (2018))
- For large molecules with aliphatic chains kinetic and entropic factors might be essential



DFT-D predicts that antiparallel stacking is 0.18 eV/mol lower in energy than the observed parallel stacking
Adv Funct Mater 28, 1702073 (2017)

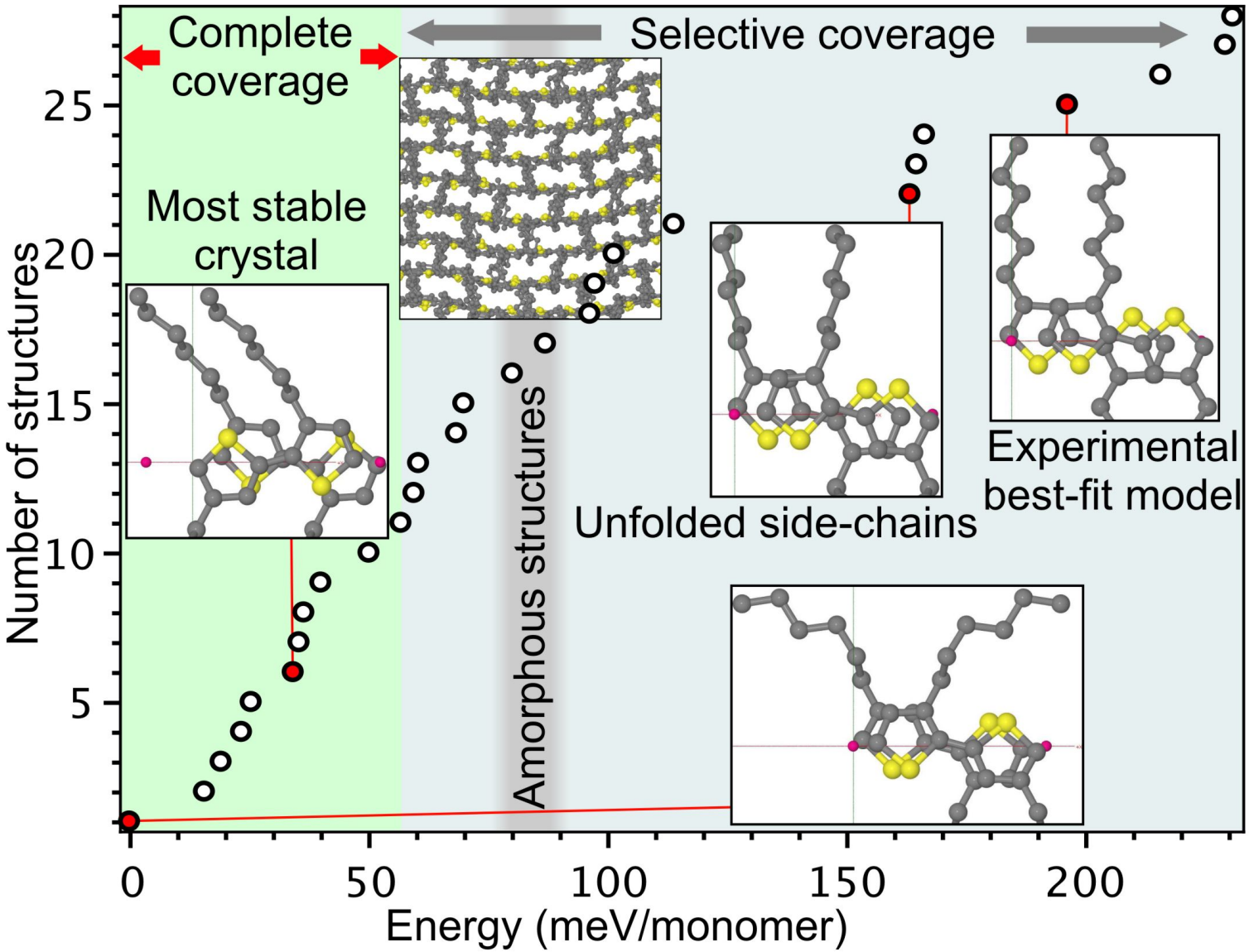
Polymorphism of bulk polymers: example of P3HT

Atomic positions remain unresolved, though structure is well known down to nanometers



Polymorphism of bulk polymers: example of P3HT

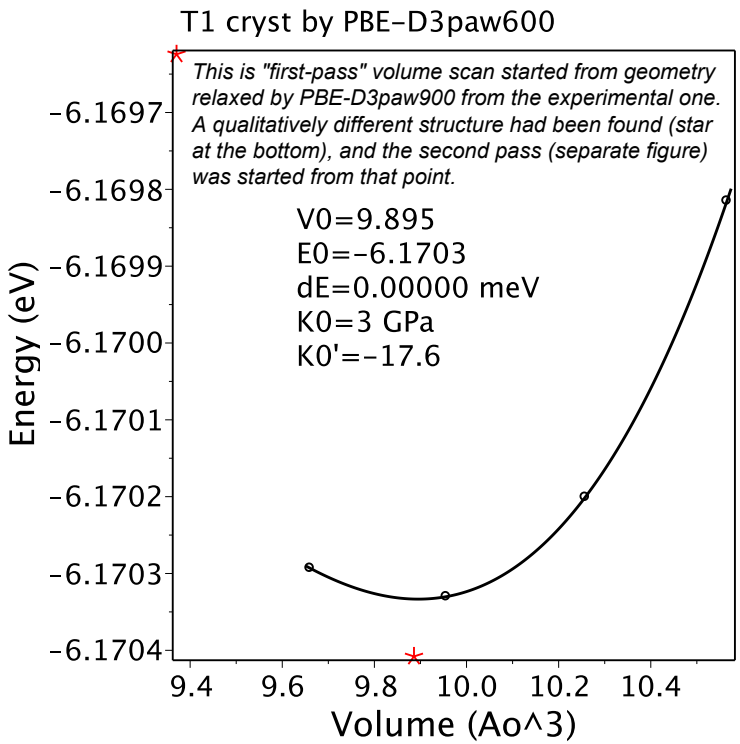
J Phys Chem C 122, 9141 (2018)

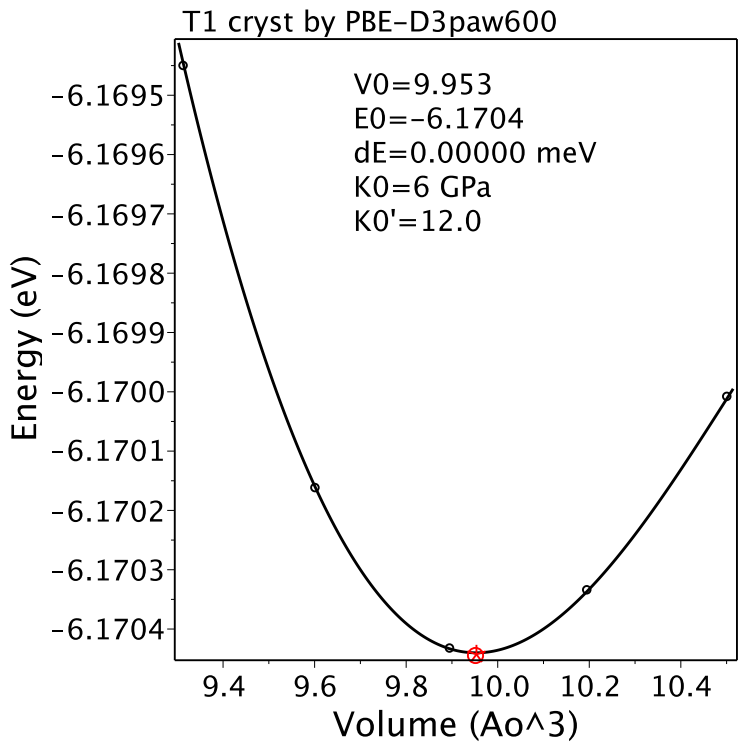


Technical recommendations in geometry optimization

Chem Mater 33, 966 (2021)

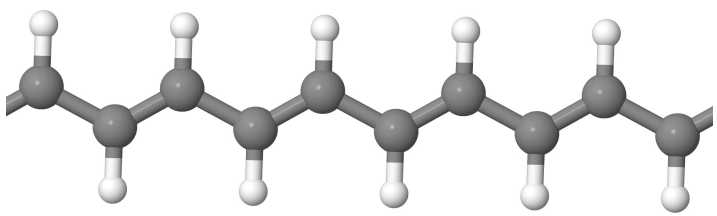
- Clean up experimental geometry: disorder, missing hydrogens
- Tighten optimization criteria and increase numerical precision
- Avoid getting stuck at false minima

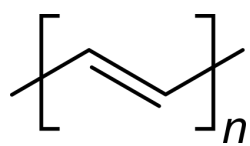


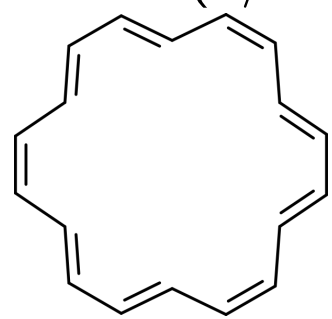


Questions

1. Compare energy density of polymorphs for P3HT and SiO_2.
2. For which crystalline systems vibrational entropy is not the most important entropic factor.
3. Explain why local density functionals fail with BLA: compare PBE/CAM-B3LYP for trans-polyacetylene (.013/.090 Å), its 32-atom oligomer (.030/.090 Å) and [18]annulene (0/.077 Å).







Electronic properties

- Wave-function
- Effective mass
- HOMO/LUMO energies, IP/EA, charge gap
- Optical gap and excitations
- Intermolecular couplings
- Small-gap systems

Electronic properties not sensitive to the method

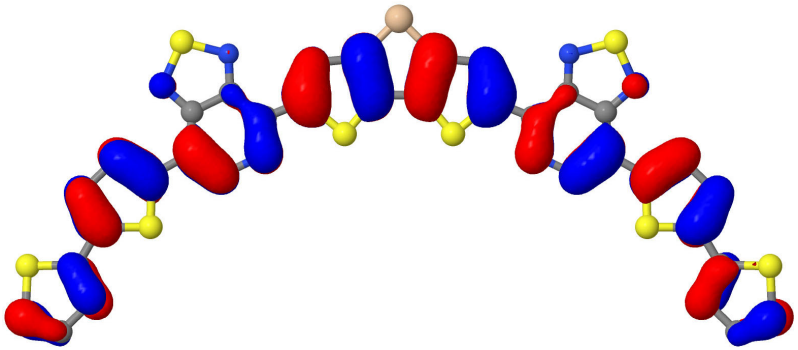
- Wave-function
- Intraband properties (e.g. effective mass)

Systematic trends with HF content $\Longrightarrow$ *use "bracketing" & IP-tuning*

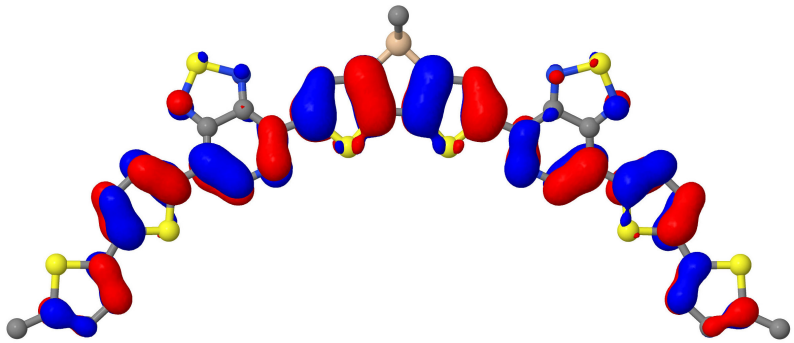
PBE(0) – B3LYP(.2) – HSE06(.25/0), APF(.23), PBE0(.25) –
– CAM-B3LYP(.19/.65) – ωB97X(.16/1)

Wave-function

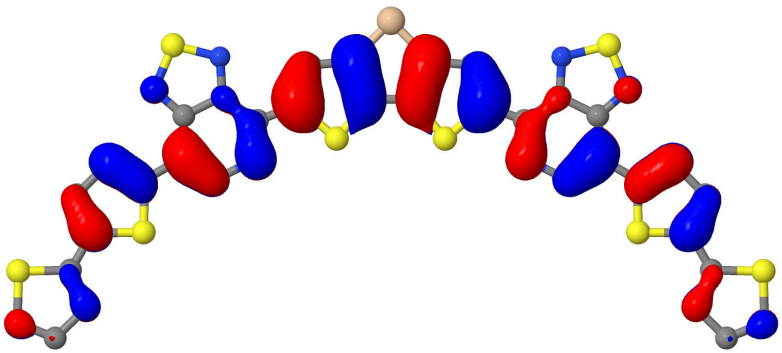
(not sensitive to the method)



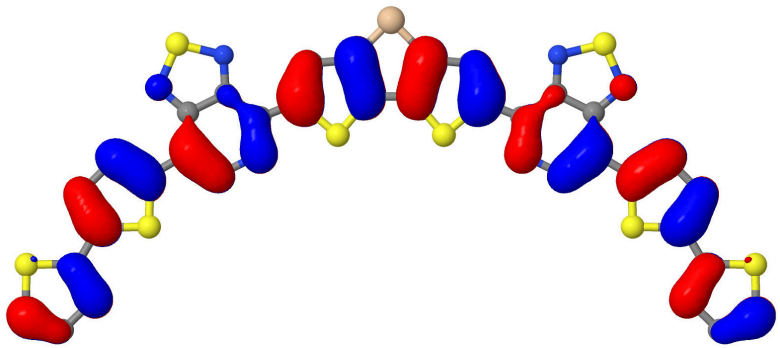
HOMO (CAM-B3LYP)



HOMO (PM6)



hole NO (CAM-B3LYP)



hole NO (B3LYP)

Wave-function follows BLA pattern, e.g. HOMO is on double bonds

Effective mass

(not very sensitive to the method)

Effective mass for holes in trans-polyacetylene:

- 0.074 – PBE
- 0.076 – HSE06
- 0.076 – B3LYP
- 0.090 – CAM-B3LYP
- 0.097 – ωB97X

Because of narrow complex-shaped bands, other intraband parameters such as bandwidths are often more informative than effective masses

HOMO/LUMO energies and IP/EA

Theoretical definitions

- Ionization Potential, IP$= E(N-1) - E(N) > 0$
- Electron Affinity, EA$= E(N) - E(N+1)$ (usually positive)
- Charge gap = IP-EA
- Absolute electronegativity = (IP+EA)/2
- Vertical IP/EA – geometry fixed at relaxed initial state
- Adiabatic IP/EA – fully relaxed geometries

Experimental determination for organic semiconductors

- Cyclic voltammetry (adiabatic)
- Photoemission spectroscopy (vertical, VDE instead of EA)

Terminology convention: Experimentalists do not use IP/EA terminology, but use HOMO/LUMO energies instead. For bulk 3D systems this gives an intrinsic property, but for systems exposed to an environment, IP/EA strongly depend on the environment.

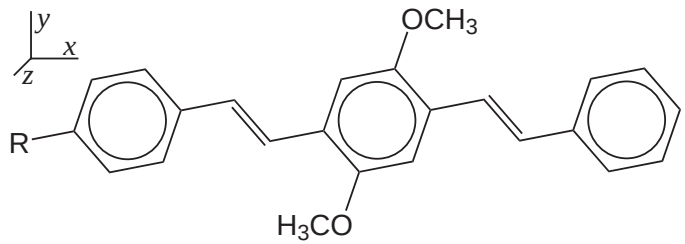
Calculation of IP/EA

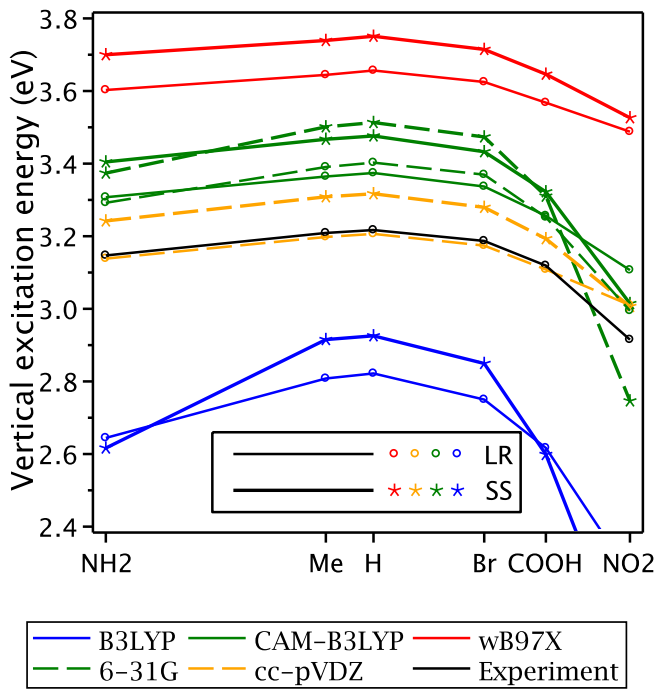
- Molecules – by definition
  - Small molecules – see JCTC 12, 595;605;615;627 (2016)
- Molecular solids
  - as molecule in a dielectric medium
  - as solid in PBC – see below
- Extended π-conjugated systems
  - use HOMO/LUMO (+GW)
  - extrapolate PRB 92, 195134 (2015)
- Relative IP/EA in same conditions – use HOMO/LUMO

Koopman's theorem and IP-tuning

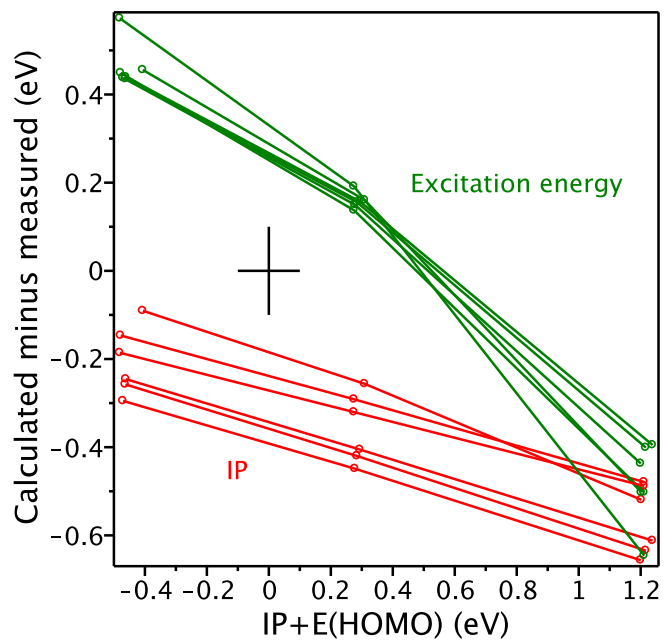
Chem Phys 481, 133 (2016) JCTC 12, 605 (2016); Acc Chem Res 47, 2592 (2014)

- Use IP+E_{HOMO}=0 to select best functional or tune its parameters
- Useless for small molecules, but works well for larger ones





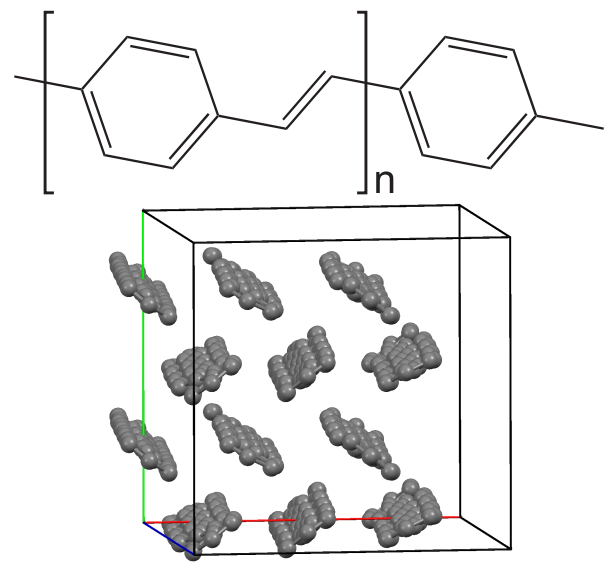
functional	IP+E_{HOMO}(eV)
B3LYP	+1.2
CAM-B3LYP	+0.3
ωB97X	−0.4



Optical gap and excitations

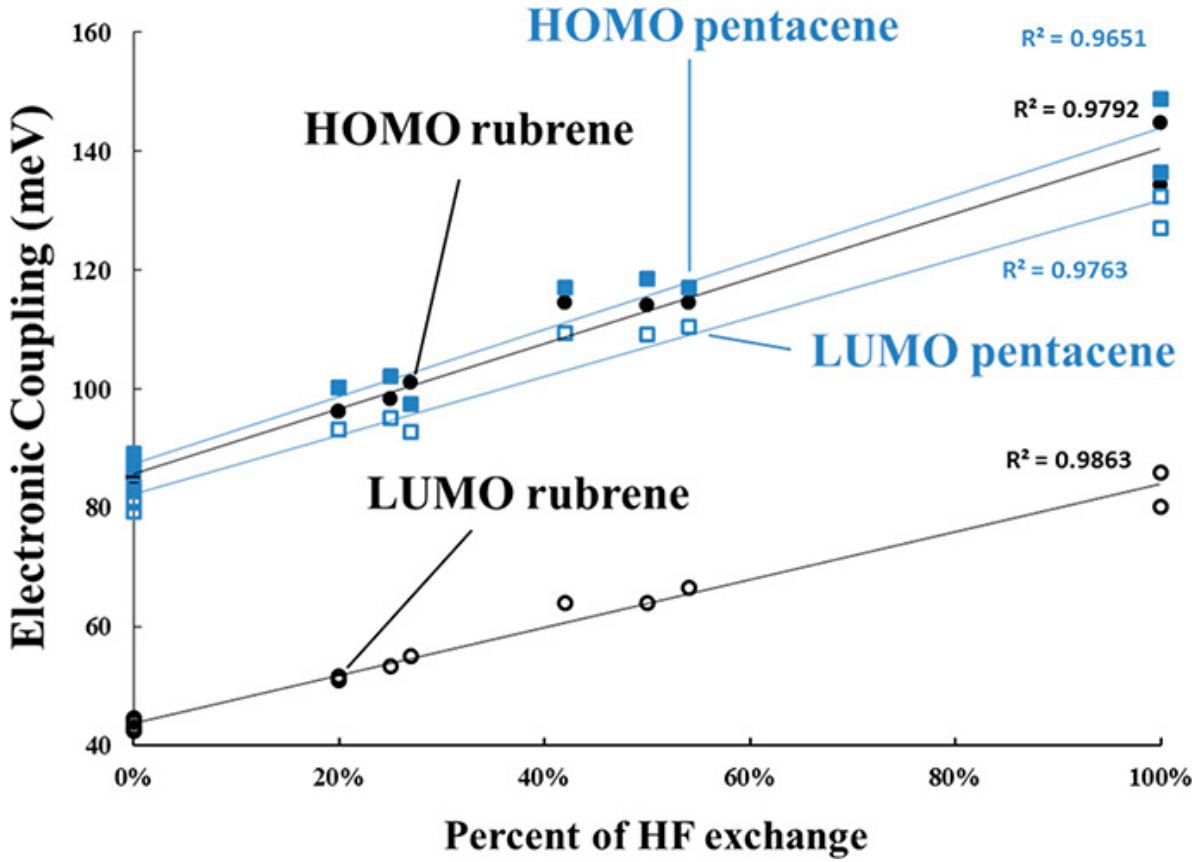
- Molecules – by TDDFT or GW(+BSE)
- Molecular solids, multimers – vibronic effects are important
- Extended π-conjugated systems – as solid in PBC
- Relative gap in same conditions – use HOMO-LUMO gap

	bandgap (eV)	
	crystal	polymer
wB97X	5.9	6.6
CAM-B3LYP	4.4	4.8
experiment	3.5	–
B3LYP	2.2	2.5
HSE06	1.7	2.1
PBE	1.1	1.3



Intermolecular couplings

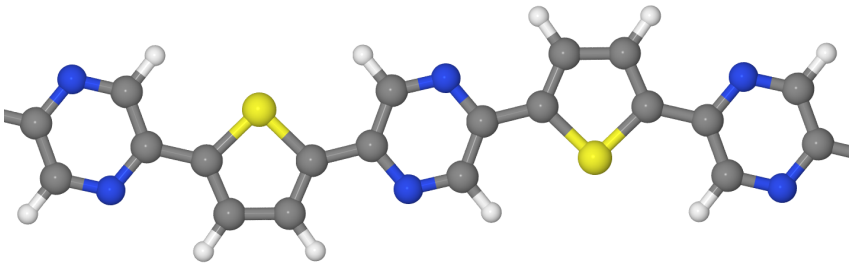
J Phys Chem Lett 4, 919 (2013)

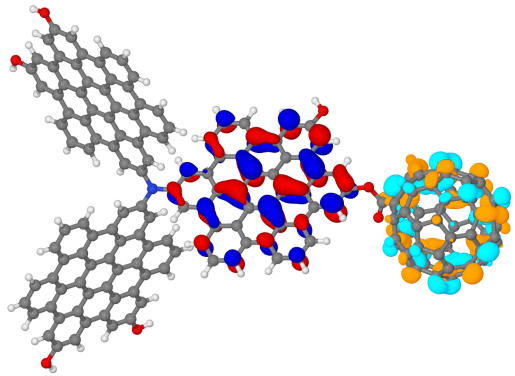


Small-gap systems

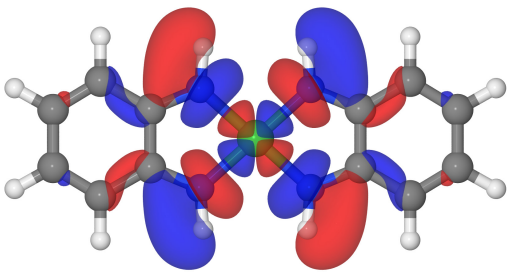
(very sensitive to the method)

- Charge transfer states (donor-acceptor systems) – use DFT





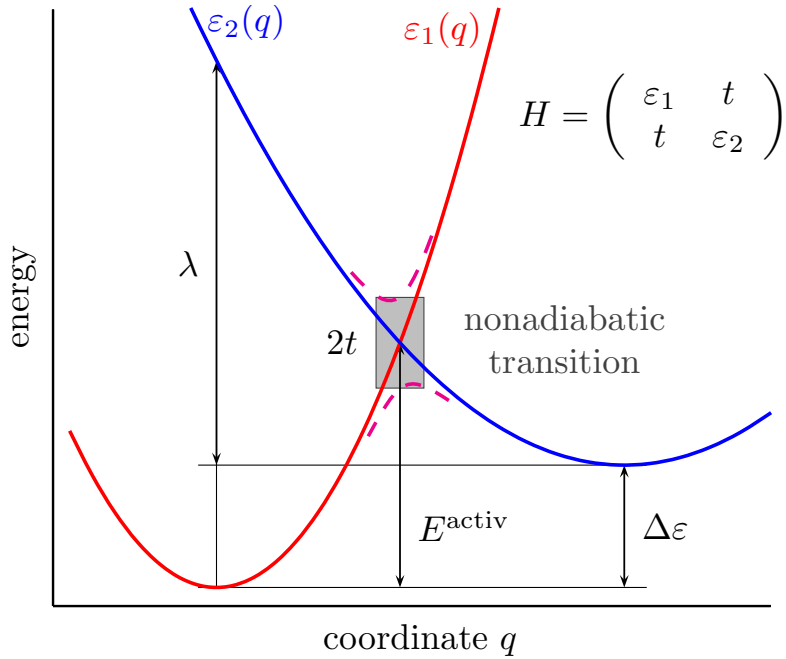
- Spin-degenerate cases (transitions metals) – use DFT with care



- Strongly correlated systems (extended π-conjugation)
  — see example of acenes J Chem Phys 148, 134112 (2018)

Questions

1. Why MO in the last slide does not follow BLA pattern?
2. When does optical gap substantially differ from charge gap?
3. Show vertical and adiabatic transitions on the figure below:



Spectroscopy

— primary experimental characterization tool for organic semiconductors

- Vibronic couplings for a single electronic state
- UV-Vis spectra
- Raman spectra
- Other optical: IR, photoemission, pump-probe ...
- Also nonoptical: XPS, NMR ...

Vibronic effects important, they are very sensitive to method

Vibronic couplings for a single electronic state

Independent boson model = Displaced harmonic oscillator model – exactly solvable

The key assumption is that separation between electronic states is larger than vibronic bandwidth $\Longrightarrow$

$$\mathsf{H} = \varepsilon \mathsf{n} + \sum_\alpha \hbar\omega_\alpha \left(\mathsf{b}_\alpha^\dagger \mathsf{b}_\alpha + \frac{1}{2} \right) + \sum_\alpha \hbar\omega_\alpha g_\alpha \left(\mathsf{b}_\alpha^\dagger + \mathsf{b}_\alpha \right) \mathsf{n}$$

here ε – electronic level, b_α – normal modes, g_α – vibronic (electron-phonon) couplings, $S_\alpha = g_\alpha^2$ – Huang–Rhys factors

Solution:

$$\tilde{\mathsf{H}} = \mathrm{e}^{\mathsf{P}} \mathsf{H} \mathrm{e}^{-\mathsf{P}} = (\varepsilon - \lambda)\mathsf{n} + \sum_\alpha \hbar\omega_\alpha \left(\mathsf{b}_\alpha^\dagger \mathsf{b}_\alpha + \frac{1}{2} \right)$$

where *displacement operator* and *electronic state relaxation energy*

$$\mathsf{P} = \mathsf{n} \sum_\alpha g_\alpha \left(\mathsf{b}_\alpha - \mathsf{b}_\alpha^\dagger \right), \quad \lambda = \sum_\alpha \hbar\omega_\alpha g_\alpha^2$$

Vibrationally resolved spectra: transition spectral density

Absorption/emission intensity:

$$I_{\mathrm{emi}}(E) = \frac{4E^3}{3\hbar^4 c^3}|d|^2\sigma^{\mathrm{excited}}(-E), \quad I_{\mathrm{abs}}(E) = \frac{4\pi^2 E}{3\hbar c}|d|^2\sigma^{\mathrm{ground}}(E)$$

Transition spectral density:

$$\sigma(E) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\hat{\sigma}(t)\mathrm{e}^{\mathrm{i}tE/\hbar}\,\mathrm{d}t$$

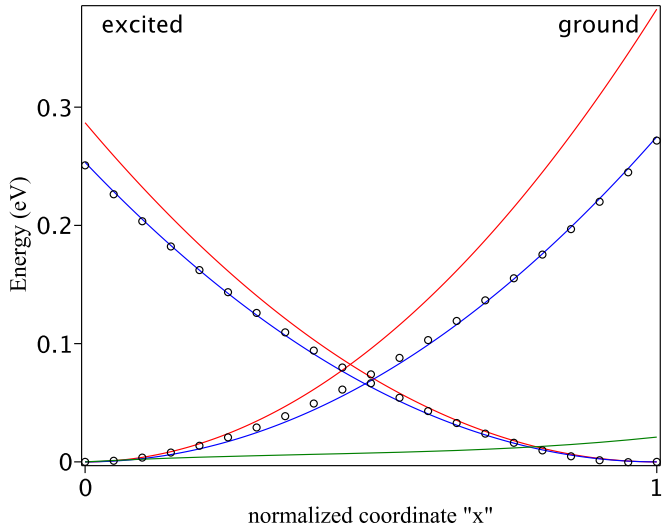
where the phonon correlator

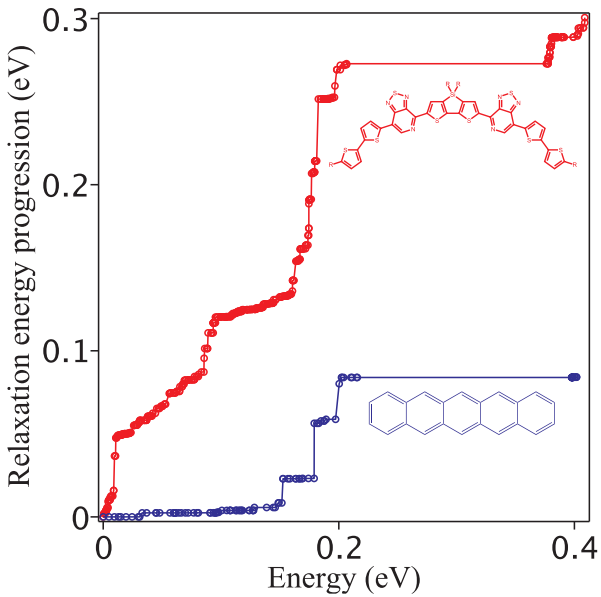
$$\hat{\sigma}(t) = \exp\left[\sum_\alpha S_\alpha \coth\frac{\hbar\omega_\alpha}{2T}(\cos\omega_\alpha t - 1) - \mathrm{i}\sum_\alpha S_\alpha \sin\omega_\alpha t - \mathrm{i}\frac{E_{00}+\lambda'}{\hbar}t - \frac{\sigma^2 + 2\lambda' T}{2\hbar^2}t^2\right]$$

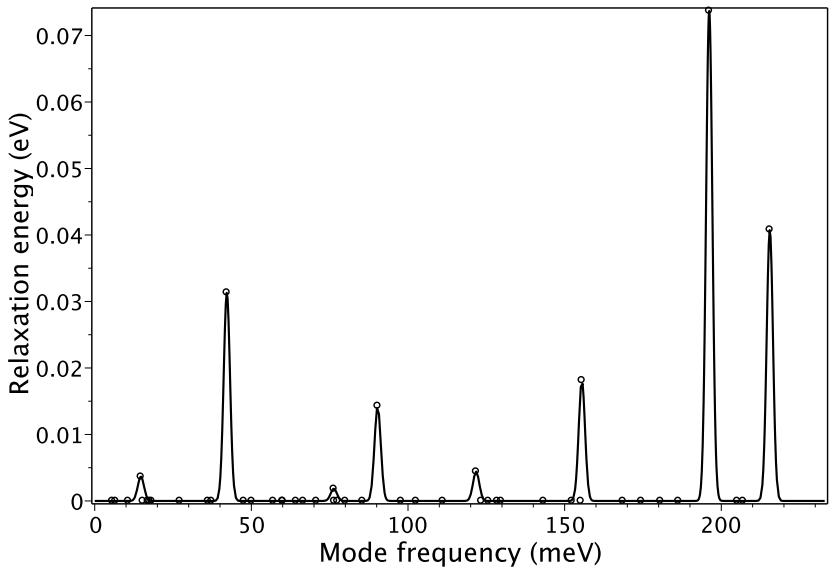
here λ' is reorganization energy due to classical modes and σ^2 is an inhomogeneous broadening

Calculating vibronic couplings

- Get two relaxed geometries: for zero and one quasiparticle at site
- Project atomic displacement onto normal modes ξ_α, then $g_\alpha = -\frac{\xi_\alpha^{(0)}}{\sqrt{2}}$
- Rescale g and ω for weak anharmonic effects



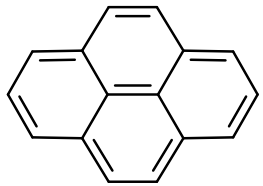


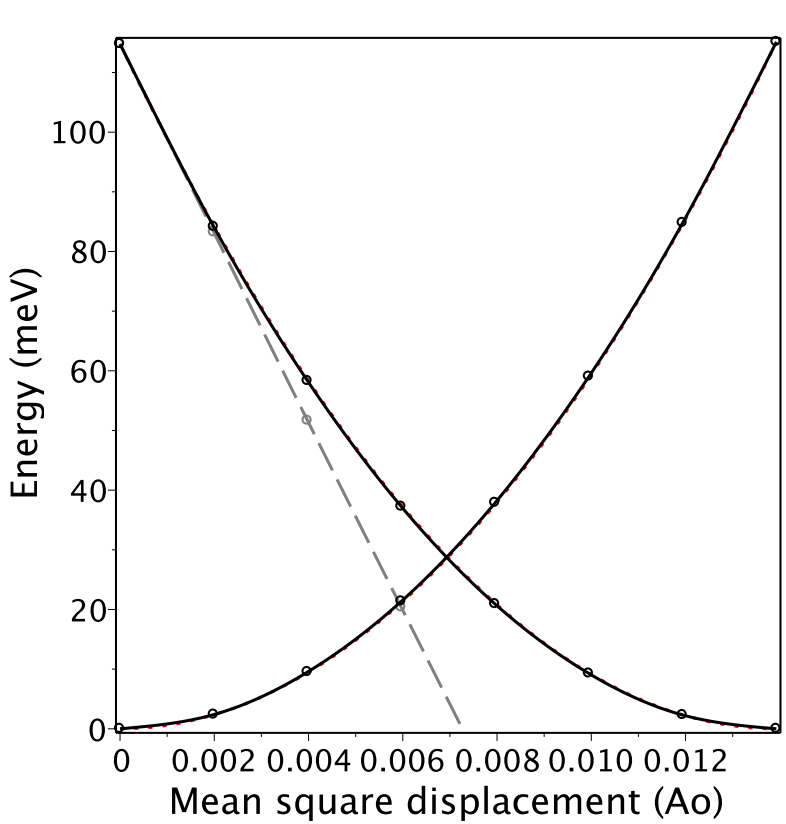


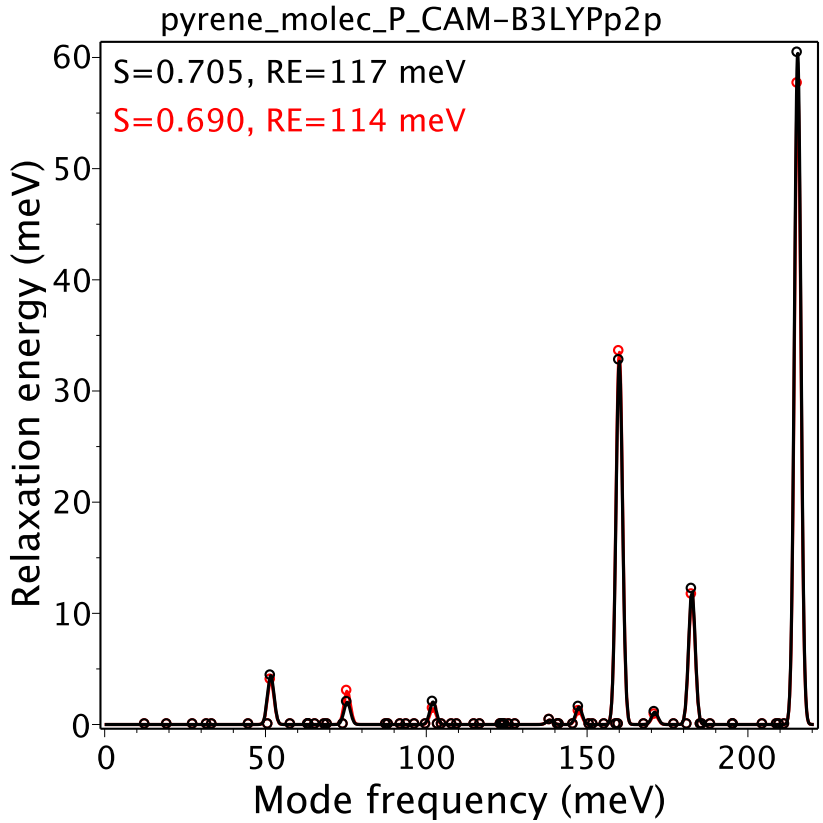
$\lambda(E) = \sum_{\hbar\omega_\alpha < E} g_\alpha^2 \hbar\omega_\alpha$

Accuracy of displaced harmonic oscillator approximation

Pyrene molecule – ideal case: curves are symmetric and harmonic, gradient can be used

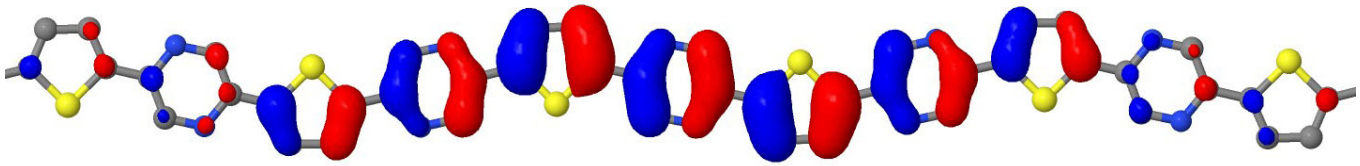


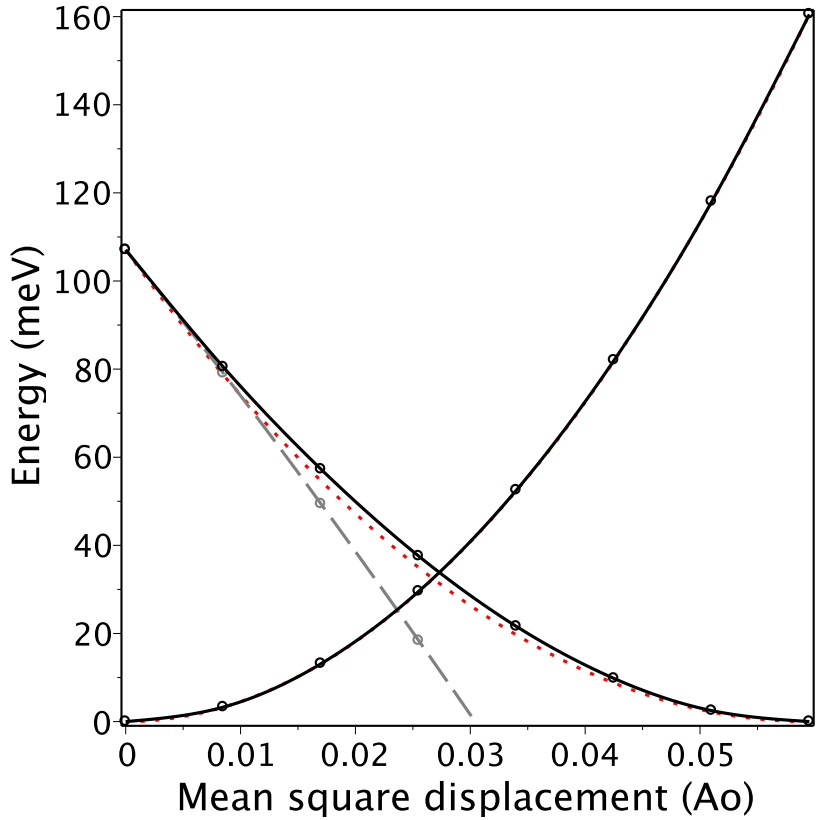




Accuracy of displaced harmonic oscillator approximation

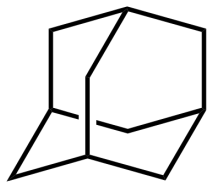
Long oligomer – works satisfactory but there is asymmetry and some anharmonicity

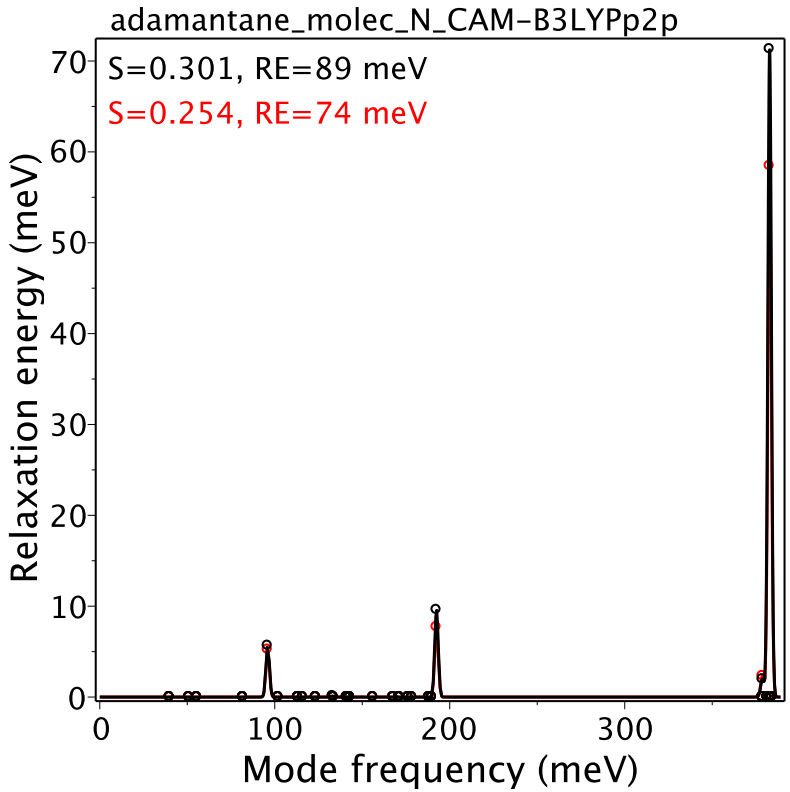


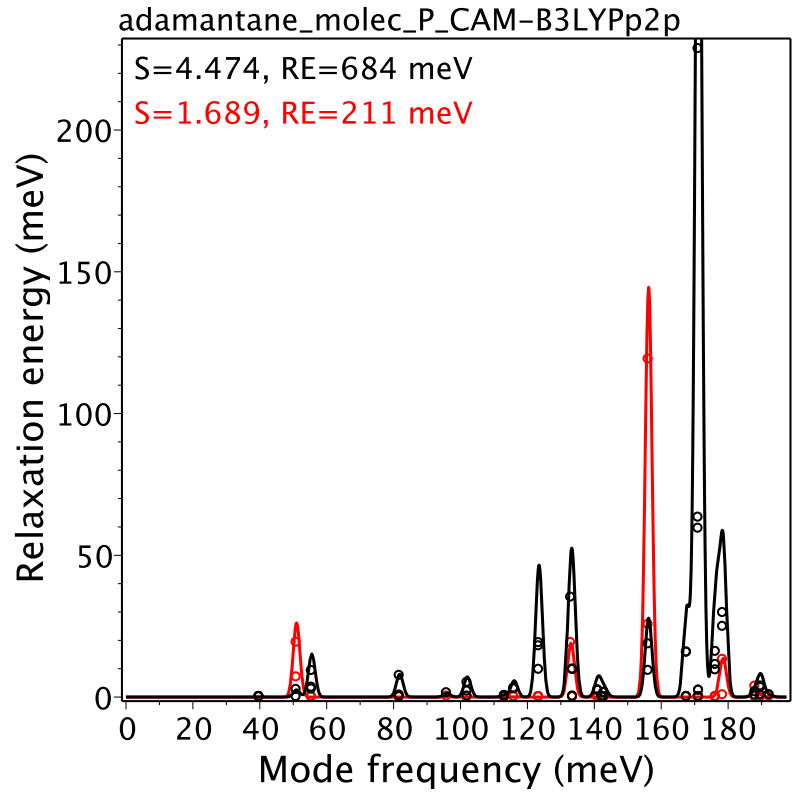


Accuracy of displaced harmonic oscillator approximation

Adamantane – anion is OK, cation is unsatisfactory – degenerate HOMO

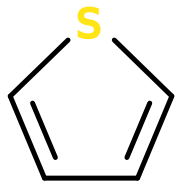


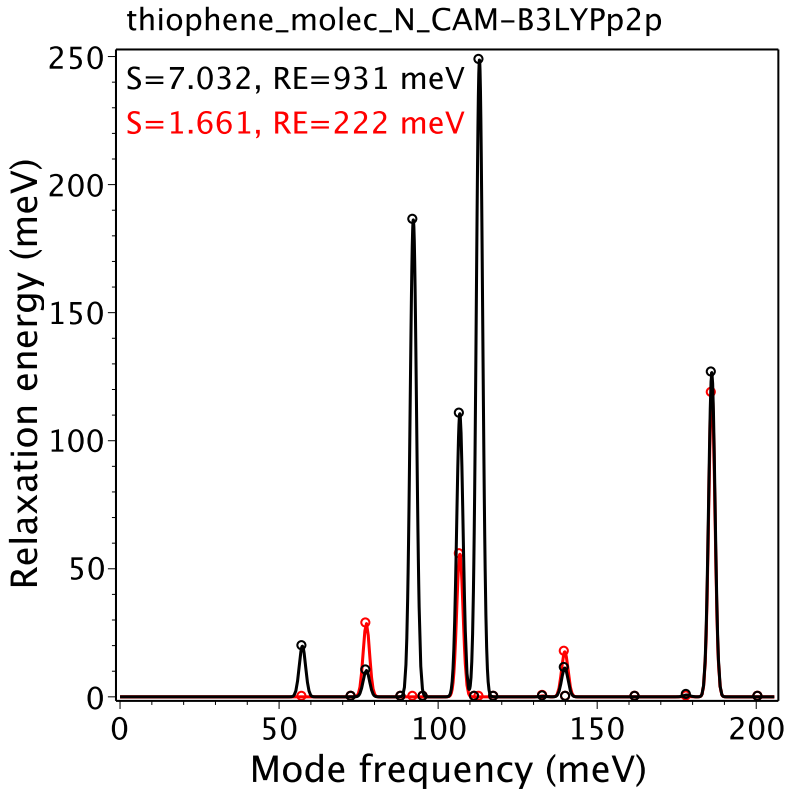


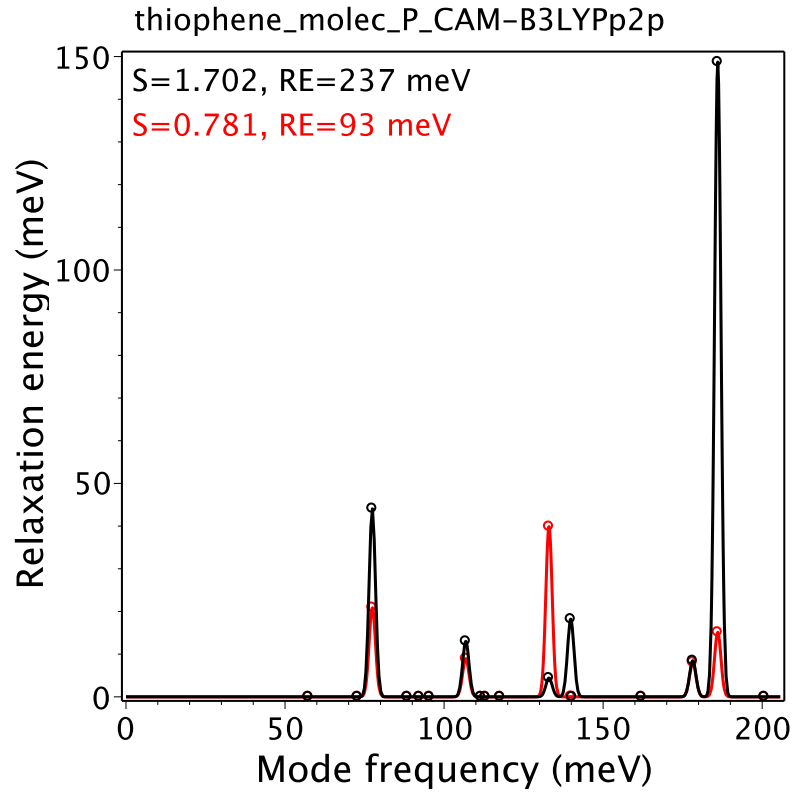


Accuracy of displaced harmonic oscillator approximation

Thiophene – unsatisfactory – anharmonic PES

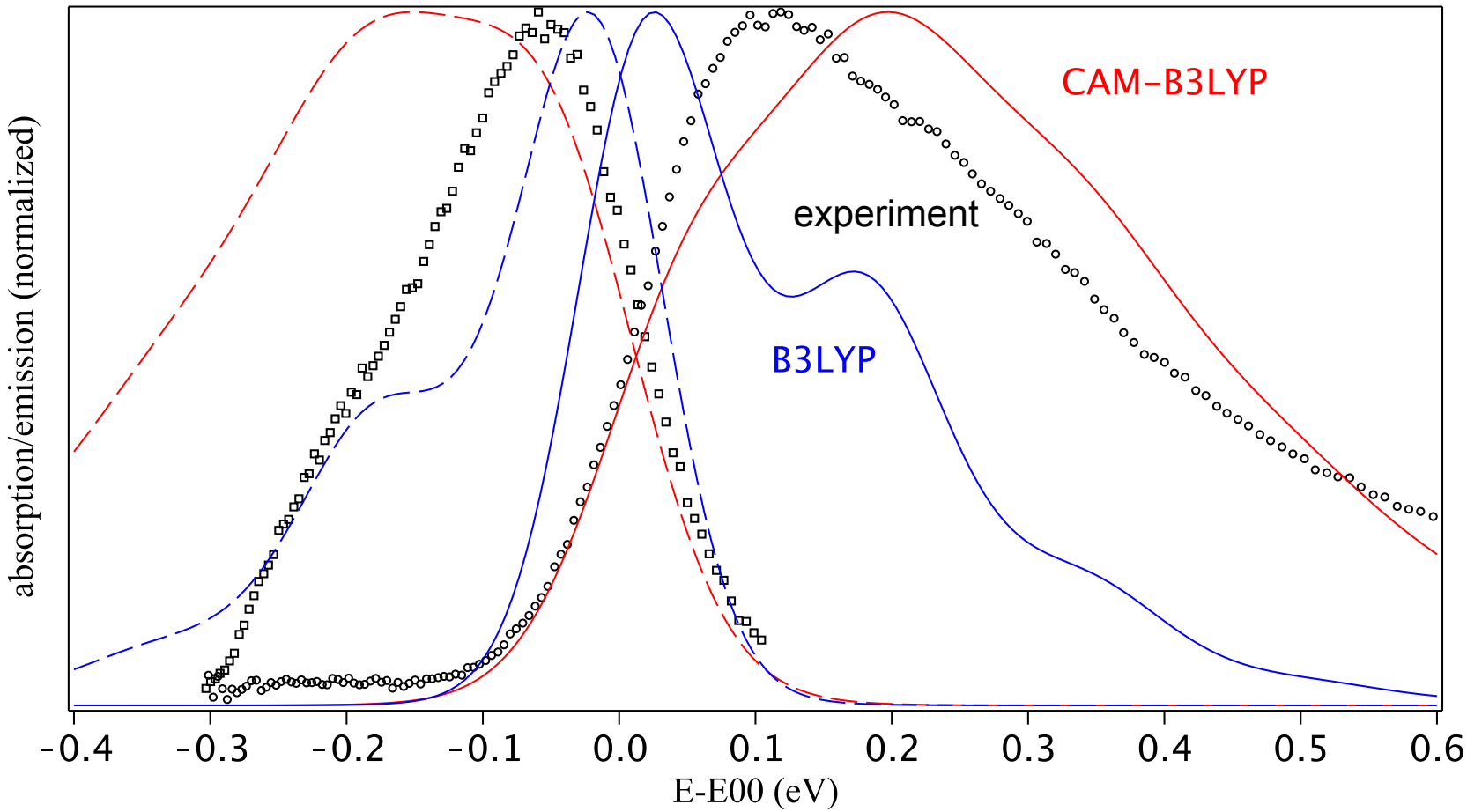






Vibrationally resolved UV-Vis spectra: example

Annu Rev Phys Chem 66, 305 (2015)



B3LYP underestimates vibronic couplings for low-ω modes

CAM-B3LYP overestimates vib. couplings for high-ω modes

Vibrationally resolved UV-Vis spectra: low-T example

J Chem Phys 116, 8569 (2002)

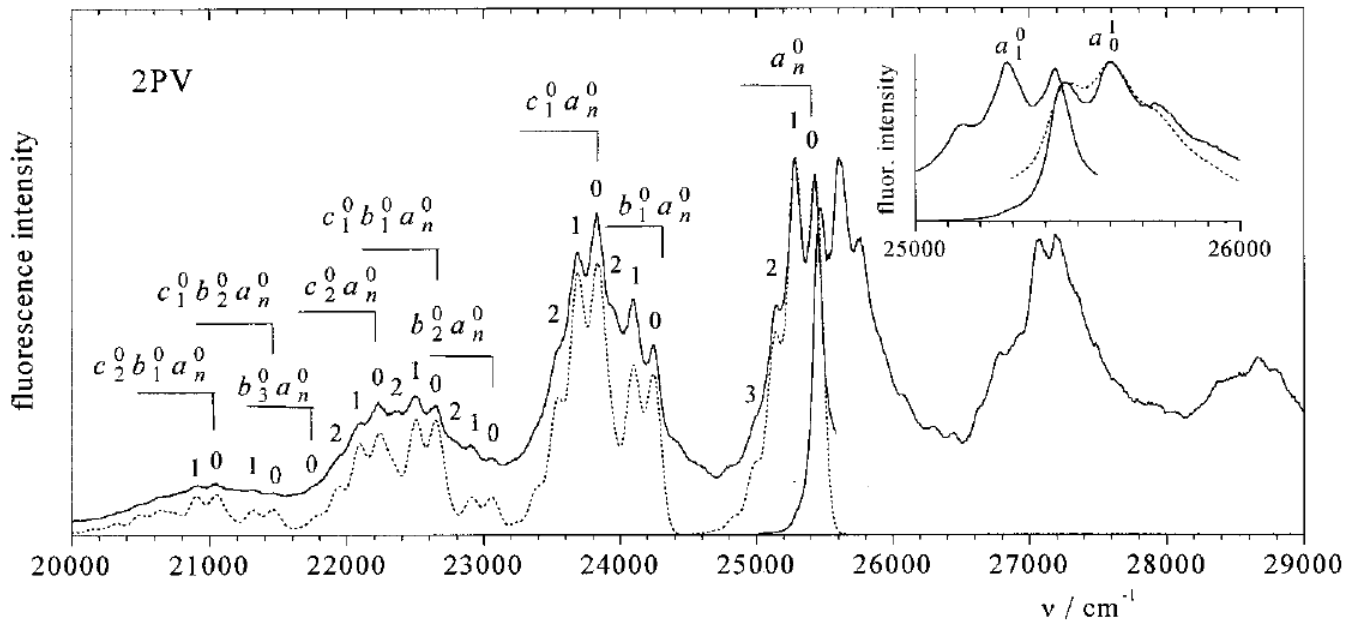
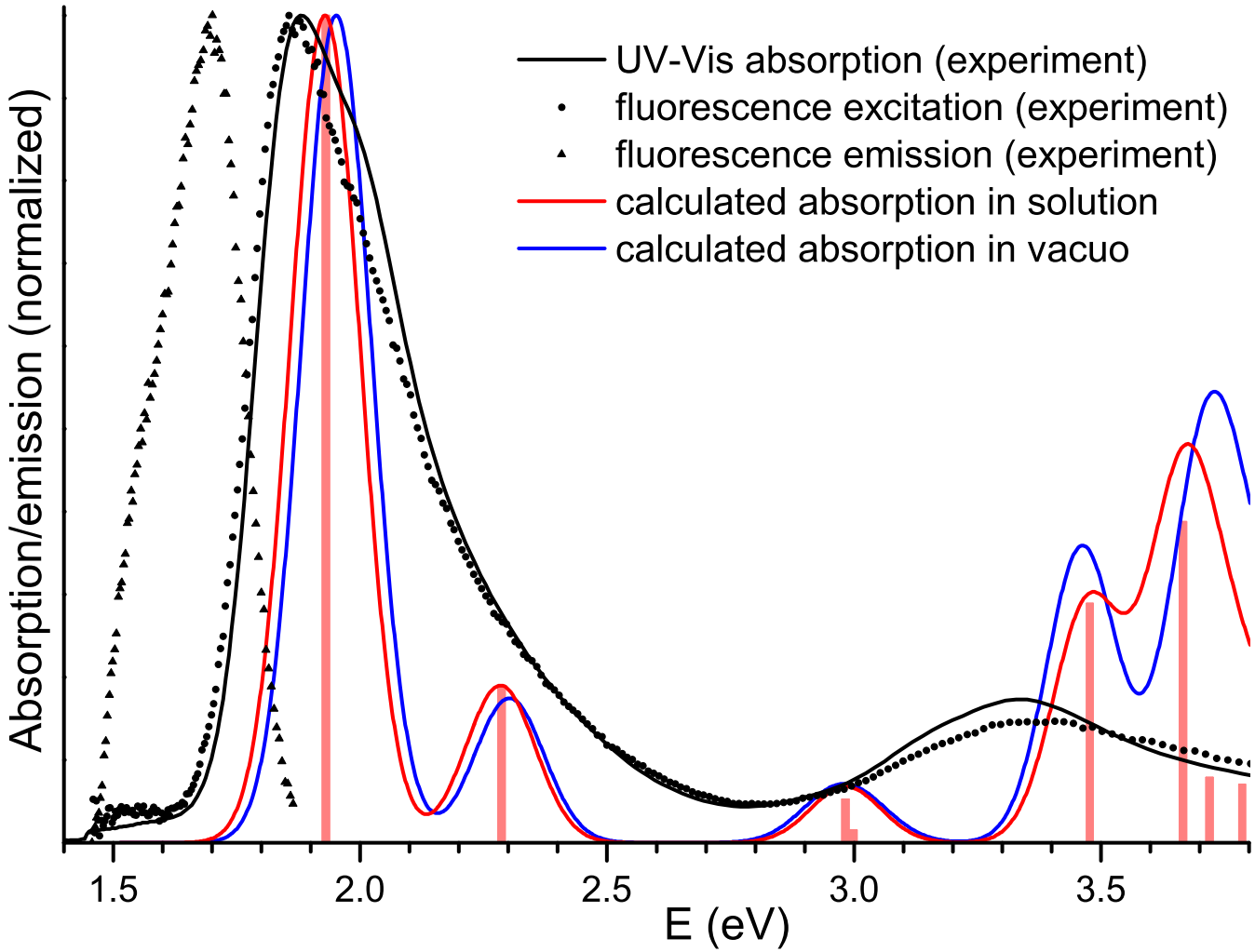


FIG. 7. Fluorescence excitation spectrum (right) and fluorescence emission spectrum (left) of 2PV in tetradecane at 15 K. Solid line: experiment; dashed line: simulation according to Eq. (1) with three modes ($\nu_a = 150\ \mathrm{cm}^{-1}$, $\nu_b = 1200\ \mathrm{cm}^{-1}$, $\nu_c = 1600\ \mathrm{cm}^{-1}$, $S_a = 1.05$, $S_b = 0.45$, $S_c = 0.67$, $\gamma = 130\ \mathrm{cm}^{-1}$). Inset: Region of the electronic origin; dashed line: simulation of the fluorescence excitation spectrum according to Eq. (10) with $T = 15$ K, $D = 5.5$.

UV-Vis spectra: multiple electronic transitions

J Phys Chem C 117, 4920 (2013)



Observe non-gaussian structure of the main absorption band

Raman spectra

- Off-resonant Raman activities can be calculated by DFPT, e.g. available in Gaussian as a black-box solution
- In experiment usually resonant Raman spectra are measured
- Resonant Raman intensities can be calculated by

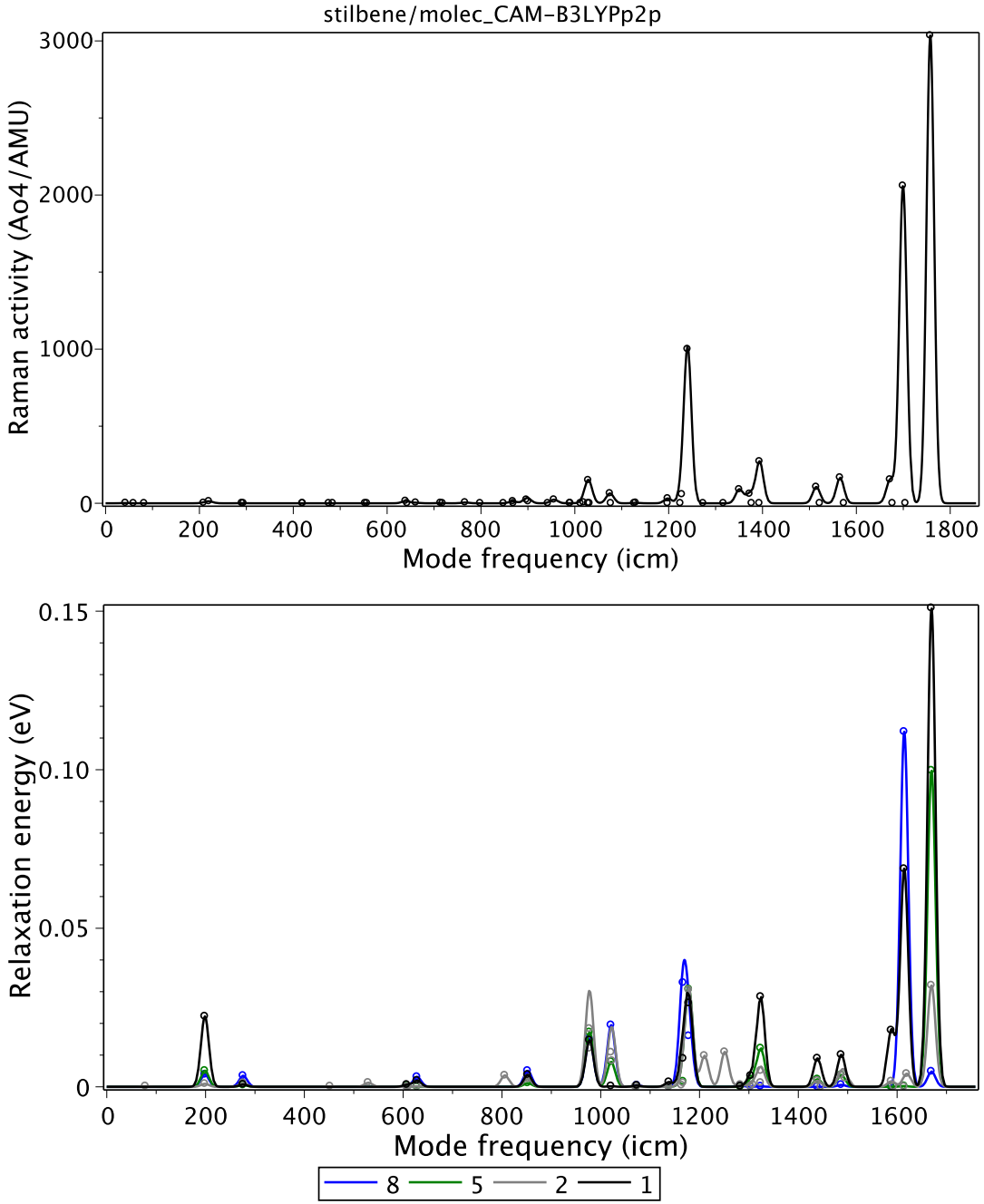
$$I_\omega \sim \lambda \omega^n d^4 / \Delta\Omega^2$$

where d is transition dipole moment, $\Delta\Omega$ is deviation from resonance, and n together with normalization factor depend on details of experiment

[J McHale, Molecular Spectroscopy (CRC, 2017)]

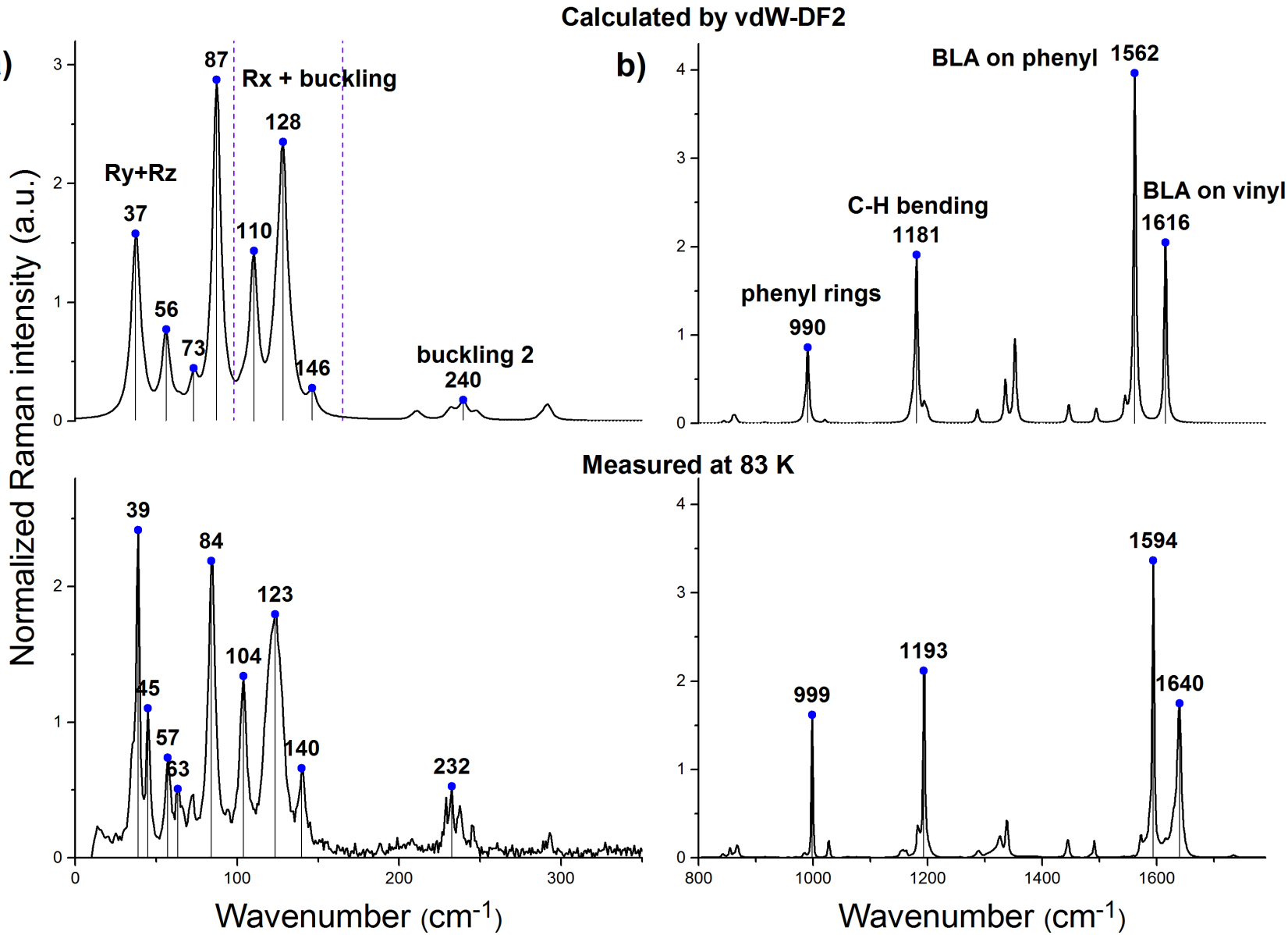
- The main challenge is to calculate vibronic couplings to higher excitations

Raman spectra of stilbene molecule



Raman spectra of stilbene crystal

J Phys Chem Lett 10, 3232 (2019)



Questions

1. Let assume that in the Raman spectra shown in the last slide we see a small peak at around 2600 cm^{-1}. There are no known vibrations at those frequencies. What can be the origin of that peak?

2. Let for a molecule the transition dipole of the lowest excitation be zero by symmetry. How will this influence molecule's properties?

3. What line broadening function would you use for UV-Vis spectra?

Energy and charge transport

- Brute force approach – nonadiabatic MD – not scalable
- Simplified scalable approach – most commonly used
- Beyond the simplified approach – ideas

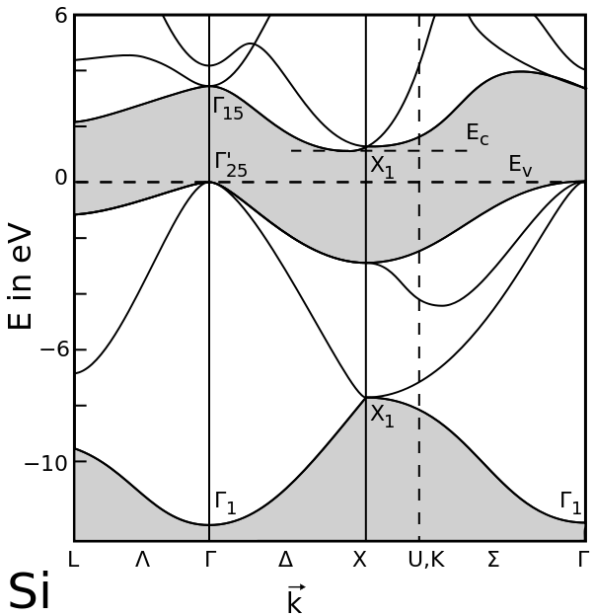
Multiple scales: how to approach

Scale	Method	Electronic processes
molecular complex (1000 atoms)	NAMD	intramolecular relaxation internal conversion intermolecular transfer redox reactions
single bulk phase (crystal,amorphous)	MF	intraband relaxation charge carrier scattering
mesoscale (up to continuum)	KMC MD ??	hopping ionic transport electronic + ionic
device	PDE	diffusive transport

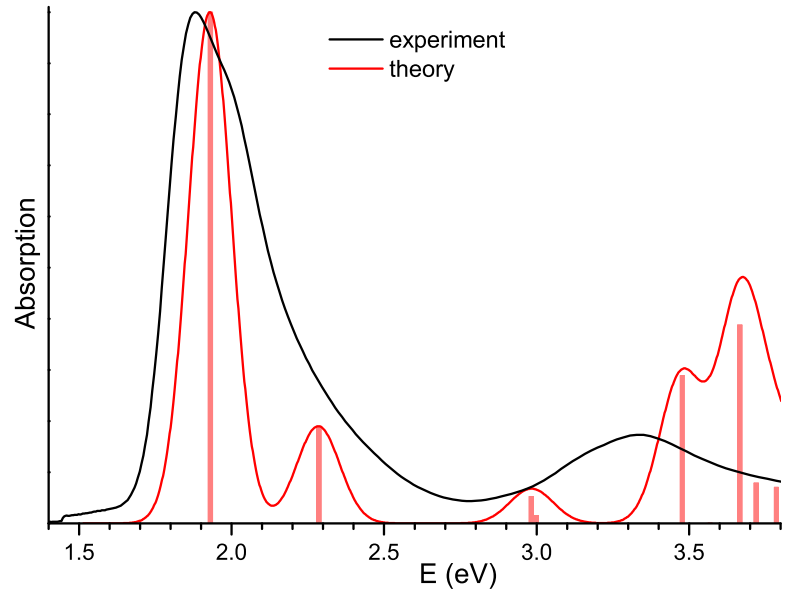
Challenge: no black-box tools, it is complex problem (combine different approaches on different scales, error accumulation through scales)

NAMD=nonadiabatic MD, MF=mean field, KMC=kinetic Monte Carlo, MD=molecular dynamics, PDE=partial differential equations

Some definitions: electronic and vibronic bandwidth



Electronic bandwidth



Vibronic bandwidth

$$W_{\text{el}}^2 = \langle \Delta\varepsilon^2 \rangle + \langle \Delta\varepsilon^2 \rangle_T$$

$$W_{\text{vib}}^2 = \sum_\alpha g_\alpha^2 \hbar^2 \omega_\alpha^2 \coth \frac{\hbar\omega_\alpha}{2T}$$

For bandwidth W, correlation function decreases as $\mathrm{e}^{-W^2 t^2/2\hbar^2}$ at small t

Electron-phonon couplings: organic vs inorganic

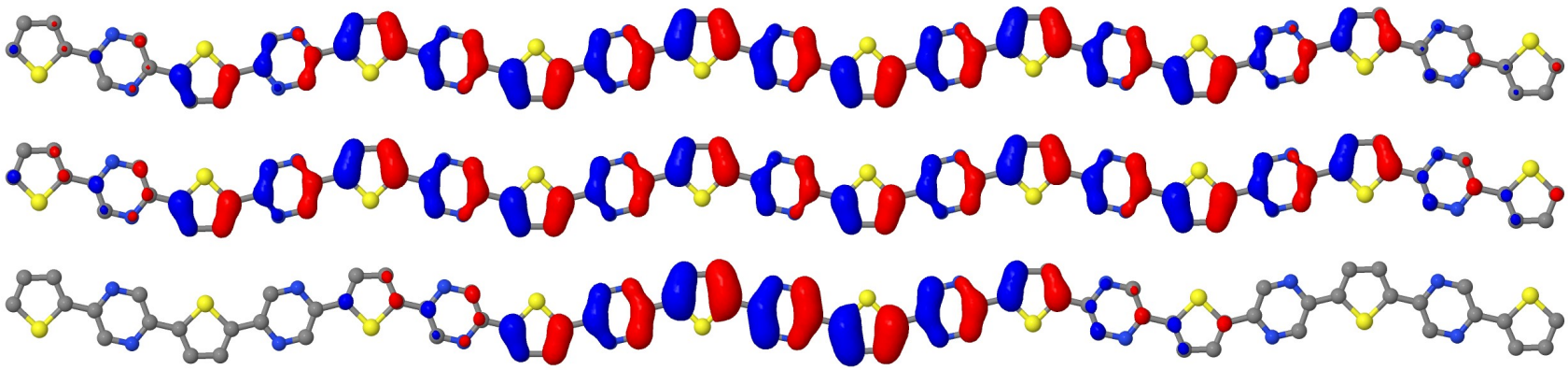
Electron-phonon couplings are always large for bonding electrons, with W_{vib} of the order of tenths of eV. The difference is in W_{el}:

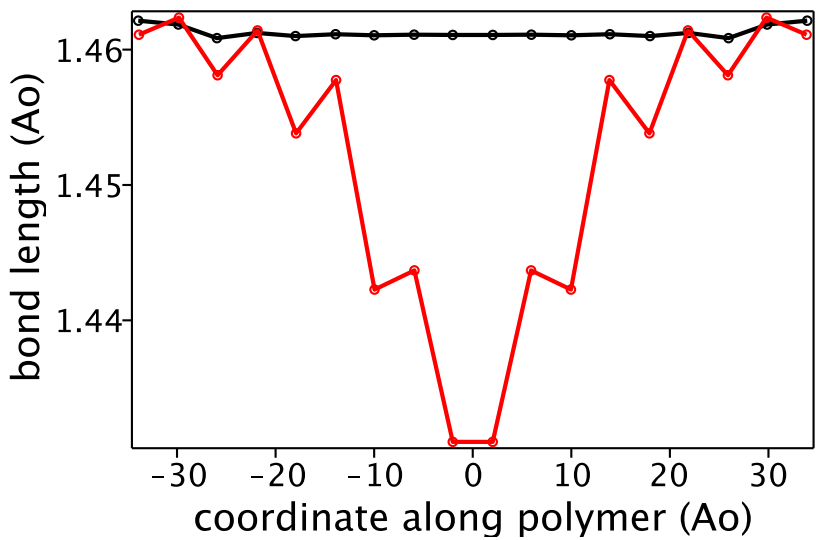
"Inorganic electronics"	"Organic electronics"
$W_{\text{el}} \gg W_{\text{vib}}$	$W_{\text{el}} \sim W_{\text{vib}}$
(weak el-ph correlations)	(strong el-ph correlations)
$\Longrightarrow$ model of free charge carriers scattered by phonons	$\Longrightarrow$ more complicated models

Additional complication: soft lattice (no rigid framework, flexible dihedrals, intermolecular motions) $\Longrightarrow$ doping and intercalation challenges (also chalcogenides, transition metal oxides)

Polaron formation

(HOMO, cation NO, polaron NO)





Charge carrier mobility

Basic equations in homogeneous medium

Current density $\quad j = \mu \cdot n \cdot e\mathcal{E}$

Free charge carriers	**Localized charge carriers**
Drude formula	Hopping
$\mu = \dfrac{e\,\tau_{\text{scattering}}}{m_{\text{effective}}}$	$\mu = \dfrac{2\pi e}{\hbar} f \cdot (aV)^2 \dfrac{J}{T}$

* Purely electronic and electron-phonon interaction terms are factorized

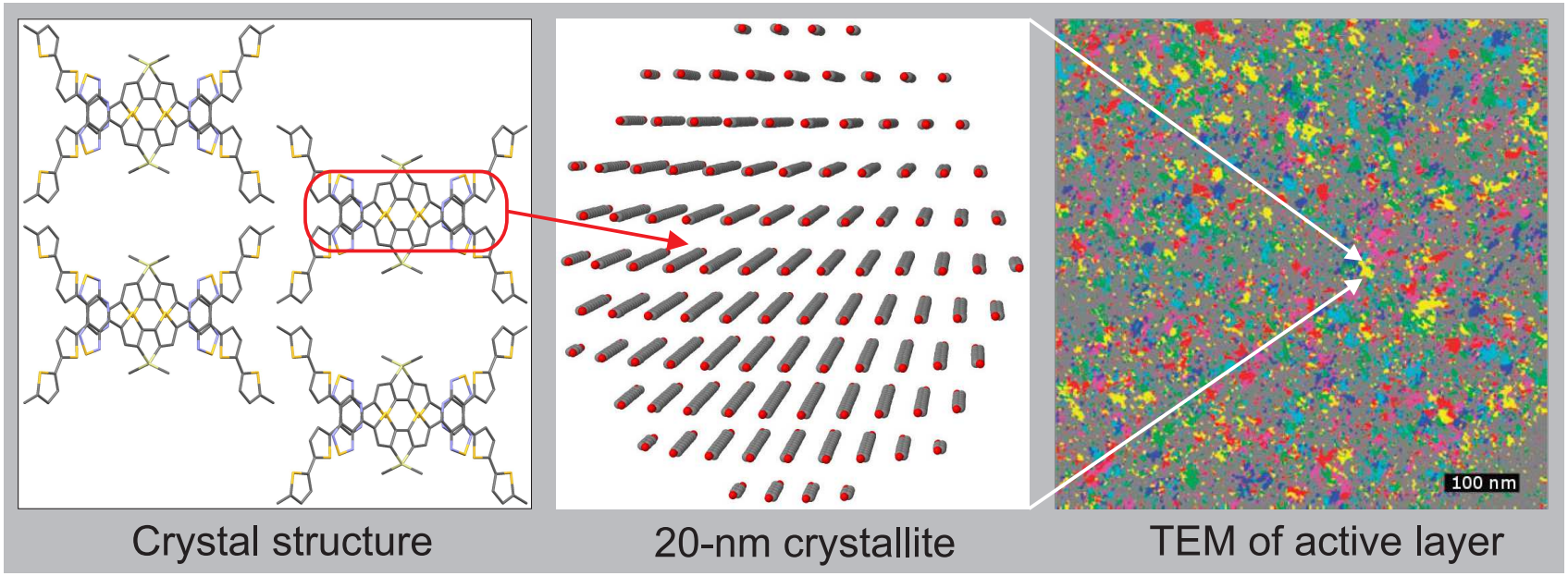
Scattering (or localization) mechanisms:

- dynamic lattice defects (phonons, intramolecular vibrations)
- extrinsic disorder: from lattice defects to mesoscopic nonhomogeneity (grain boundaries, interfaces, composites)
- carrier-carrier interaction

---

f = lattice form-factor, a = lattice spacing, V = electronic inter-site coupling, J = spectral overlap, mobility definition $v = \mu\mathcal{E}$, zero-field mobility = eD/T, exciton diffusion length = $\sqrt{D \cdot \text{lifetime}}$

Simplified approach for a molecular solid



- Coarse grain electrons to one site per molecule
- Simplify molecular motions to harmonic vibrations
- Linearize coupling between electrons and molecular motions

$$\Longrightarrow \sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_{\alpha} \hbar\omega_\alpha \left(b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar\omega_\alpha g_{ij\alpha} \left(b_\alpha^\dagger + b_\alpha \right) c_i^\dagger c_j$$

Then solve this Hamiltonian (e.g. in small polaron hopping approximation)

Annu Rev Phys Chem 66, 305 (2015)

Holstein–Peierls Hamiltonian

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar\omega_\alpha \left(b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar\omega_\alpha g_{ij\alpha} \left(b_\alpha^\dagger + b_\alpha \right) c_i^\dagger c_j$$

here c_i – quasiparticles (excitons, holes etc.) described by coarse-grained Hamiltonian, b_α – normal modes or phonons,

$$H_{ij}^{1p} = \delta_{ij}\varepsilon_i + (1 - \delta_{ij}) t_{ij},$$

ε_i – onsite energy, t_{ij} – transfer integral, $g_{ij\alpha}$ – electron-phonon coupling (local for $i = j$, nonlocal otherwise)

Approximations:

- mean field approximation for electrons (one may add interaction terms)
- harmonic approximation for atomic motion (essential for quantum modes)
- linear electron-phonon coupling

For calculation of nonlocal (intermolecular) couplings see [Phys Stat Sol B 248, 511]

Calculating coarse-grained electronic Hamiltonian

See also [Chem Rev 117, 10319 (2017)]

Definition: For all possible atomic configurations, the lowest eigenvalue of H^{1p} should match the exact electronic energy

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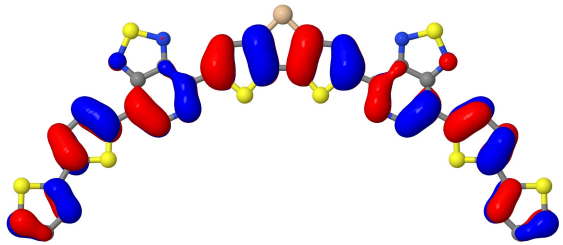
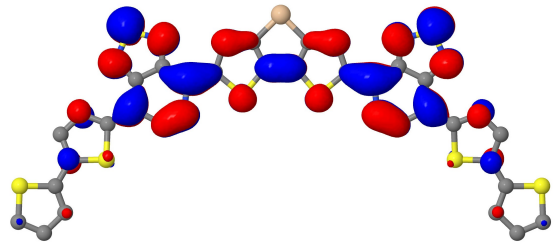
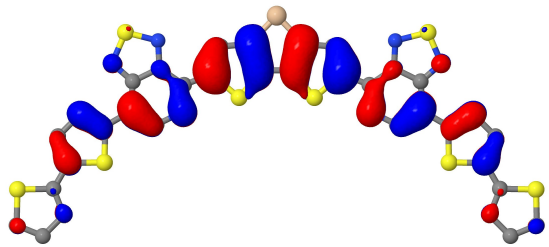
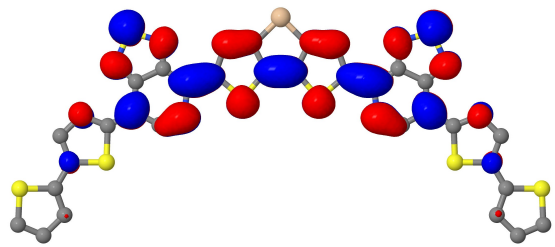
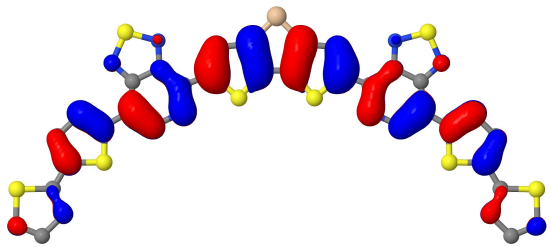
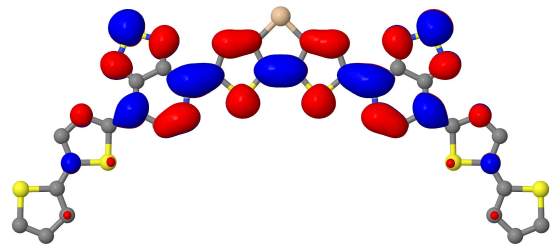
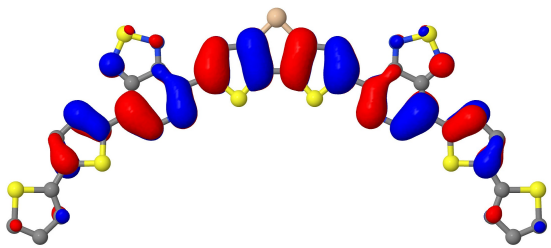
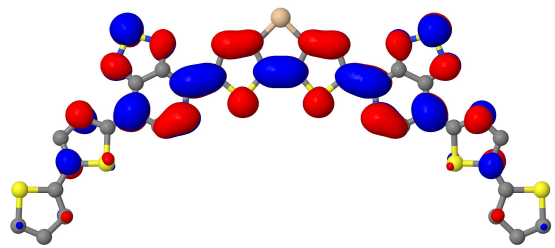
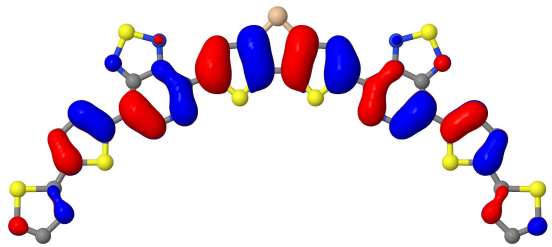
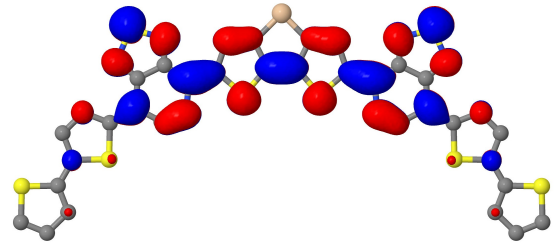
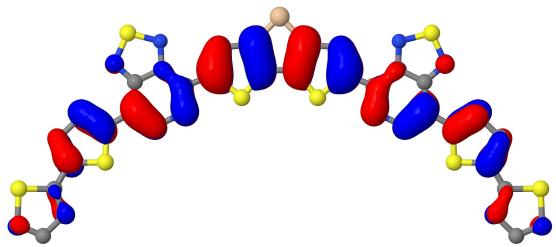
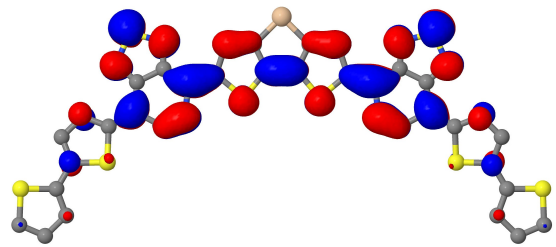
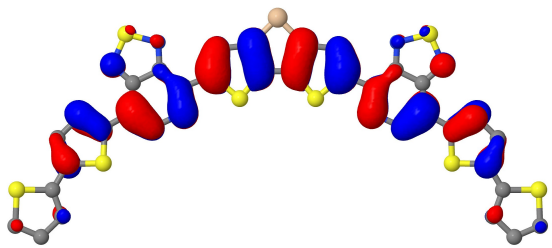
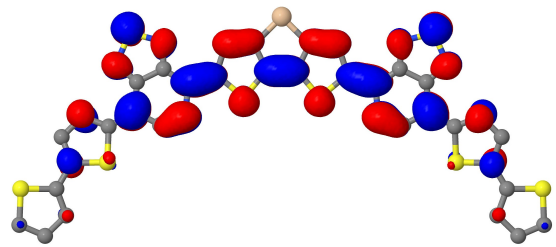
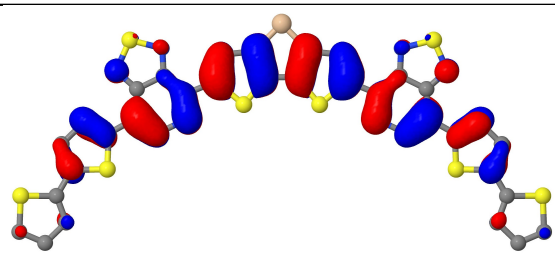
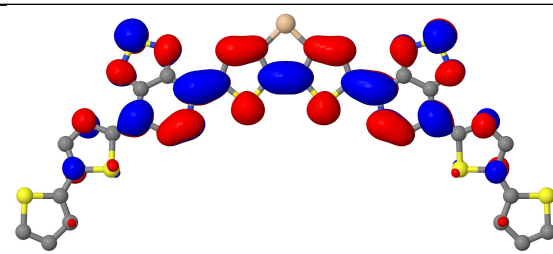
Dimer approximation:

- Frenkel excitons: from excitations energies and transition dipoles [J Phys Chem C 117, 4920]
- Electrons/holes: from DFT Fock matrices [JPCC 117, 4920] (HOMO/LUMO=hole/electron, HOMO×LUMO=exciton)
- Semiempirical approaches [Int J Q Chem 108, 51; JACS 127, 4744]

Hole=HOMO, electron=LUMO, exciton=HOMO×LUMO

	HOMO	LUMO
ground state $n_h = 2$ $n_e = 0$		
	hole NO	electron NO
cation/anion $n_{h/e} = 1$ $\Delta n_2 = .07/.06$		
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		

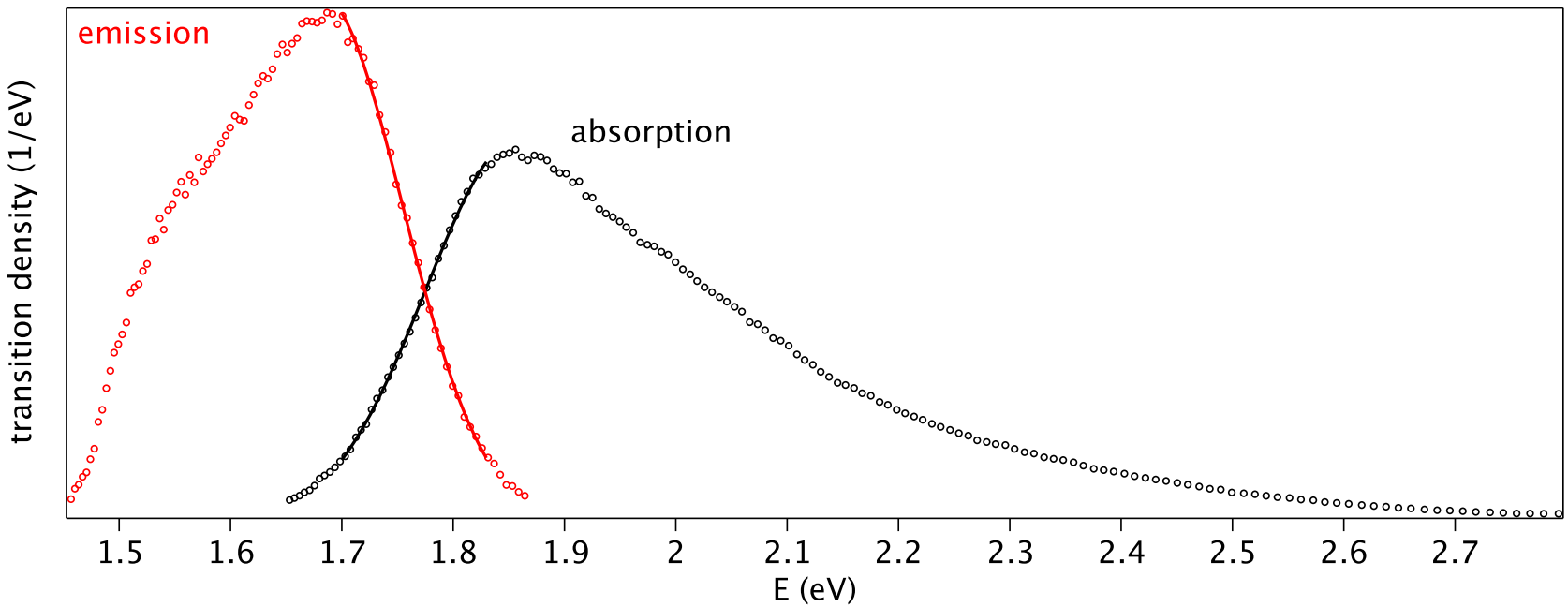
Excitation=exciton

	hole NTO/NO	electron NTO/NO
singlet exciton $n_h = 1 + .12$ $n_e = 1 - .12$		
singlet transition $n_{h/e} = 1 \pm .17$		
triplet exciton $n_h = 1 + .17$ $n_e = 1 - .18$		
triplet transition $n_{h/e} = 1 \pm .25$		

Solving Holstein–Peierls Hamiltonian: hopping regime

Calculate hopping rates using Fermi's golden rule:

$$w_{(i\to j)} = \frac{2\pi}{\hbar}|t_{ij}|^2 J_{ij}, \quad J_{ij} = \int \rho_i^{\mathrm{emi}}(E)\rho_j^{\mathrm{abs}}(E)\,\mathrm{d}E \text{ is spectral overlap}$$



Details: charge/energy transfer in donor-acceptor model

(two-site Holstein model by perturbation theory in inter-site electronic coupling)

Fermi's golden rule:

$$w = \frac{2\pi}{\hbar} \sum_{nn'} \rho_n \left| H^{\text{int}}_{nn'} \right|^2 \delta(E_{nn'}), \quad E_{nn'} = E_{n'} - E_n,$$

where ρ_n is initial population and δ is spectral lineshape function.
For local electron-phonon couplings (Holstein model)

$$H^{\text{int}}_{nn'} = t \, \langle n_{\text{D}} | n'_{\text{D}} \rangle \langle n_{\text{A}} | n'_{\text{A}} \rangle, \quad \rho_n = \rho^{\text{D}}_{n_{\text{D}}} \rho^{\text{A}}_{n_{\text{A}}}, \quad E_n = E_{n_{\text{D}}} + E_{n_{\text{A}}},$$

where $n_{\text{D/A}}$ ($n'_{\text{D/A}}$) denotes initial (final) state of donor/acceptor and vibrational overlaps $\langle n | n' \rangle$ are called Franck–Condon factors.

$$\Longrightarrow \quad w = \frac{2\pi}{\hbar} |t|^2 J, \quad \text{where}$$

$$J = \int \sigma^{\text{D}}(-E) \sigma^{\text{A}}(E) \, \mathrm{d}E \quad \text{is spectral overlap}$$

$$\sigma(E) = \sum_{nn'} \rho_n \langle n | n' \rangle^2 \delta(E - E_{nn'}) \quad \text{is transition spectral density,}$$

whose Fourier transform is correlator between initial and final states.

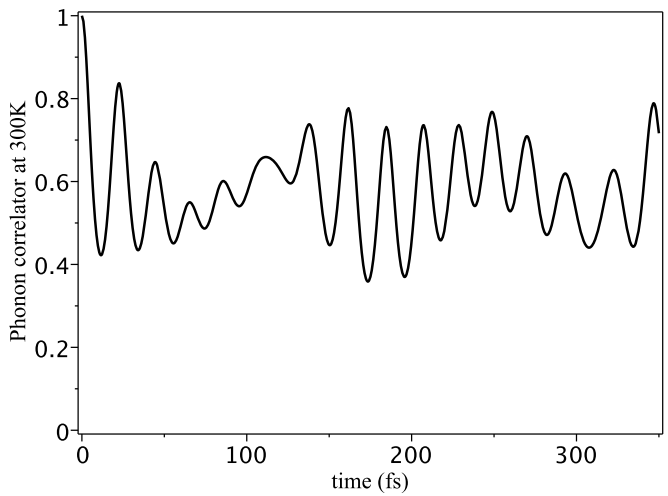
Spectral overlap via phonon correlator

$$J_{ij} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left\langle \mathrm{e}^{\mathrm{i}t\mathsf{H}_i^{\mathsf{vib}}/\hbar}\ \mathrm{e}^{-\mathrm{i}t\mathsf{H}_j^{\mathsf{vib}}/\hbar} \right\rangle \mathrm{d}t$$

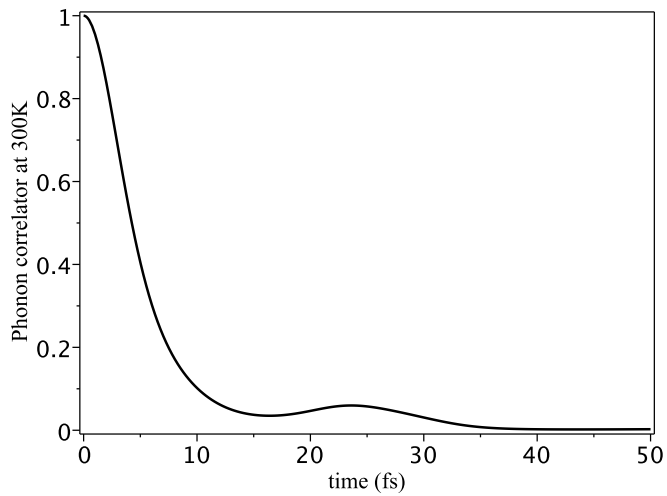
Independent boson model (displaced harmonic oscillator):

$$J_{ij} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \hat{\delta}(t)\mathrm{e}^{-\mathrm{i}\omega_{00}t} \prod_{\alpha} C_\alpha(t)\,\mathrm{d}t,$$

where $C_\alpha(t) = \exp\left[g_\alpha^2\left(\coth\frac{\hbar\omega_\alpha}{2T}\left(\cos\omega_\alpha t - 1\right) - \mathrm{i}\sin\omega_\alpha t\right)\right]$,
$\hbar\omega_{00}$ is 0-0 transition energy,
$\hat{\delta}$ is line shape function (inhomogeneous broadening) e.g. $\mathrm{e}^{-\sigma^2 t^2/2\hbar^2}$



rigid vs. soft molecule

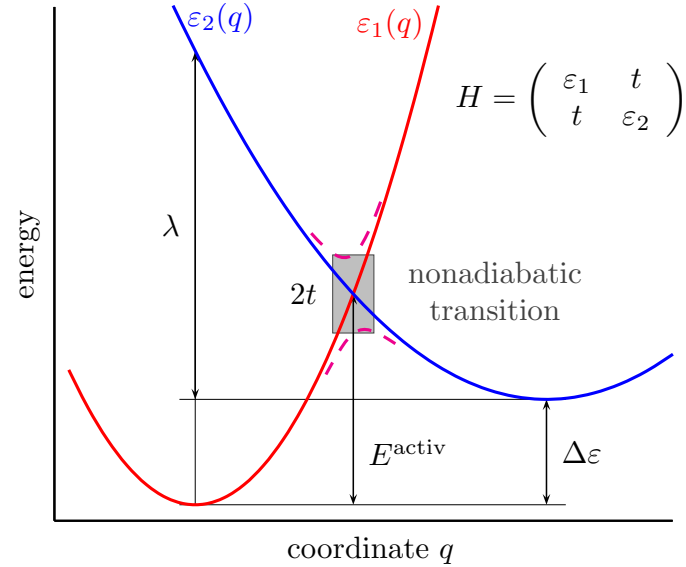


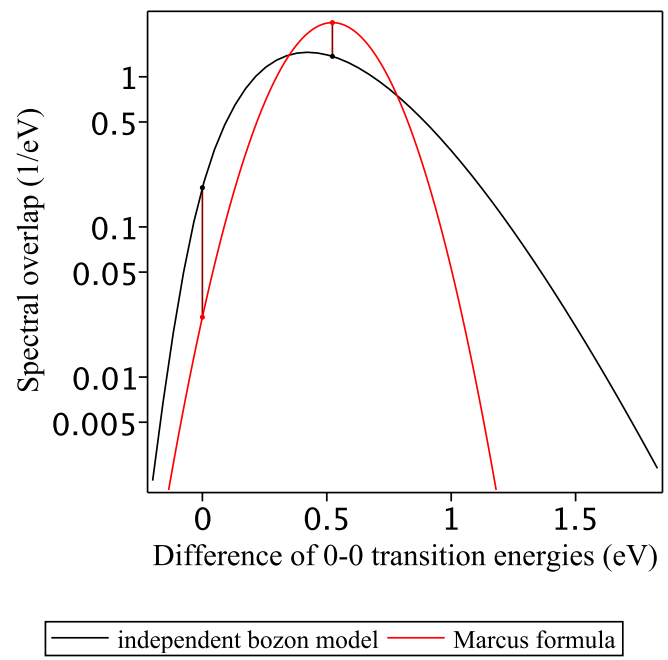
Spectral overlap in high temperature limit: Marcus formula

If $T \gg \hbar\omega$ then

$$J_{ij} = \frac{1}{\sqrt{4\pi\lambda T}} \exp\left[-\frac{(\lambda + \varepsilon_j - \varepsilon_i)^2}{4\lambda T}\right],$$

where $\lambda = E_i^{\text{polaron}} + E_j^{\text{polaron}}$ is the reorganization energy





Final step: solving master equation for hopping

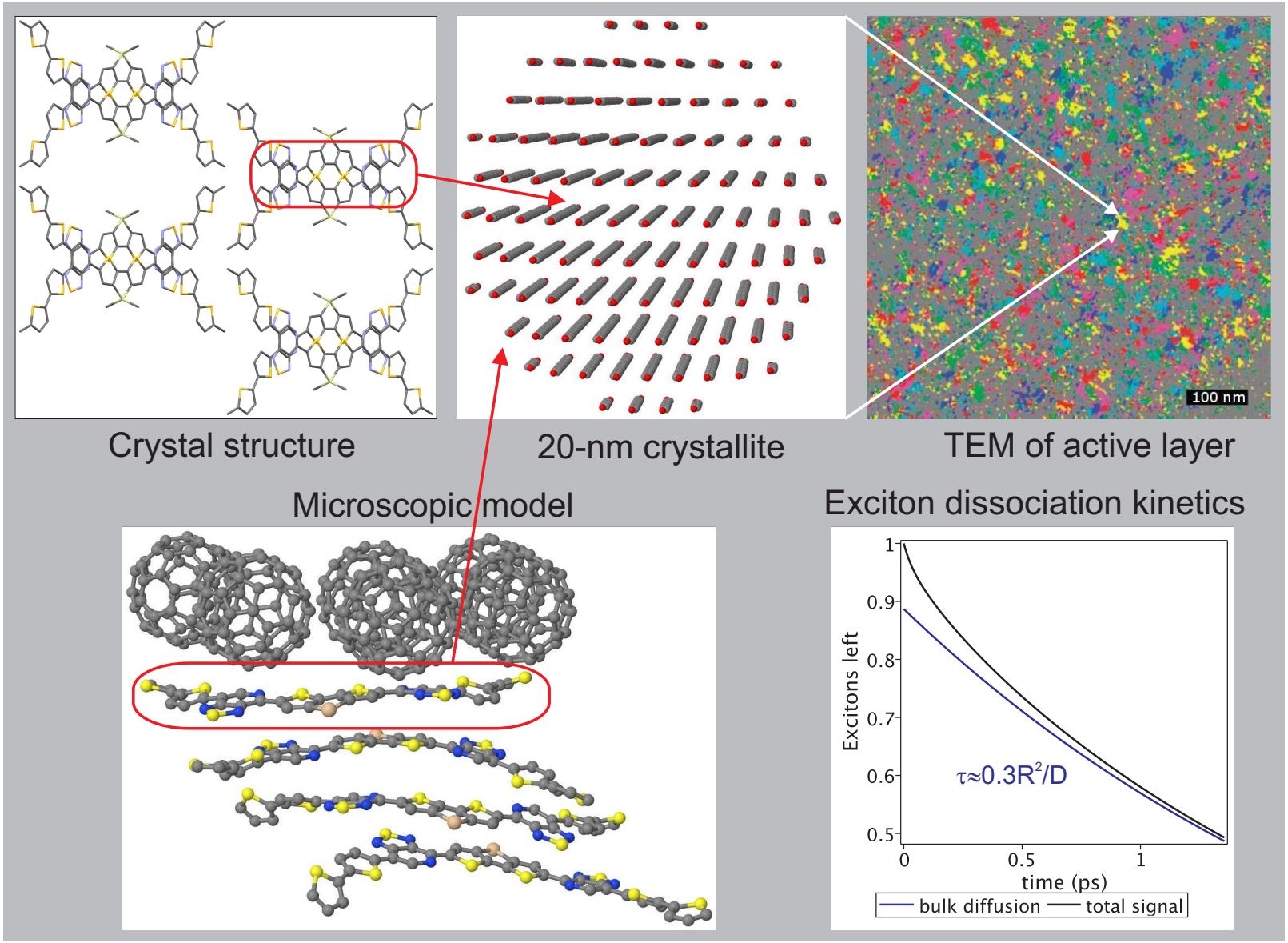
Master equation for average site occupation $n_i(t)$:

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \sum_j (n_j w_{ji} - n_i w_{ij})$$

Kinetic Monte Carlo (KMC) or direct solution?

- Use direct formulas whenever is possible, see [JPCC 117, 4920]
- If system size is too large for matrix methods or if the problem is nonlinear use KMC

Example: Modeling exciton dissociation



In absence of traps exciton dissociation proceeds in picoseconds

Beyond hopping: Mean-field polaron approximation

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar\omega_\alpha \left(b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{i\alpha} \hbar\omega_\alpha g_{i\alpha} \left(b_\alpha^\dagger + b_\alpha \right) n_i$$

1. Do polaron transformation:

$$H \to e^P H e^{-P}, \text{ where } P = \sum_{i\alpha} g_{i\alpha} \left(b_\alpha - b_\alpha^\dagger \right) n_i$$

$$\implies H^{\text{electron}} + H^{\text{phonon}} + H^{\text{int}} \to H^{\text{polaron}} + H^{\text{phonon}}$$

but H^{polaron} includes phonon operators.

2. Take "late" thermal average over phonons in H^{polaron}
$\implies$ renormalized onsite energies and transfer integrals:

$$\varepsilon_i^{\text{polaron}} = \varepsilon_i - \lambda_i, \qquad t_{ij}^{\text{polaron}} = r_{ij} t_{ij}$$

here
$\lambda_i = \sum_\alpha g_{i\alpha}^2 \hbar\omega_\alpha$ is polaron relaxation energy,
$r_{ij} = \exp\left(-\frac{1}{2} \sum_\alpha g_{i\alpha}^2 \coth \frac{\hbar\omega_\alpha}{2kT} - \frac{1}{2} \sum_\beta g_{j\beta}^2 \coth \frac{\hbar\omega_\beta}{2kT} \right)$ is band narrowing factor.

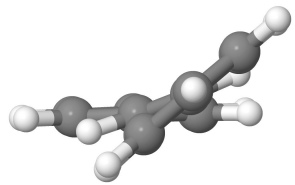
Beyond the simplified approach

(not intended to cover all research groups and all recent publications)

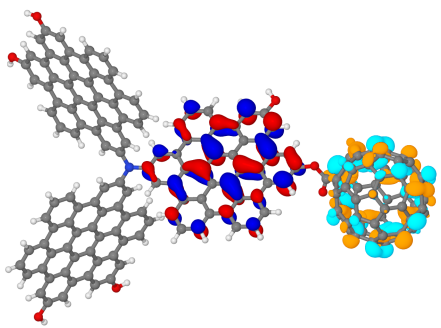
- More accurate model (*up to all-quantum dynamics*)
  - J.Blumberger [Nat Comm 10, 3843 (2019)]
  - S.Tretiak [Acc Chem Res 47, 1155 (2014)]
  - O.Prezhdo, [J Chem Theory Comp 12, 1436 (2016)]
  - P.Rossky [J Chem Phys 142, 244112 (2015)]
- Larger scales (*up to empirical models*)
  - D.Andrienko [J Chem Theory Comp 10, 2508 (2014)]
  - *empirical*: H.Bassler, many others
- Electron-phonon correlations (*up to solvable models*)
  - F.Spano [Chem Rev 118, 7069 (2018)]
  - K.Hannewald, F.Ortmann [Phys Stat Sol B 248, 511 (2011)]
  - I.Burghardt [Z Phys Chem 225, 541 (2011)]
  - S.Fratini, S.Ciuchi, [Adv Funct Mater 26, 2292 (2016)]
  - A.Bakulin [Nat Comm 6, 7880 (2015)]

Why do we need more accurate model

- Realistic potential energy surface
  (intramolecular librations, intermolecular motions)
  - Nonadiabatic molecular dynamic (NAMD)
    – classical molecular dynamics with
    nonadiabatic electronic transitions
    [Acc Chem Res 47, 1155]



- Realistic electron-electron interaction
  (ultrafast photodynamics, charge separation)
  - NAMD
  - Hubbard–Peierls models
- Coarse-grained electronic sites are ill-defined
  (large molecules, polymers)
  - NAMD
  - Better coarse-graining



Current NAMD implementations: 1) not scalable; 2) systematic error due to classical dynamics of atoms (nuclei)

Larger scales

Challenges:

- absence of well parameterized force fields
- accurate intra/inter-molecular geometry & realistic mesoscale

Approaches:

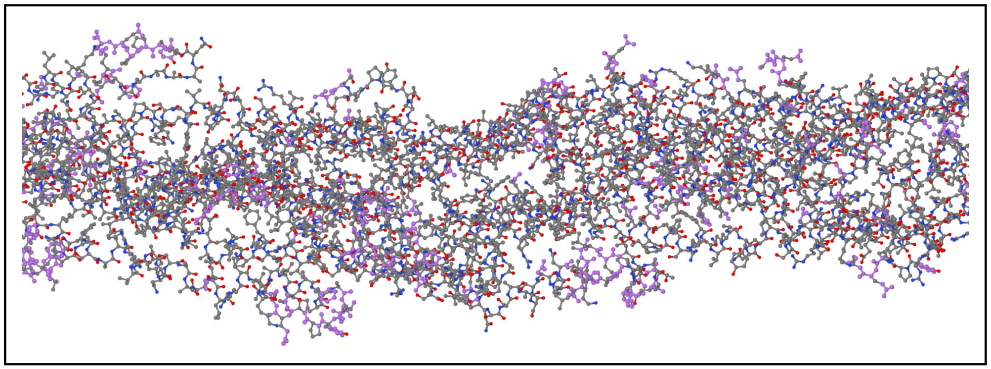
- Efficient/accurate DFT-based parameterization of force fields
- First-principle parameterization of empirical models
  [J Chem Theory Comput 10, 2508]
- Upscaling NAMD and effective Hamiltonian methods

Electron-phonon correlation effects

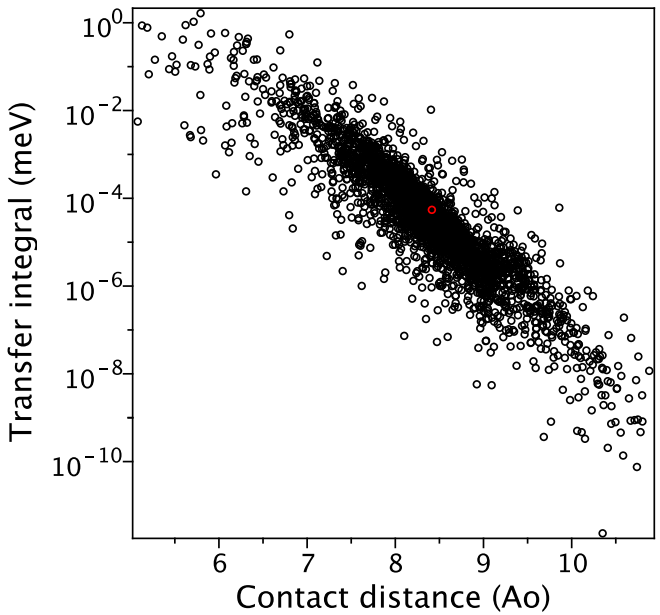
(e.g. effective hopping rate $\neq$ average rate)

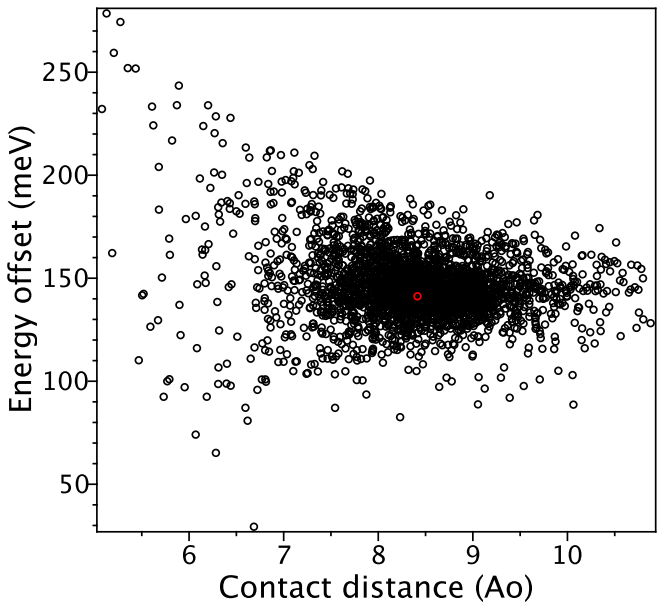
- Statistical correlations
  - Phonon population fluctuations – usually small effect
  - Nonequilibrium phonon population:
    - pumping Nat Comm 6, 7880 (2015)
    - photoexcitation Phys Rev Lett 116, 057402 (2016)
- Dynamic correlations
  - Strong deviations from rate theory, coherences in ultrafast energy transfer JACS 137, 11637 (2015)
  - Large rate fluctuations Adv Mater 27, 1908 (2015)
  - Localization in a perfect crystal Adv Funct Mater 26, 2292 (2016)

Dynamic correlations: Intermolecular fluctuations



$B(\text{Å}^2)$	$\lg\langle V^2\rangle$	$-\lg\langle V^{-2}\rangle$
2.5	-4.1	-5.0
12	-3.4	-6.2
23	-2.8	-7.0
34	-1.4	-8.5

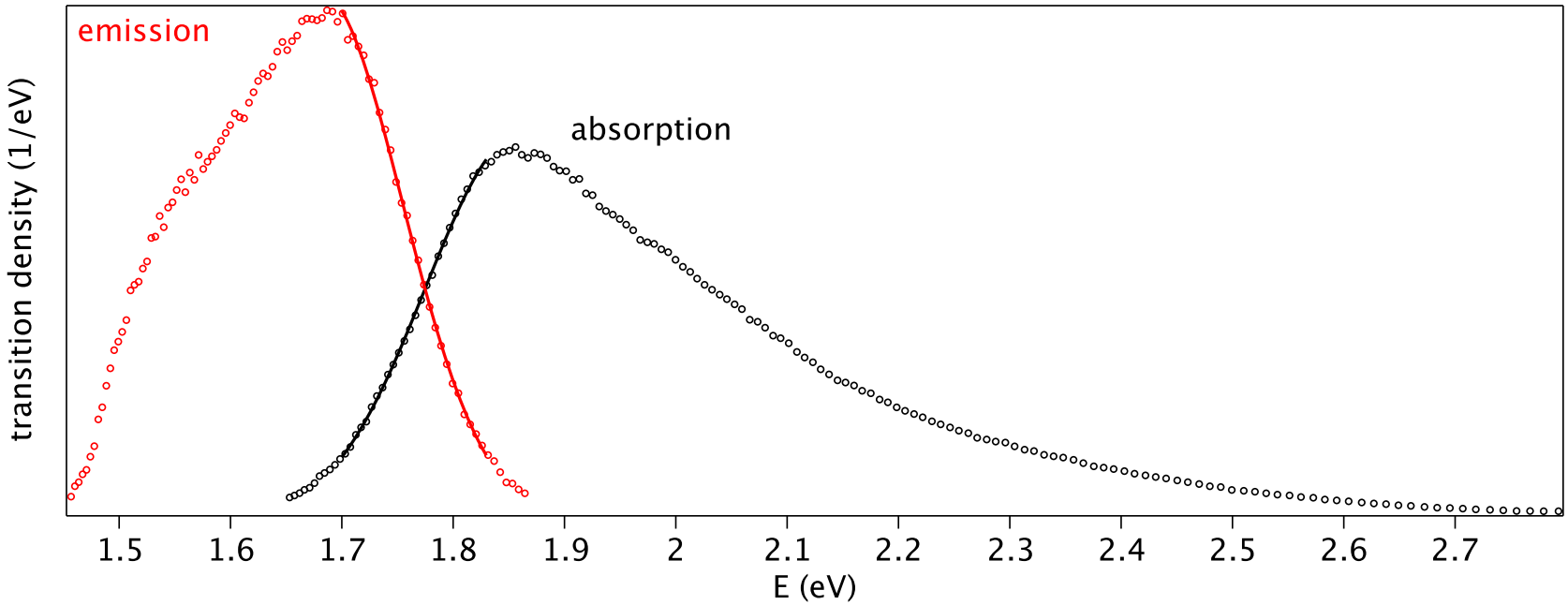




H Yan, C Chuang, A.Z., S Tretiak, F W Dahlquist, G C Bazan, Adv Mater 27, 1908 (2015)

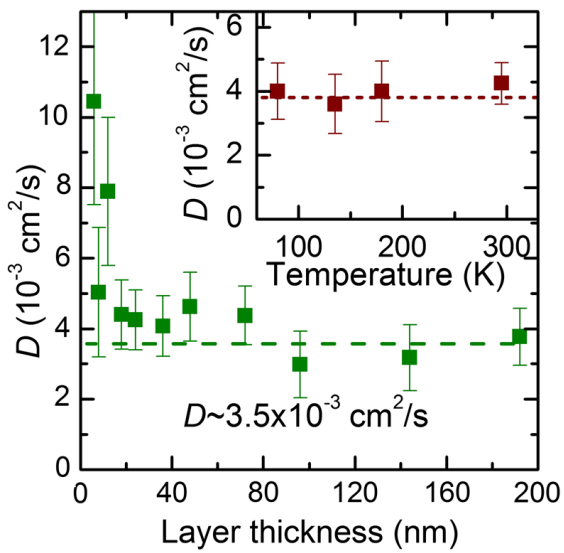
B is Debye–Waller factor (experimentally 20-50 Å^2), V – electronic coupling

Statistical correlations: Nonequilibrium initial population



$$\exp\left(-\frac{\lambda}{4T}\right) \rightarrow \exp\left(-\frac{\lambda}{16T}\right)$$

Rate increase factor 1.6 for the shown transition density



Phys Rev Lett 116, 057402 (2016) →

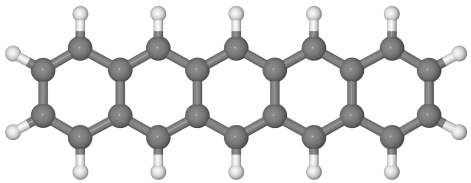
λ – Stokes shift (Frenkel exciton reorganization energy), T – temperature

Exciton/charge carrier localization in molecular crystals

Holes in pentacene

OFET applications

rigid



$V \sim 100$ meV, $W^{\text{bare}} \sim 600$ meV

Intramolecular modes:
$\lambda = 50\text{-}80$ meV, $W^{\text{polaron}} \sim 350$ meV

Intermolecular modes [1]:
$\hbar\omega = 5\text{-}20$ meV, $g^2_{\text{total}} \sim 0.2$

Experiment at 75 K [2]: $W = 250$ meV

W=bandwidth

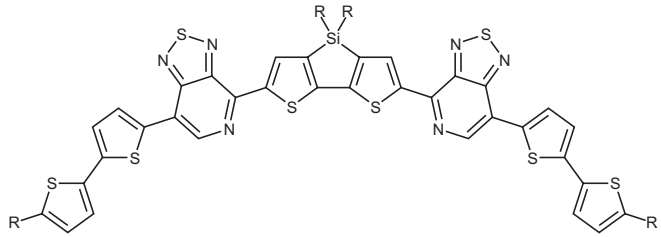
[1] Phys Rev B 69, 075211 (2004)

[2] Phys Rev Lett 108, 256401 (2012)

Excitons in DTS($PTTh_2$)$_2$

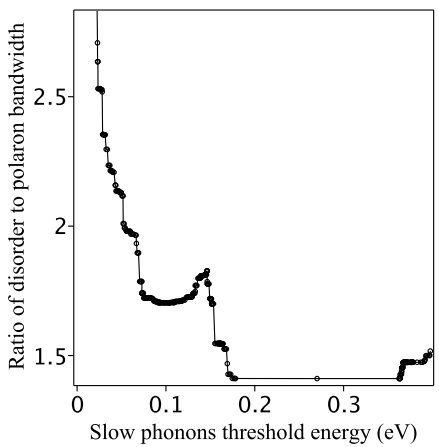
OPV applications

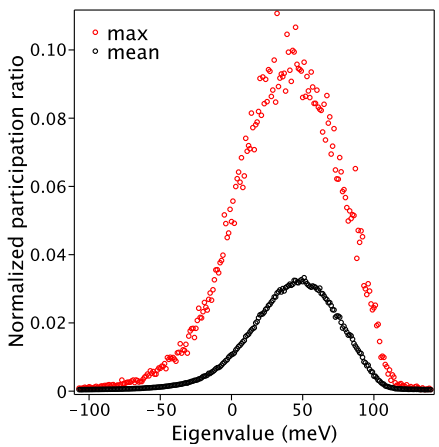
flexible



$V = 60$ meV, $W^{\text{bare}} = 260$ meV

Intramolecular modes:
$\lambda = 110\text{-}260$ meV, $W^{\text{polaron}} = 0$





Two localization mechanisms: band narrowing and quasistatic disorder

Challenges (small-molecule solid)

- Structure prediction (polymorphism, accurate force field)
- Multiple sites per molecule (benzene, C60, large molecules)
- Nonlocal couplings (accuracy vs. feasibility)
- Efficient implementation of mean field polaron approach
- ... combine with deformation potential theory
- Slow and anharmonic molecular motions
- Charge transport in polycrystals
- Upscaling NAMD

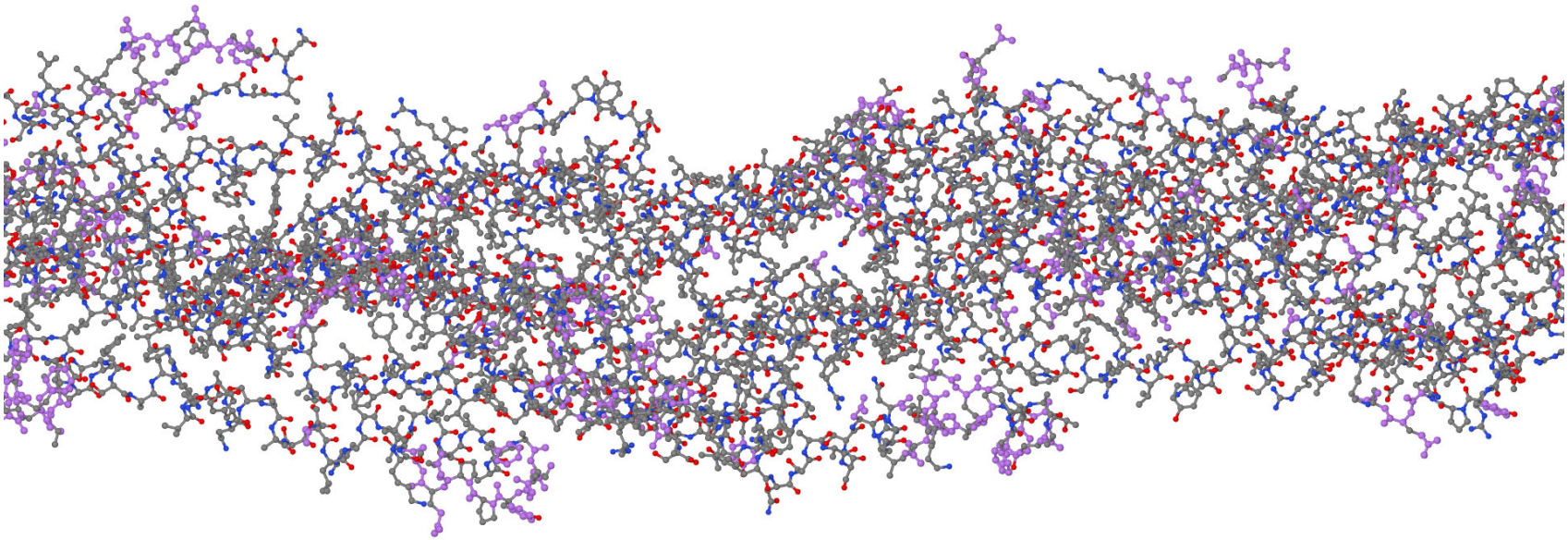
Questions

1. Calculated by the above approach mobilities are systematically higher than the observed ones. Explain this trend.

2. Is the polaron shown at the beginning of this section large or small?

3. For ultrashort distances between electrodes the charge transport is qualitatively different. Explain.

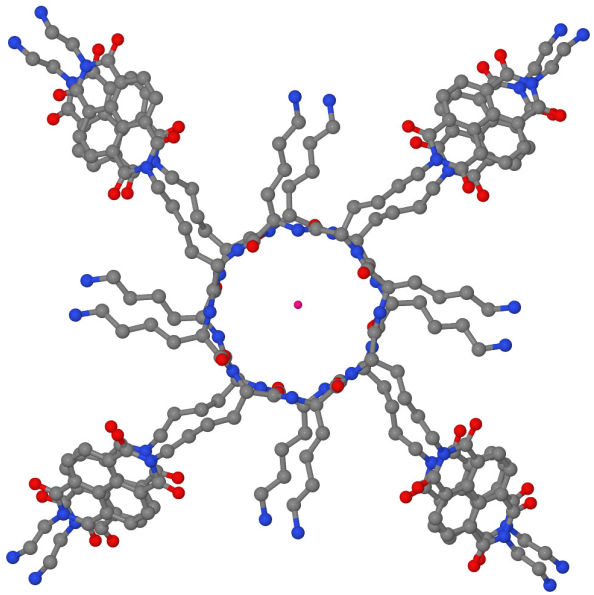
Electronic coarse-graining

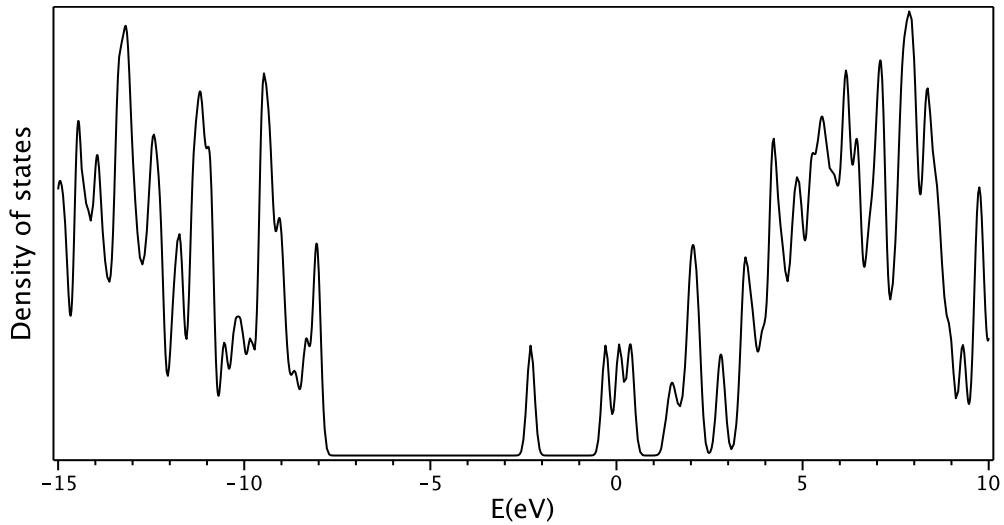


17k atoms, 50k valence electrons $\Longrightarrow$ $\sim$50k 'frontier' MOs

Do we need all of them to describe a particular phenomenon?

Electronic coarse-graining





Which orbitals are important for

- light absorption
- electron transport
- hole transport
- protonation
- structural changes

Coarse-graining: tight binding Hamiltonian

(mean field approximation for electrons, you can add explicit ee-interaction later)

$$\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j$$

here i, j enumerate coarse-grained sites, c_i describe quasiparticles (electrons, holes, excitons[1] etc.)

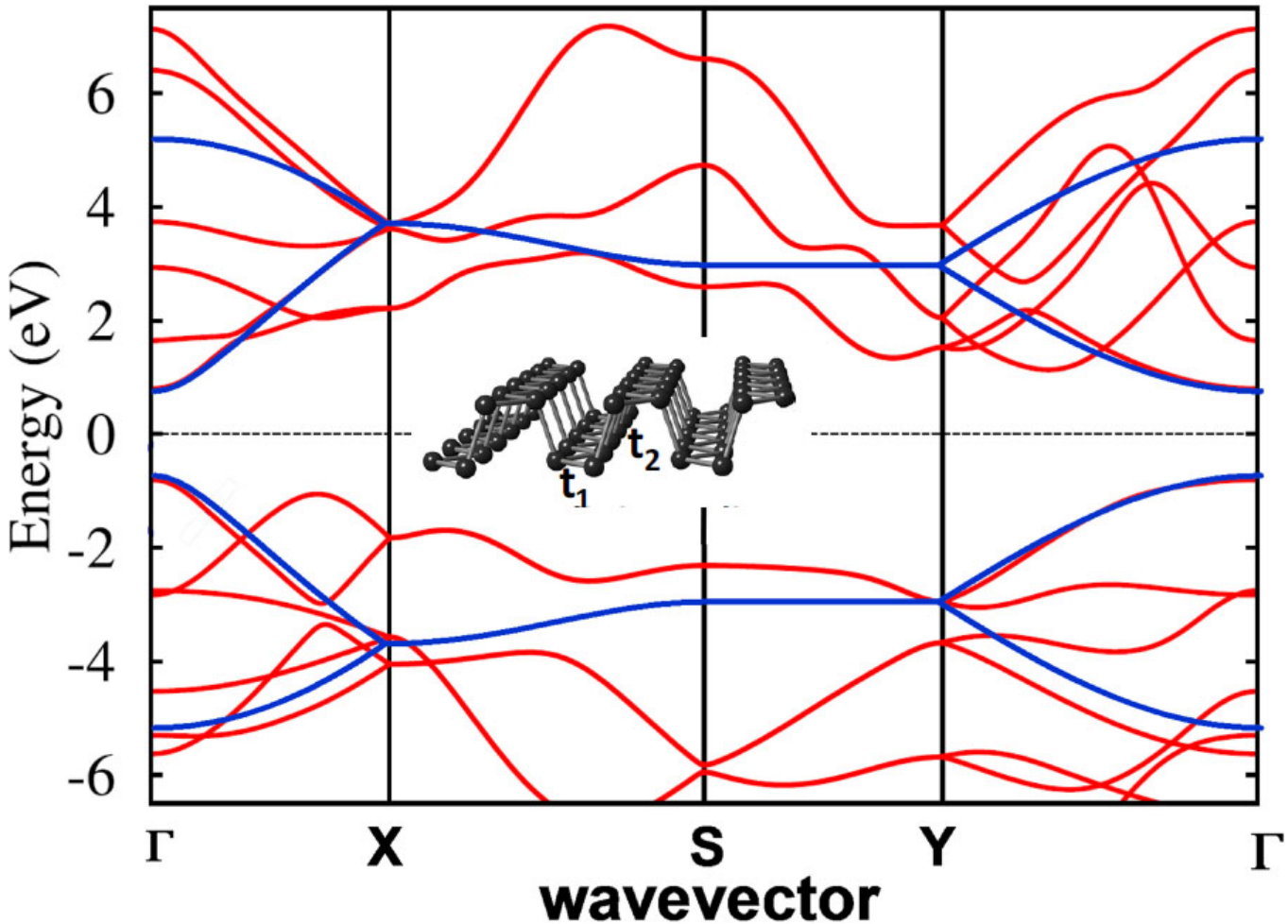
$$H_{ij}^{1p} = \delta_{ij}\varepsilon_i + (1 - \delta_{ij})t_{ij},$$

ε_i – onsite energy, t_{ij} – transfer integral

[1] See e.g. J Phys Chem C 117, 4920 (2013)

Approach 1: Fitting tight binding Hamiltonian

PRB 95, 075436 (2017)



Great for simple systems, not readily extendable to complex ones

Approach 2: Use localized molecular orbitals

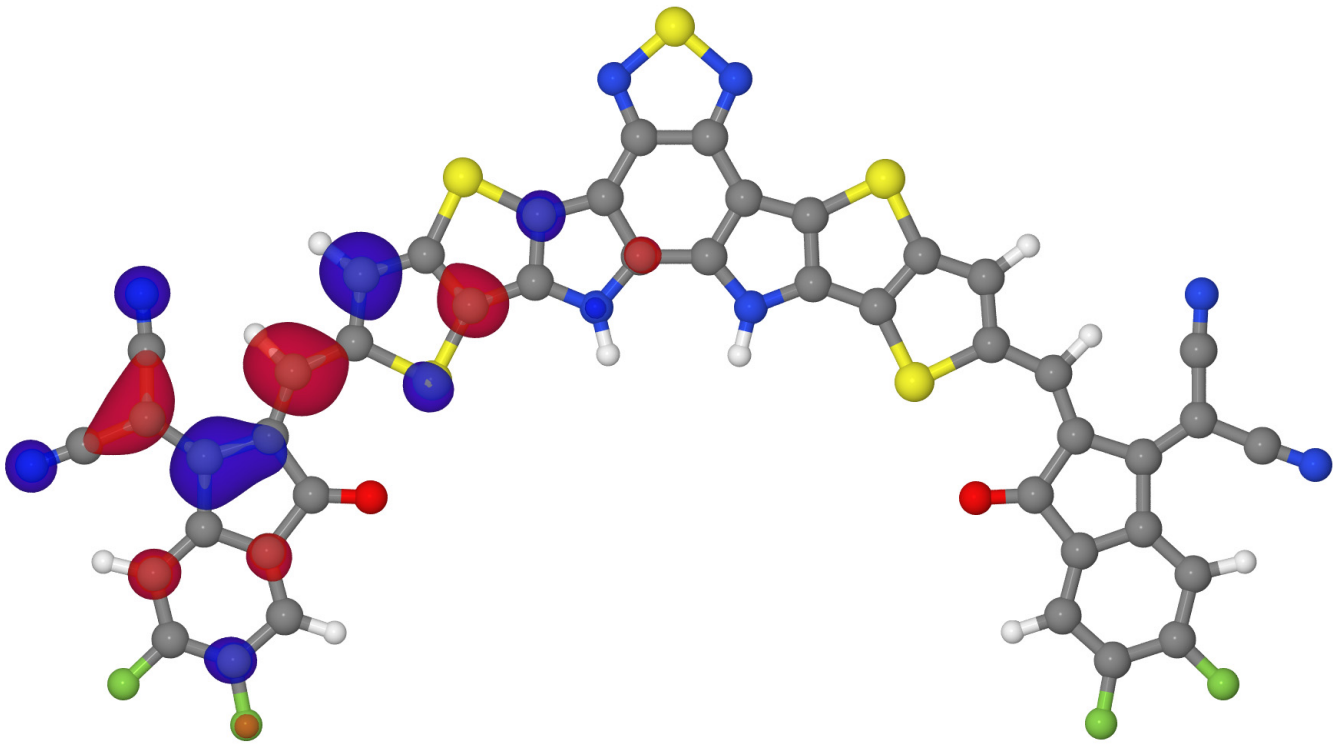
- Use localized MO to get SCF
  - MOZYME code in MOPAC
  - fragmentation methods Chem Rev 112, 632 (2012)
- Get SCF and then localize
  - many localization algorithms Acc Chem Res 47, 2758 (2014)

$\Longrightarrow$ Obtain overlap and Fock (H^{1p}) matrices in LMO basis. Then do coarse-graining: select active space and renormalize H^{1p} by eliminating inactive LMOs.

Easy to do for small-molecule solids: 'site' = molecule

Nontrivial coarse-graining: Large molecules

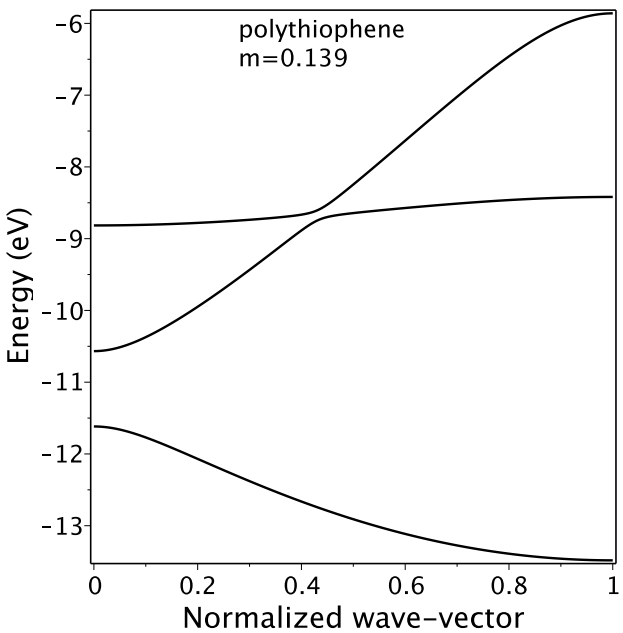
(in particular novel non-fullerene acceptors for high-efficiency solar cells)

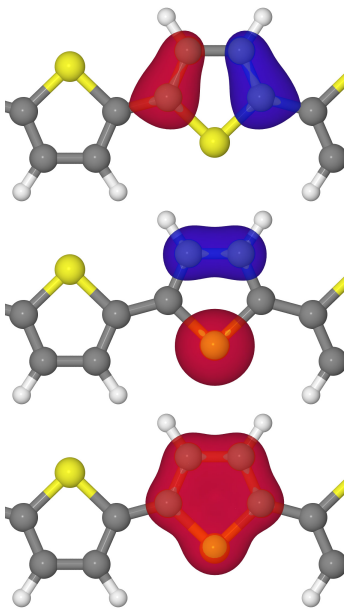


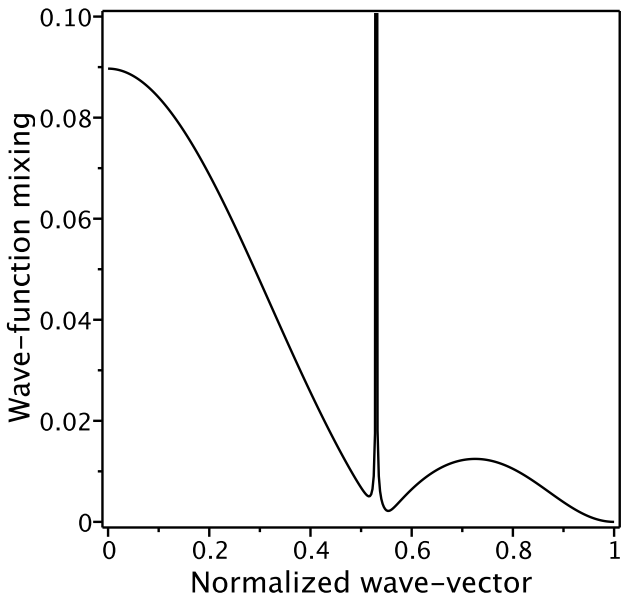
Chem Mater 33, 966 (2021)

Nontrivial coarse-graining: Conjugated polymers

Problem: There are no static well-separated coarse-graining sites
Solution, electronic part: Use of localized molecular orbitals $\rightarrow$ get coarse grained tight-binding Hamiltonian

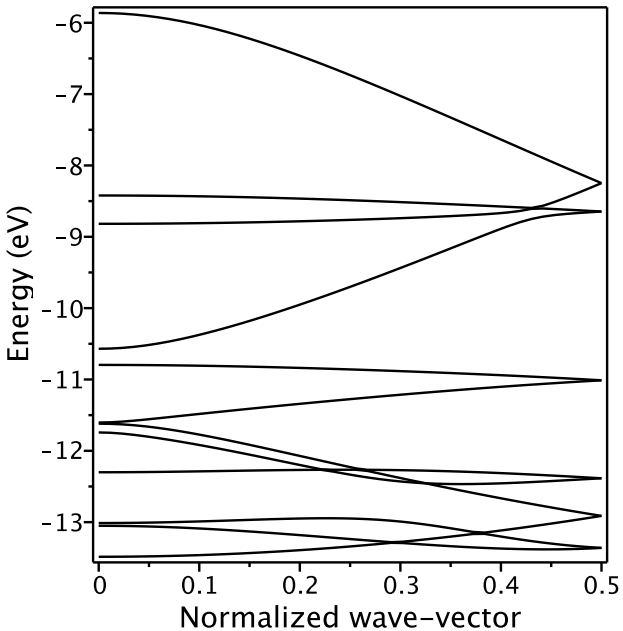


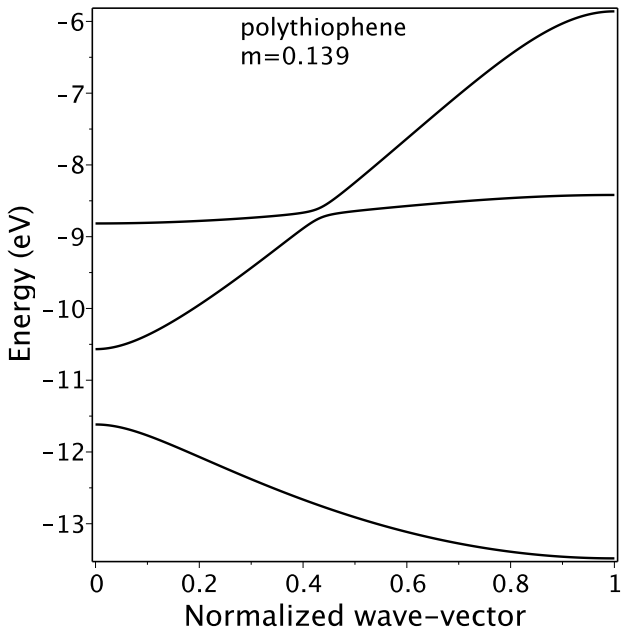


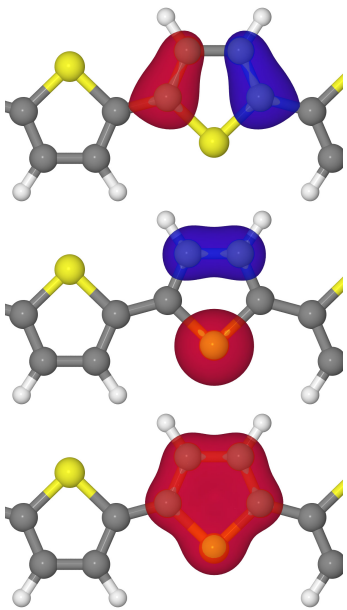


Comparison: full bands vs π-bands

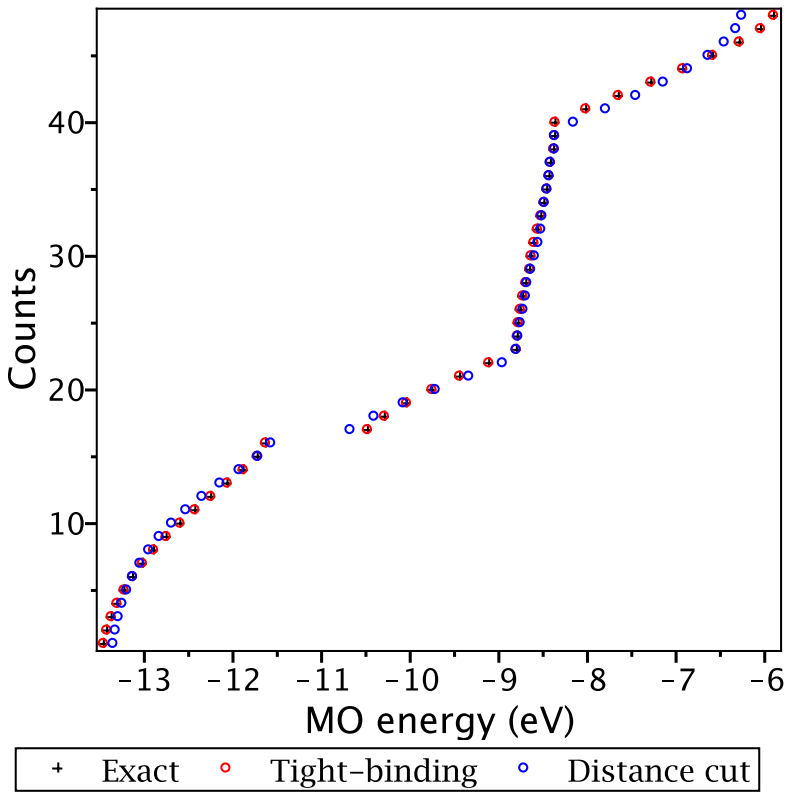
(CAM-B3LYP/6-31G*)

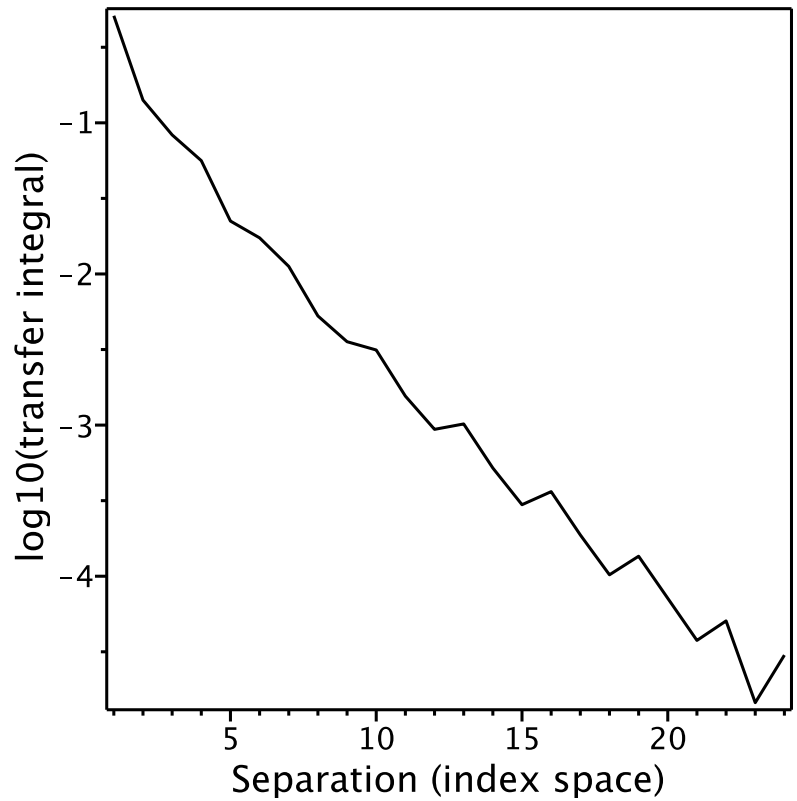






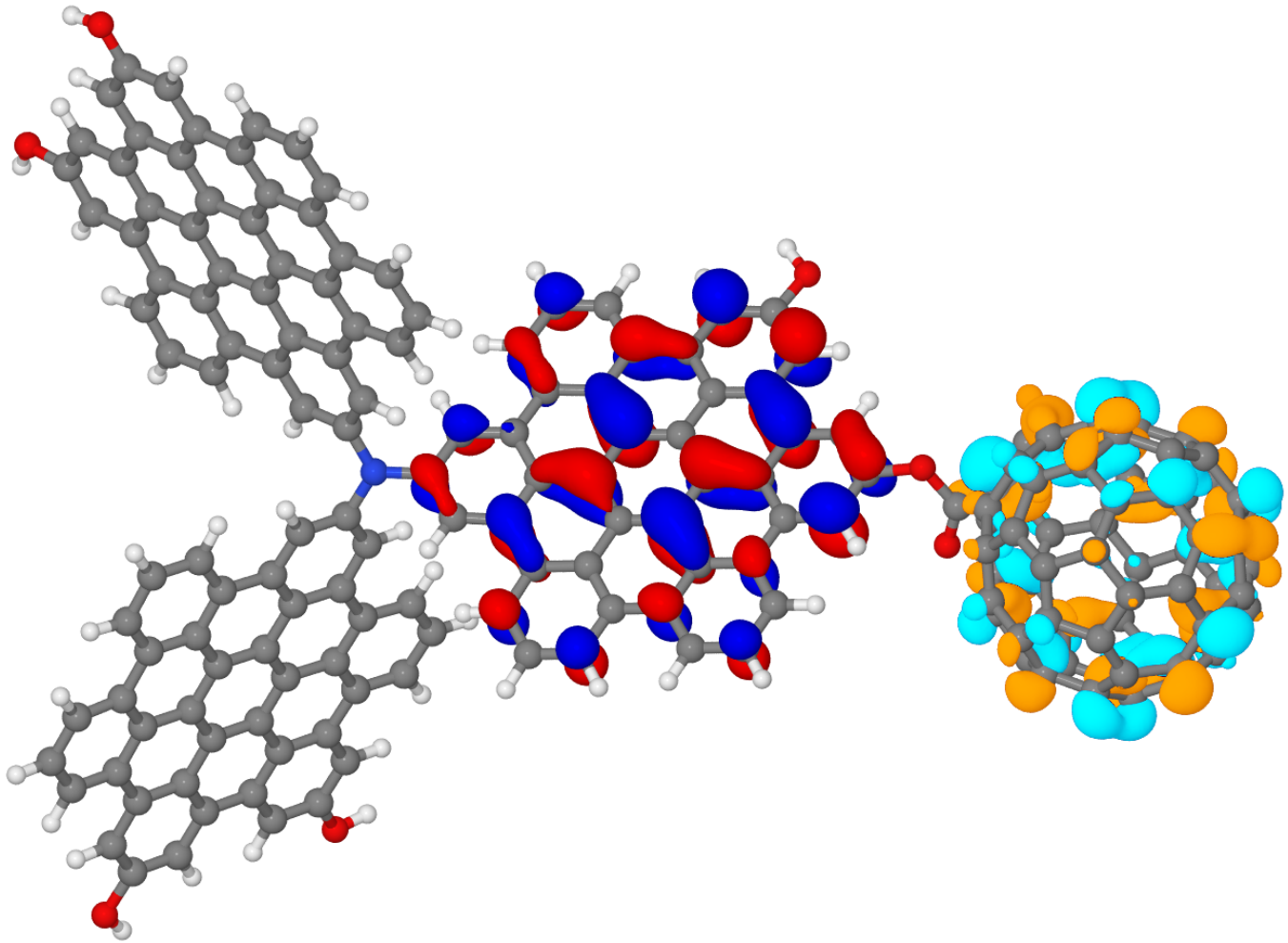
Model reduction: ignore small couplings





Application: charge transfer routes in large molecules

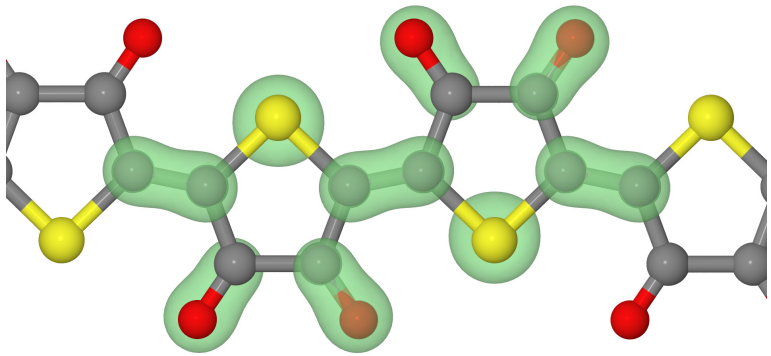
(fixed geometry)

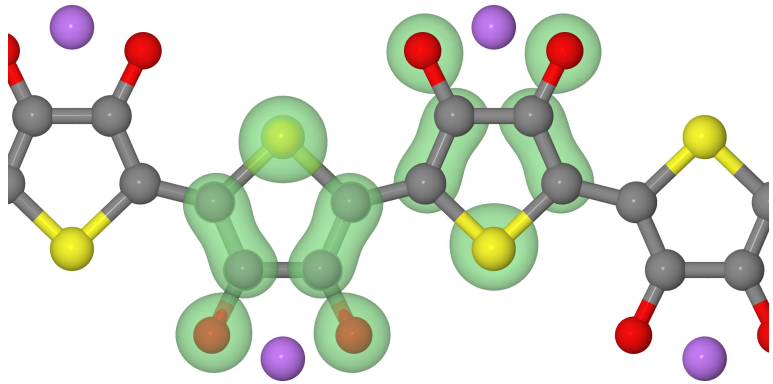


The two localized MO have large coupling and small energy offset

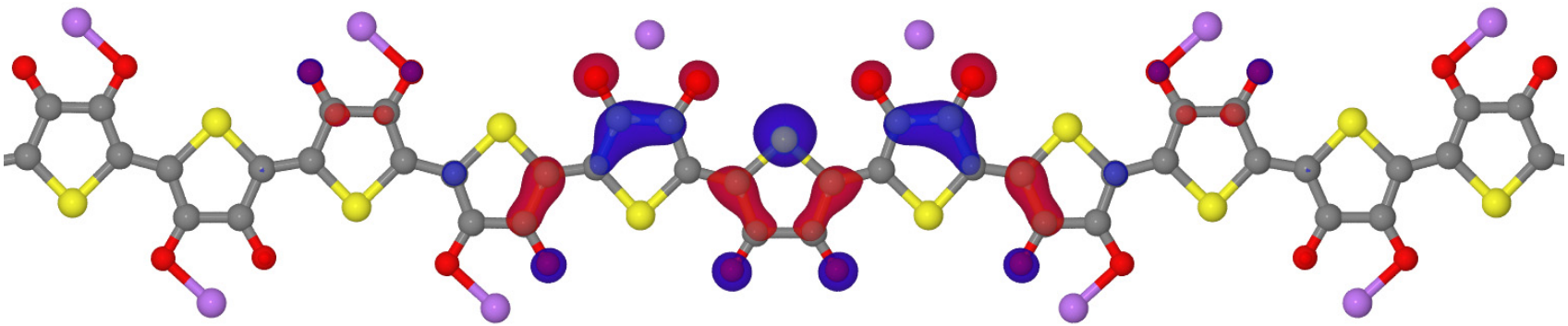
Application: organic Li-ion batteries

Problem: poor electronic conduction





Upon Li-intercalation bonding pattern changes dramatically

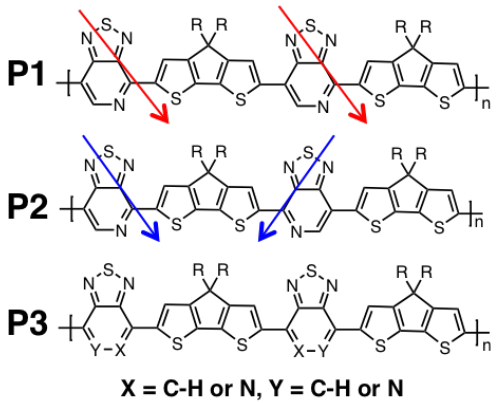


Localized electronic states appear on Li-deficient monomers (-0.5 eV)

Example: Influence of regiochemistry

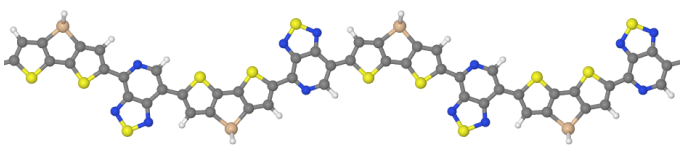
Chem Sci 8, 1146 (2017)

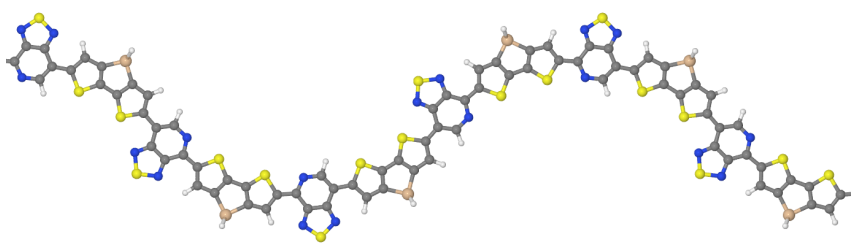
Experiment: L Ying JACS 133, 18538 (2011):



polymer	P1	P2	P3
$E_{HOMO}/E_{LUMO}{}^{a}$ [eV]	−5.07/−3.70	−5.16/−3.70	−5.23/−3.69
$E_g{}^{cvb}$ [eV]	1.37	1.46	1.54
$\lambda_{max}{}^{sol}/\lambda_{max}{}^{filmsc}$ [nm]	930/920	885/885	880/870
$E_g{}^{optd}$ [eV]	1.09	1.12	1.15
$\mu_{sat}{}^{e}$ [$cm^2\ V^{-1}\ s^{-1}$]	0.4 (0.3)	0.6 (0.5)	0.005 (0.005)
I_{on}/I_{off}	2×10^3	2×10^4	1×10^4

Theory: Electronic structure of ideal polymer is insensitive to regiochemistry $\Longrightarrow$ The difference is in intramolecular conformations influencing also intermolecular packing





Resources

- List of references
- A Koehler, H Bassler, Electronic Processes in Organic Semiconductors: An Introduction (Wiley, 2015) *in library*
- A Zhugayevych, S Tretiak, Theoretical Description of Structural and Electronic Properties of Organic Photovoltaic Materials, Annu Rev Phys Chem 66, 305 (2015) pdf