

Organic Materials for Energy and Optoelectronics

# Lecture on Modeling of organic semiconductors for non-theoreticians

Andriy Zhugayevych

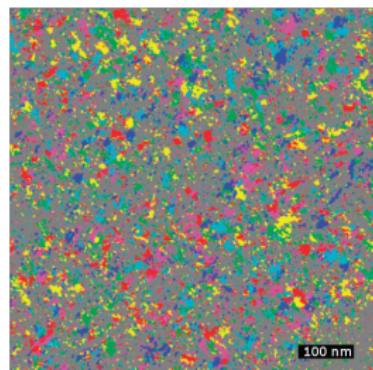
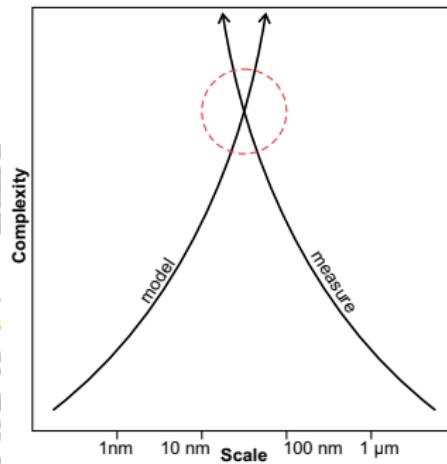
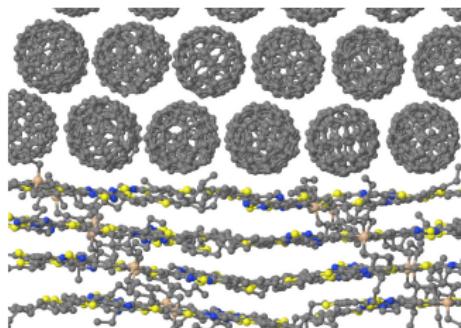
*February 18, 2022*

## *Outline*

- Introduction
- Overview of approaches
- Illustrative examples

# Why modeling is important

## Scale gap problem

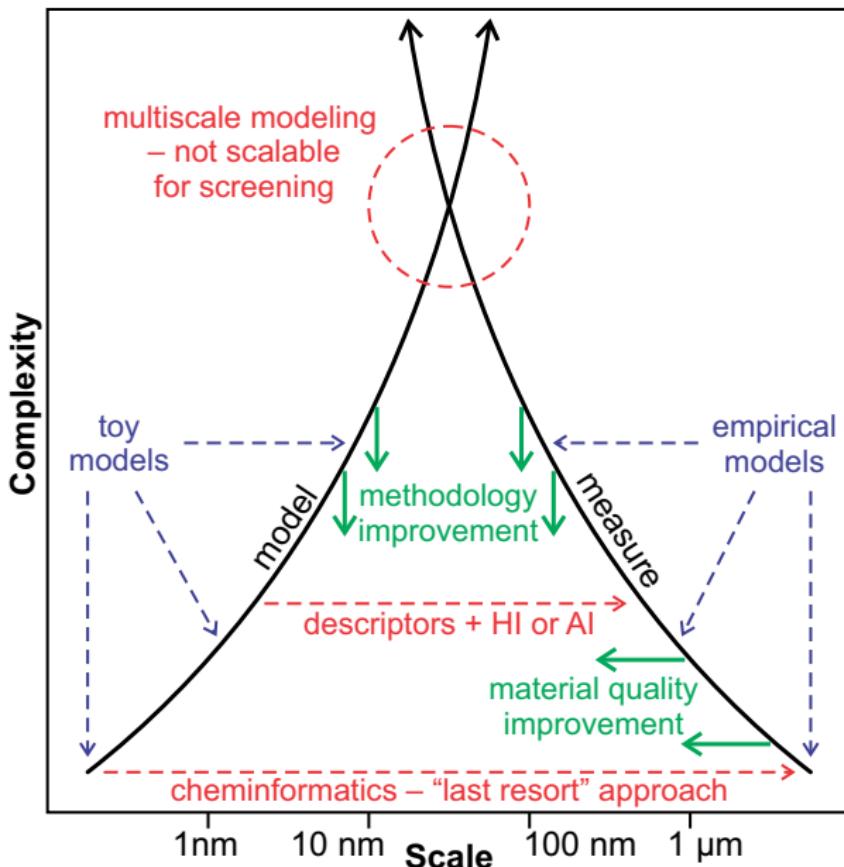


## Expected learning outcomes

(for non-theoreticians)

- Ability to communicate with computational materials scientists efficiently and constructively
- Ability to understand computational results (from articles, collaborators, databases), their reliability, and relation to measurements
- Understanding of what can be modeled at what level of accuracy
- Basic knowledge of computational approaches
- Basic skills in analysis of raw computational results (Lab)

# Bridging the scale gap



# Computational approaches

- First-principle modeling
  - ▶ Coupled clusters
  - ▶ Density functional theory (DFT)
  - ▶ Semiempirical methods
  - ▶ Molecular dynamics with empirical potentials
  - ▶ Multiscale modeling
- Empirical modeling
  - ▶ Kinetic Monte Carlo (KMC)
  - ▶ Continuum models
- Materials data science
  - ▶ Cheminformatics
  - ▶ Descriptors
  - ▶ Machine Learning (ML)

# What can be modeled from first principles

(no experimental data are required)

- Almost any property of isolated molecules  
(in vacuum or in solution)
- Complex response of simple molecular systems  
(e.g. pump-probe)
- Electronic and vibrational spectra, XPS, NMR etc
- Crystal structure, sampling of amorphous structures
- Charge carrier mobility

## Questions

1. How many  $\pi$ -orbitals are there per transition metal atom?
2. What if we replace some C atoms by Si and N by P – will we get  $\pi$ -conjugated system?

## Why there is a separate lecture on organic materials

Different classes of materials require different approaches

*Depends on type of chemical bonding and phenomena of interest*

# 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<sup>†</sup> – consider nonadiabatic processes
- Complex multiscale morphology (up to 100 nm) – scale gap<sup>††</sup>
- Complex device structure – multiscale multi-material modeling
- Large repeating unit (10s-100s of atoms) – no high level methods

⇒ *Brute force (material-nonspecific) approach is rarely used*

To model them efficiently one has to take advantage of

- Only one  $\pi$ -orbital per  $\pi$ -conjugated atom
- Consist of small rigid closed- $\pi$ -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\*

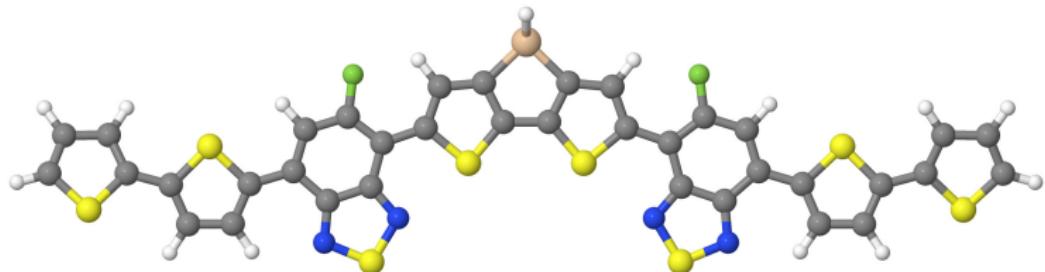
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<sup>†</sup> Compared to electronic bandwidth

<sup>††</sup> What is measured is not what is modeled

## Example: molecular solids and polymers

(quasi-1D  $\pi$ -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

$\Rightarrow$  Success of simple force fields

- The  $\pi$ -conjugated system of each block is closed-shell
- Inter-block couplings  $\sim 1 \text{ eV} \ll$  band gap of blocks
- Intermolecular couplings  $\sim 0.1 \text{ eV} \ll$  band gap of molecules

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

# Commonly used first-principle methods:

## Density functional theory (DFT)

- Best approximation by molecular orbitals (MO)
- Time-dependent DFT (TDDFT) for excited states
- Dispersion-corrected DFT (DFT-D) for vdW interactions
- Functionals:
  - ▶ PBE – avoid except for PBE-D such as PBE-D3
  - ▶ 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
  - ▶ HSE06 – best available for plain waves
- Basis sets
  - ▶ 6-31G\* – safe choice for organic semiconductors
  - ▶ Def2-TZVP – for high accuracy

*Electronic structure methods are well-benchmarked*

# Commonly used first-principle methods:

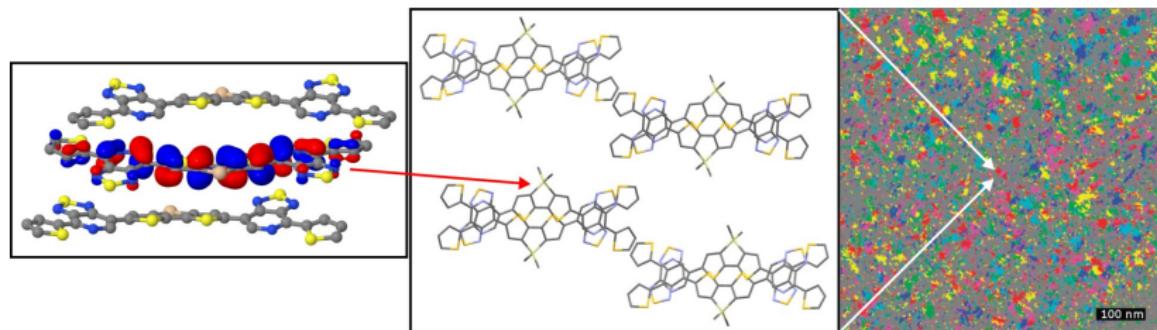
Scalable to thousands of atoms

- Semiempirical – if you need electronic properties
  - ▶ Semiempirical – no accurate parameterization yet
  - ▶ DFTB – very promising but needs to be well parameterized
  - ▶ TB – yes but always requires parameterization
- Empirical potentials – if you do not need electronic properties
  - ▶ Force fields – no accurate parameterization
  - ▶ OPLS – good starting point
  - ▶ ML potentials – under development
- QM+MM – naturally the best (for conjugated systems)

*Parameterization is the main problem*

# First-principles multiscale modeling: bird's eye view

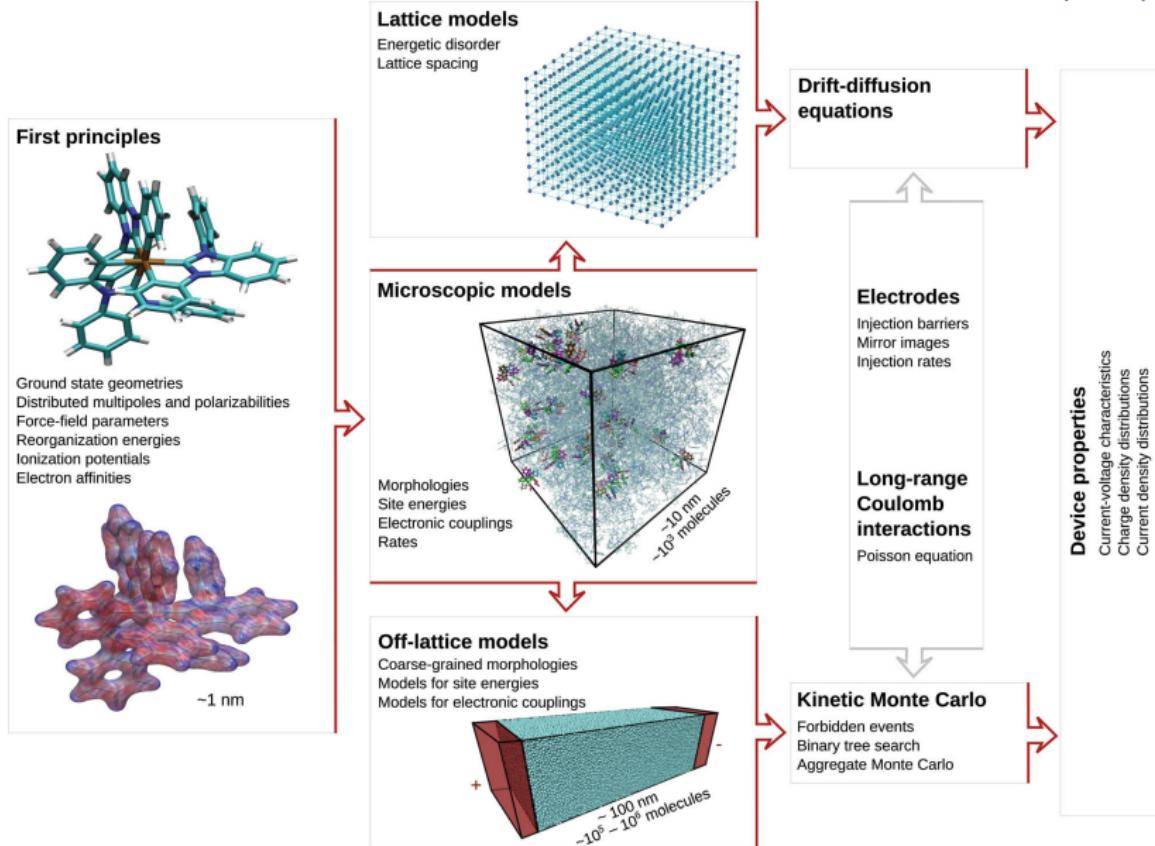
- Combine different approaches on different scales
- Control the accuracy (errors accumulate through the scales)



- 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: 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. Give examples of  $\pi$ -conjugated systems without scale gap problem.

## Structural studies

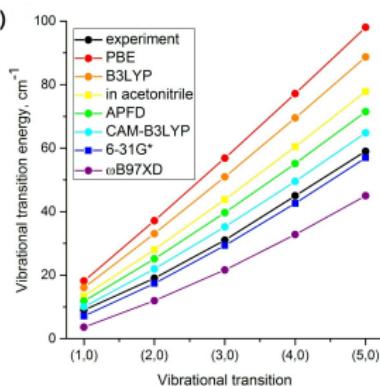
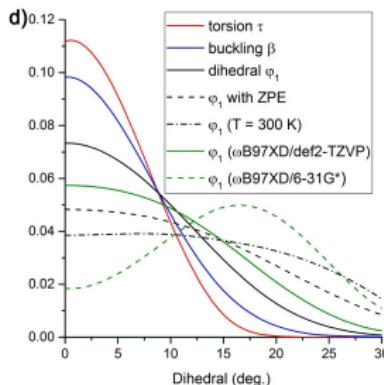
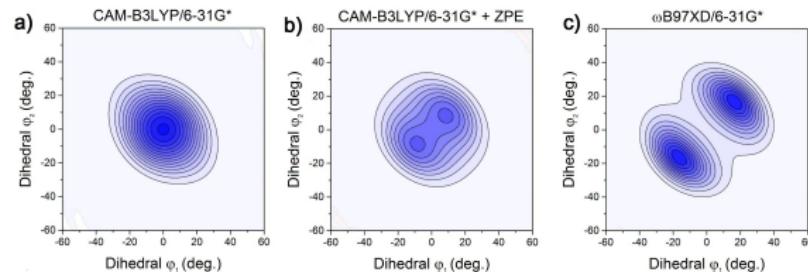
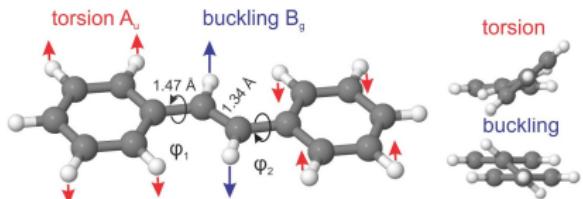
- Refine guessed or measured structure
- Study dependence of structure on parameters
- Establish structure-property relationships
- Predict structure
- Determine or sample conformations and polymorphs

### Structural properties sensitive to the method

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

# BLA and dihedrals

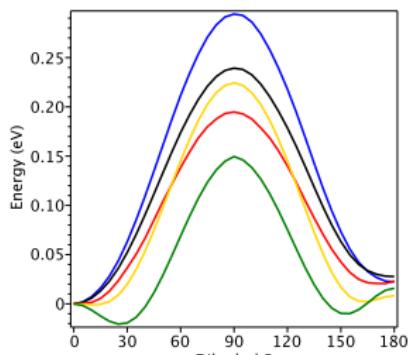
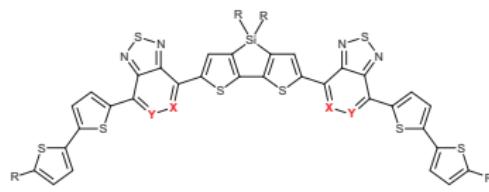
J Phys Chem Lett 10, 3232 (2019)



*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. |
| <b>planarized conjugated base</b>   |       |         |         |
| B3LYP                               |       | 2       | 2       |
| CAM-B3LYP                           |       | 9       | 9       |
| ωB97X                               |       | 17      | 17      |
| MP2                                 |       | 96      | ...     |
| MM3                                 |       | 130     | 251     |
| <b>dihedrals #3,4 are flipped</b>   |       |         |         |
| ωB97X                               |       | 119     | 38      |
| MP2                                 |       | 123     | ...     |
| CAM-B3LYP                           |       | 129     | 128     |
| B3LYP                               |       | 132     | 34      |
| MM3                                 |       | 132     | 21      |
| ωB97X                               | clf   | 119     | 22      |
| CAM-B3LYP                           | clf   | 128     | 33      |
| B3LYP                               | clf   | 128     | 19      |
| <b>dihedrals #1,3,4 are flipped</b> |       |         |         |
| ωB97X                               |       | 147     | 65      |
| CAM-B3LYP                           |       | 159     | 105     |
| B3LYP                               |       | 165     | 67      |
| ωB97X                               | clf   | 142     | 242     |
| CAM-B3LYP                           | clf   | 155     | 102     |
| B3LYP                               | clf   | 158     | 64      |
| <b>saddle point for dihedral #3</b> |       |         |         |
| 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  $\sigma_h$  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)

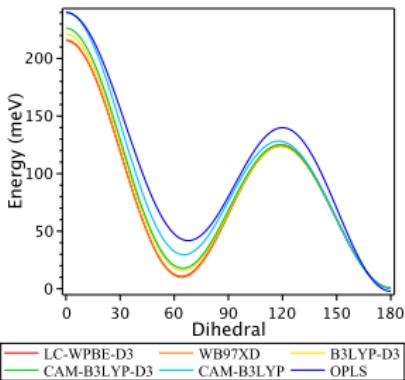
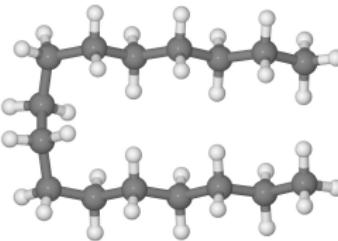


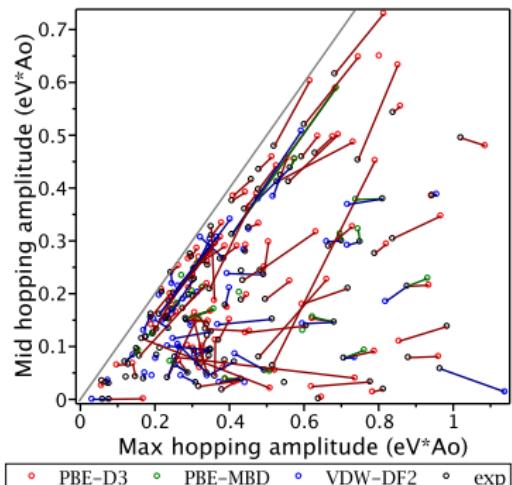
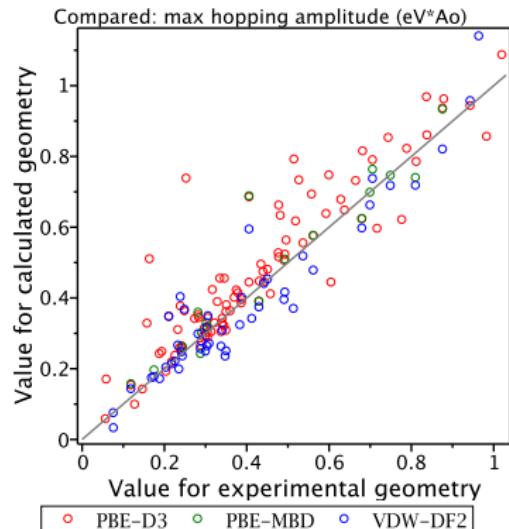
Table S4: Comparison of different methods estimating the relative, hairpin minus trans, energy for a set of polyethylene oligomers (8 to 18 carbons). The geometry is fixed at MP2/cc-pVTZ geometry obtained in Ref.,<sup>2</sup> except for the last block in the table. The entries correspond to energies in meV. Here  $\sigma$  is RMSD with respect to the reference method which is CCSD(T)/cc-pVTZ.<sup>2</sup> “Optimized OPLS” means optimized C-C-C-C dihedral. The supercell size for plane waves is  $40 \times 20 \times 20 \text{ \AA}$ . 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

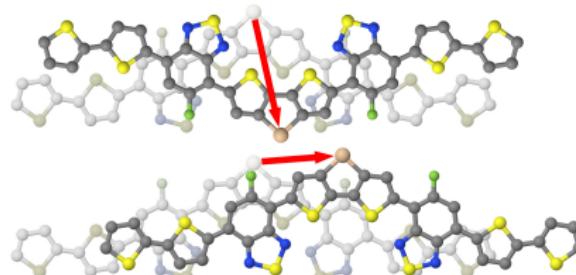
Test set: > 50 crystals, including all high- $\mu$  from Chem Soc Rev 47, 422 (2018)



# Polymerization of molecular crystals

Sci Adv 5, eaau3338 (2019)

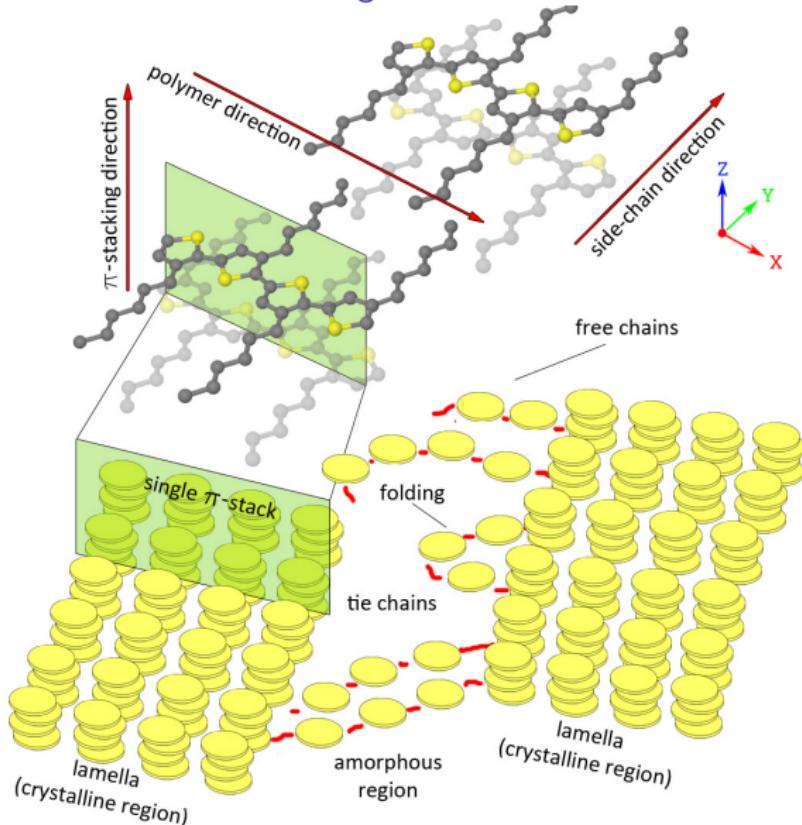
- DFT-D correctly predicts relative energy of polymorphs for small-molecule crystals (TCNQ, indigo, rubrene)
- Force fields can be used for prescreening (MM3 in [J Phys Chem Lett 5, 2700 \(2014\)](#), OPLS in [J Phys Chem C 122, 9141 \(2018\)](#))
- For large molecules with aliphatic chains kinetic and 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 \(2017\)](#)

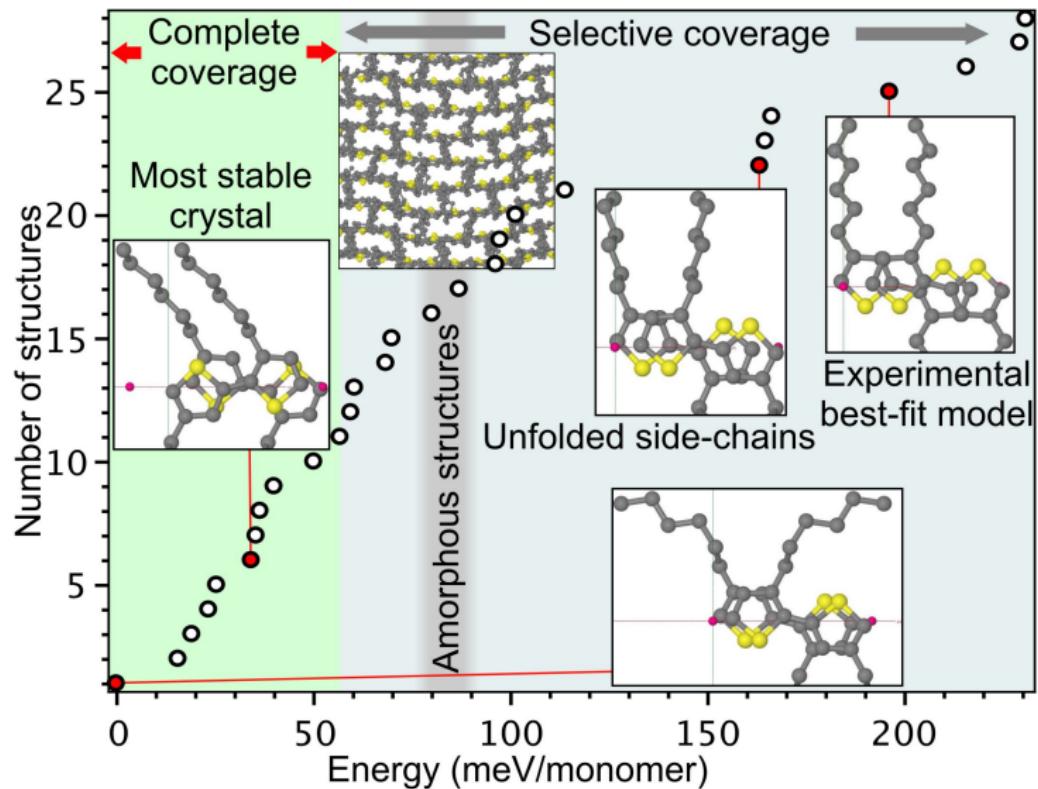
# Polymerization of bulk polymers: example of P3HT

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



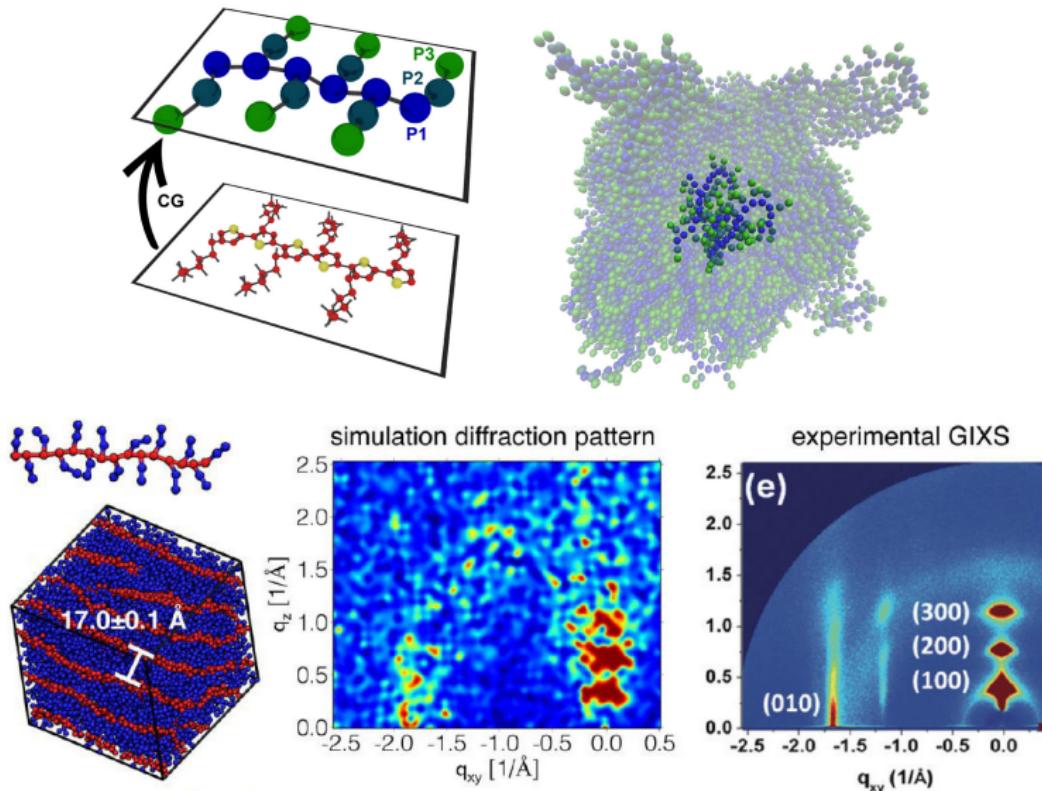
# Polymerization of bulk polymers: example of P3HT

J Phys Chem C 122, 9141 (2018)



# Example: coarse-graining molecular degrees of freedom

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



## 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

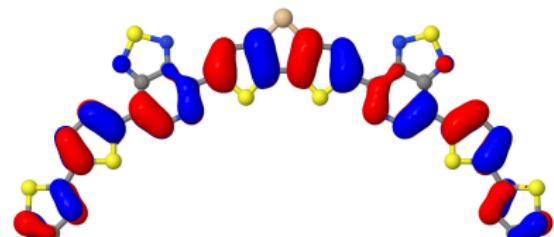
- Wave-function
- Intraband properties (e.g. effective mass)

*Systematic trends with HF content  $\Rightarrow$  use “bracketing” & IP-tuning*

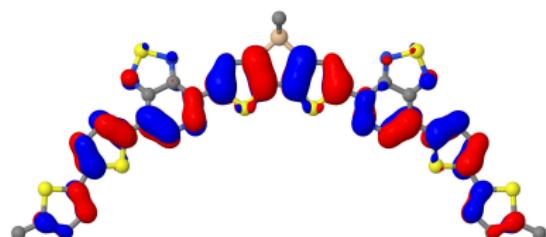
PBE(0) – B3LYP(.2) – HSE06(.25/0), APF(.23), PBE0(.25) –  
– CAM-B3LYP(.19/.65) –  $\omega$ B97X(.16/1)

# Wave-function

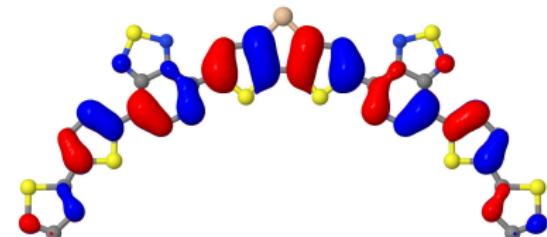
(not sensitive to the method)



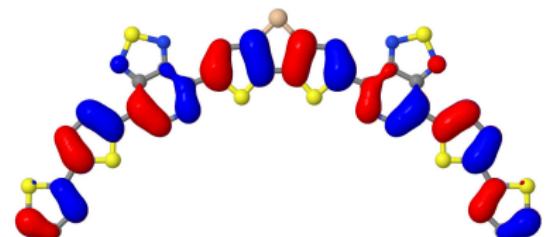
HOMO (CAM-B3LYP)



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 –  $\omega$ B97X

*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,  $\text{IP} = E(N - 1) - E(N) > 0$
- Electron Affinity,  $\text{EA} = E(N) - E(N + 1)$  (usually positive)
- Charge gap = IP-EA
- Absolute electronegativity =  $(\text{IP}+\text{EA})/2$
- 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.

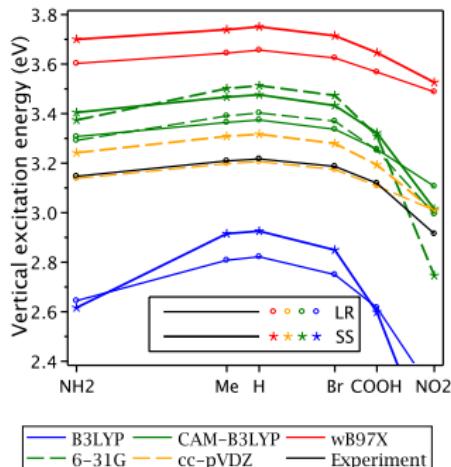
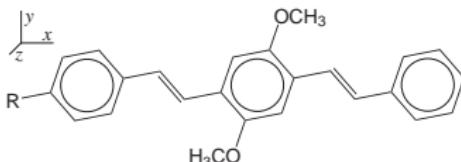
# Calculation of IP/EA

- 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  $\pi$ -conjugated systems
  - ▶ use HOMO/LUMO (+GW)
  - ▶ extrapolate PRB 92, 195134 (2015)
- Relative IP/EA in same conditions – use HOMO/LUMO

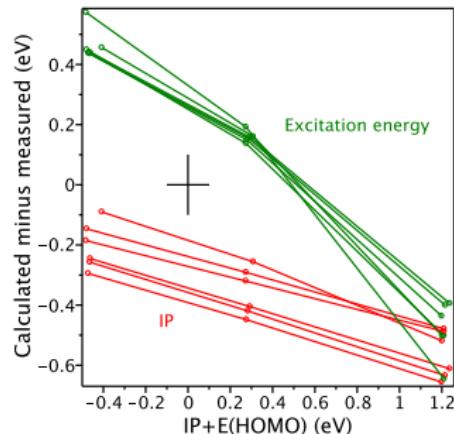
# Koopman's theorem and IP-tuning

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



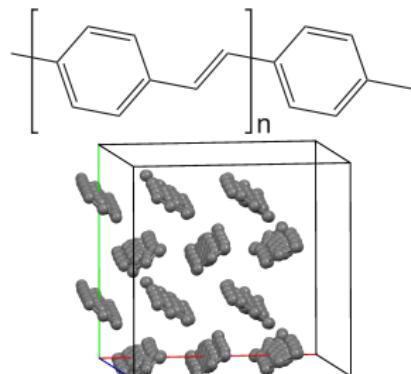
| functional    | $IP + E_{HOMO}$ (eV) |
|---------------|----------------------|
| B3LYP         | +1.2                 |
| CAM-B3LYP     | +0.3                 |
| $\omega$ B97X | -0.4                 |



# Optical gap and excitations

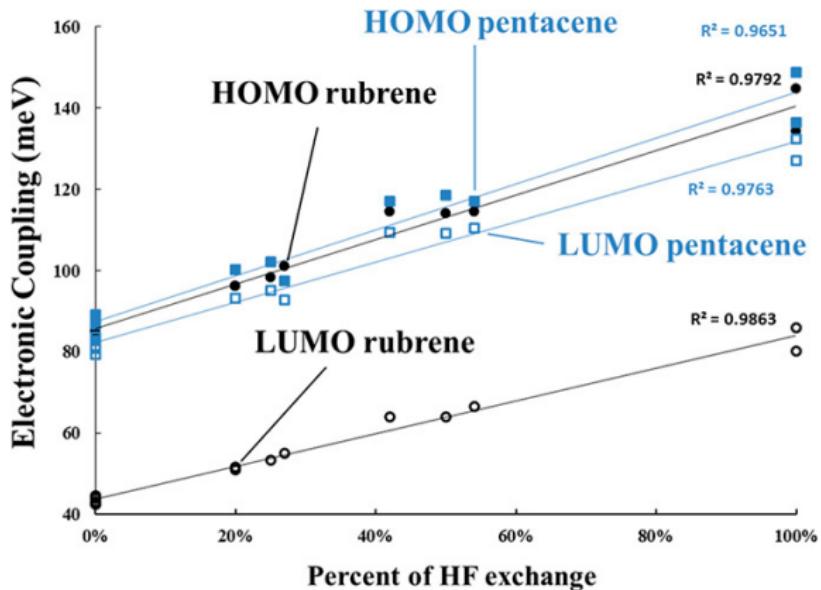
- Molecules – by TDDFT or GW(+BSE)
- Molecular solids, multimers – vibronic effects are important
- Extended  $\pi$ -conjugated systems – as solid in PBC
- Relative gap in same conditions – use HOMO-LUMO gap

|            | 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

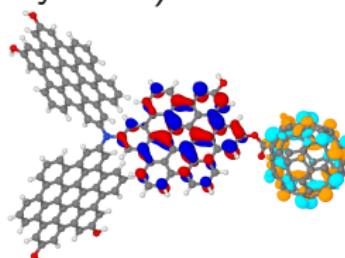
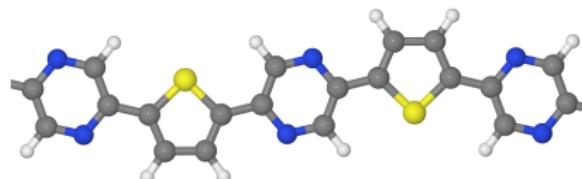
J Phys Chem Lett 4, 919 (2013)



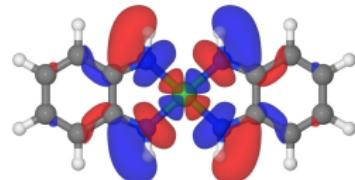
# Small-gap systems

(very sensitive to the method)

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



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



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

# 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  $\Rightarrow$

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

here  $\varepsilon$  – electronic level,  $b_{\alpha}$  – normal modes,  $g_{\alpha}$  – vibronic (electron-phonon) couplings,  $S_{\alpha} = g_{\alpha}^2$  – Huang–Rhys factors

Solution:

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

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

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

## Vibrationally resolved spectra: transition spectral density

Absorption/emission intensity:

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

Transition spectral density:

$$\sigma(E) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \hat{\sigma}(t) e^{itE/\hbar} dt$$

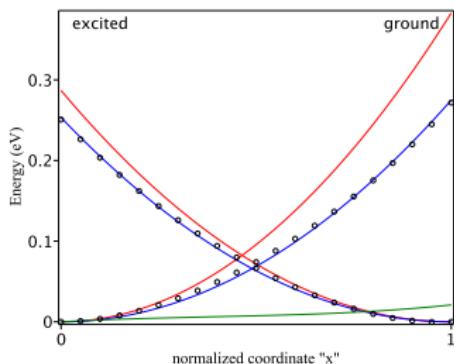
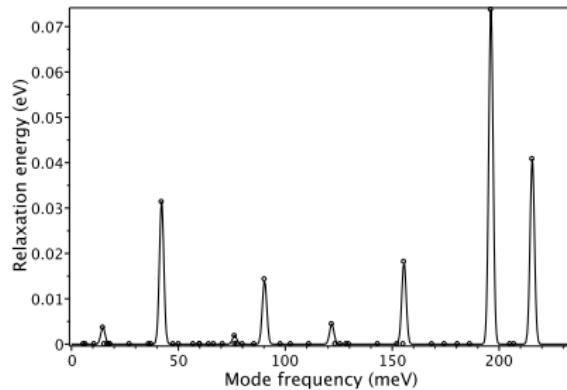
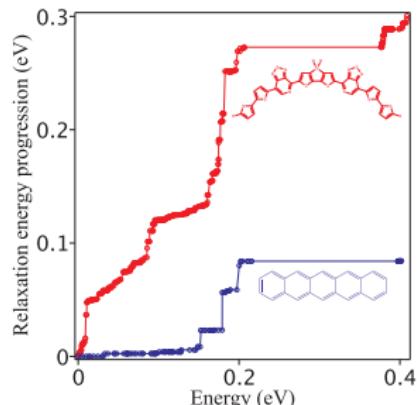
where the phonon correlator

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

here  $\lambda'$  is reorganization energy due to classical modes and  $\sigma^2$  is an inhomogeneous broadening

# Calculating vibronic couplings

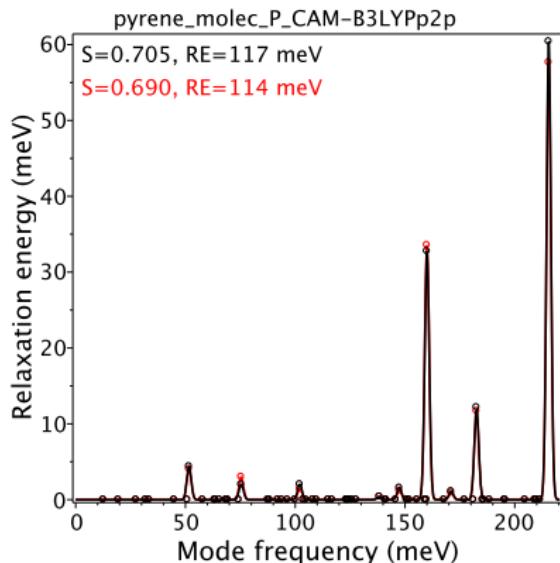
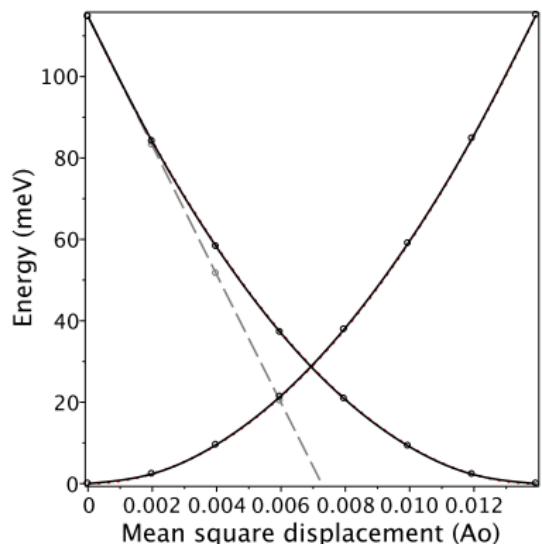
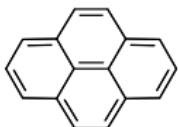
- Get two relaxed geometries: for zero and one quasiparticle at site
- Project atomic displacement onto normal modes  $\xi_\alpha$ , then  $g_\alpha = -\frac{\xi_\alpha^{(0)}}{\sqrt{2}}$
- Rescale  $g$  and  $\omega$  for weak anharmonic effects



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

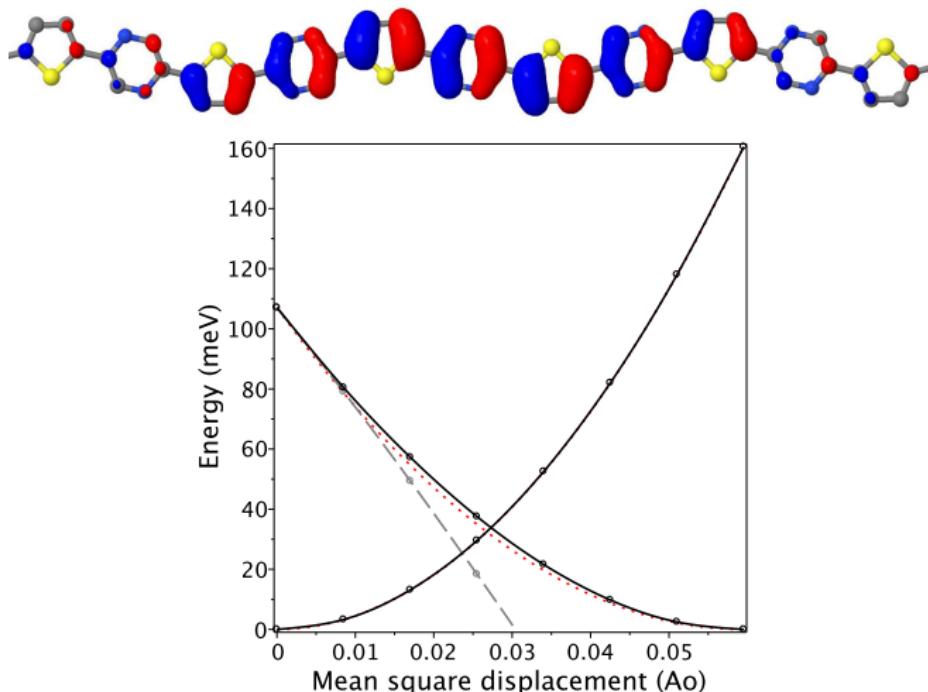
# Accuracy of displaced harmonic oscillator approximation

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



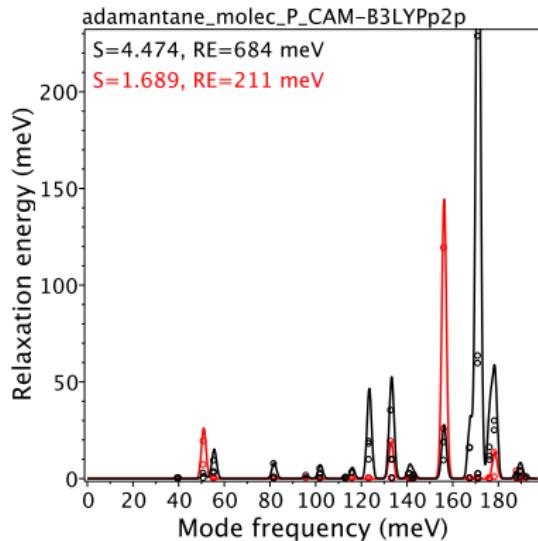
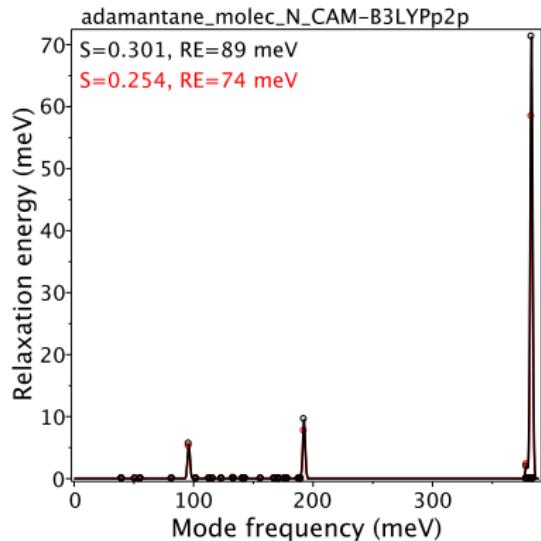
# Accuracy of displaced harmonic oscillator approximation

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



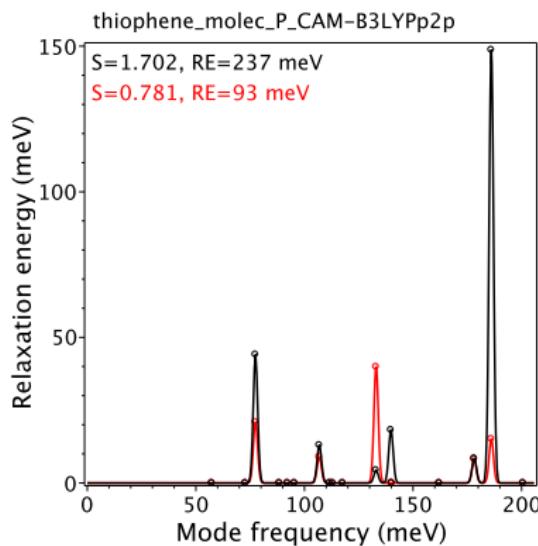
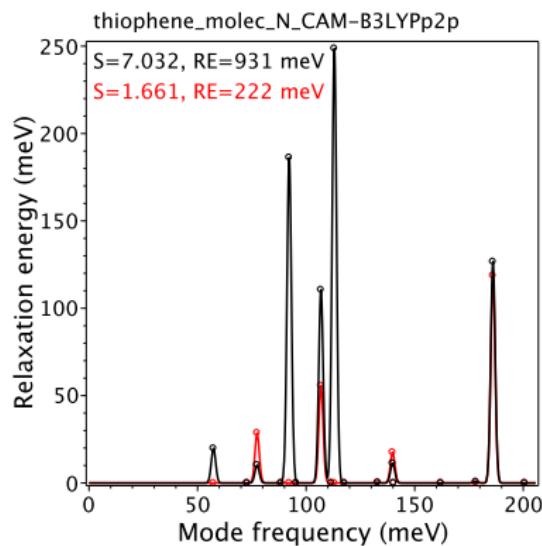
# Accuracy of displaced harmonic oscillator approximation

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



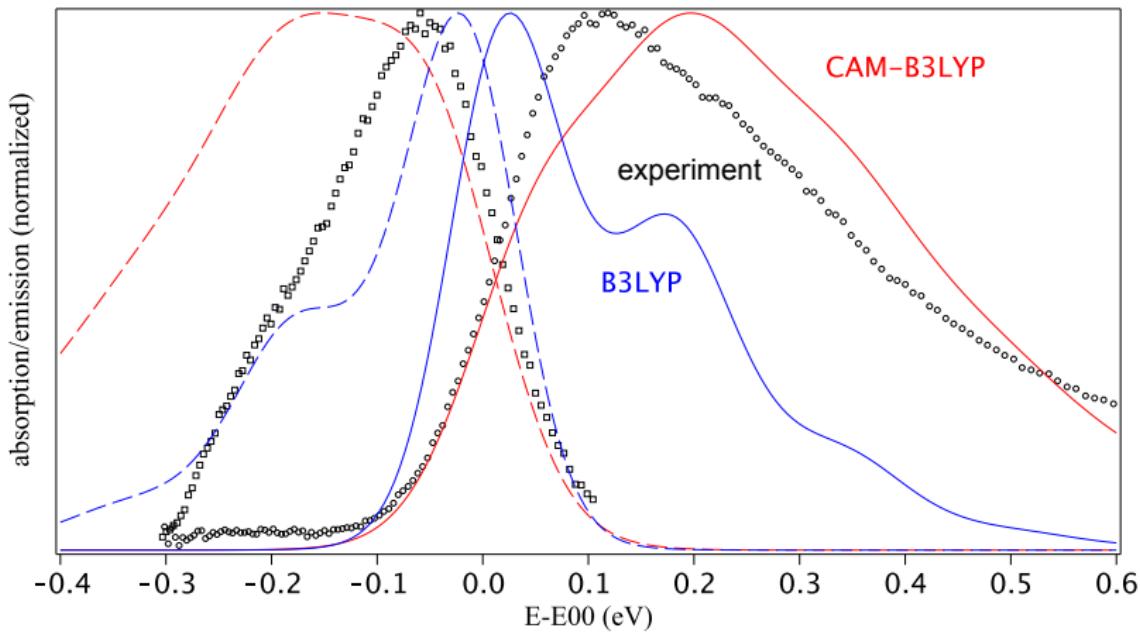
# Accuracy of displaced harmonic oscillator approximation

Thiophene – unsatisfactory – anharmonic PES



# Vibrationally resolved UV-Vis spectra: example

Annu Rev Phys Chem 66, 305 (2015)



B3LYP underestimates vibronic couplings for low- $\omega$  modes  
CAM-B3LYP overestimates vib. couplings for high- $\omega$  modes

# Vibrationally resolved UV-Vis spectra: low-T example

J Chem Phys 116, 8569 (2002)

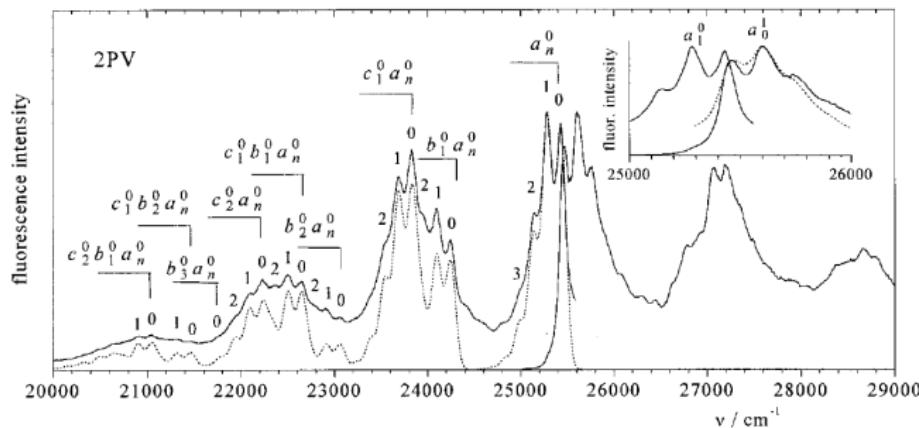
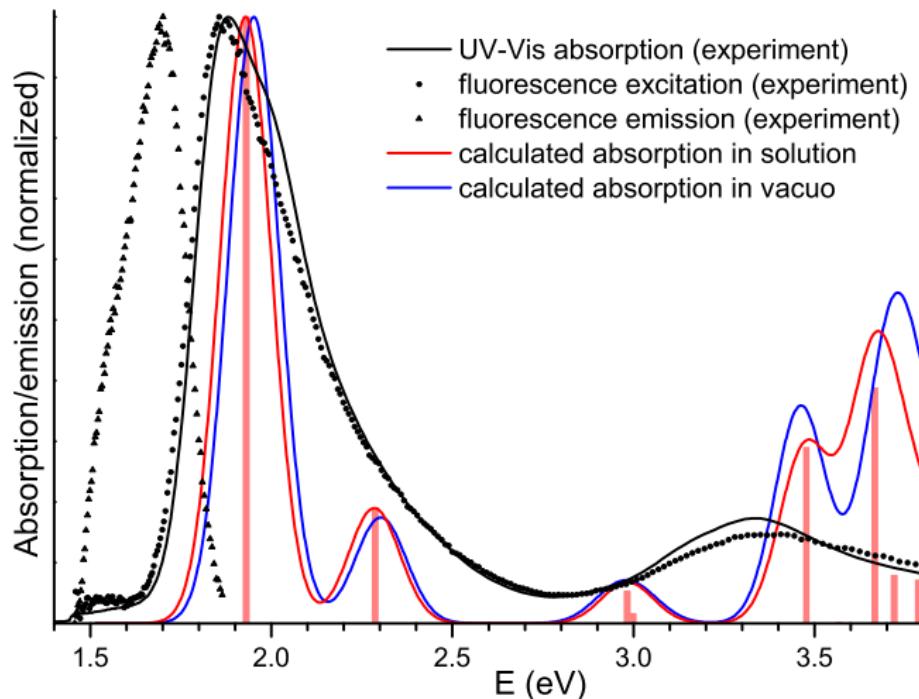


FIG. 7. Fluorescence excitation spectrum (right) and fluorescence emission spectrum (left) of 2PV in tetradecane at 15 K. Solid line: experiment; dashed line: simulation according to Eq. (1) with three modes ( $\nu_a = 150 \text{ cm}^{-1}$ ,  $\nu_b = 1200 \text{ cm}^{-1}$ ,  $\nu_c = 1600 \text{ cm}^{-1}$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

# 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

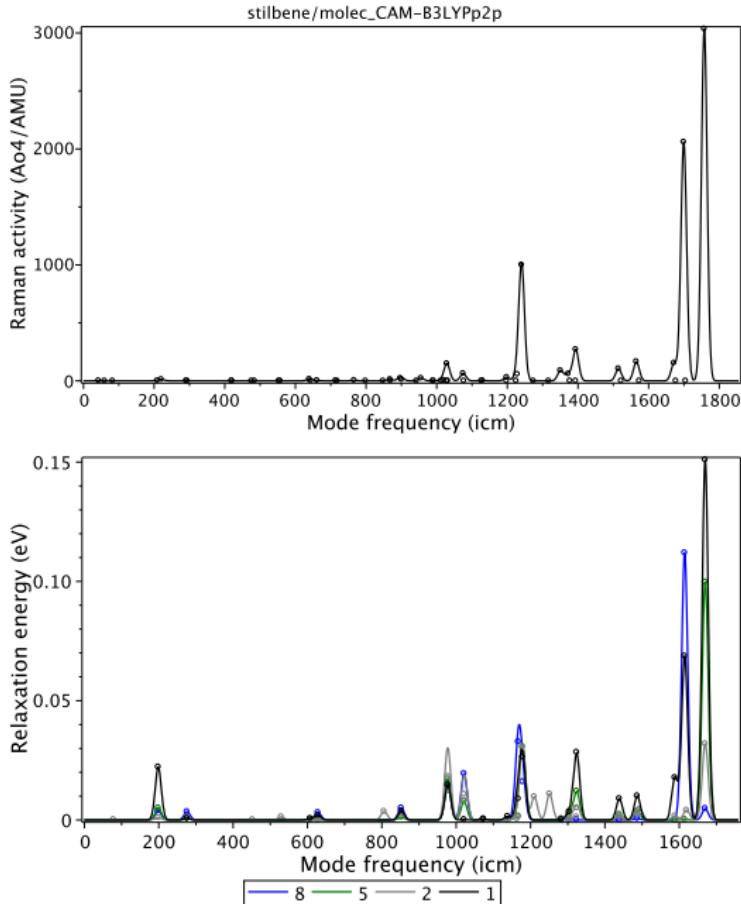
$$I_\omega \sim \lambda \omega^n d^4 / \Delta\Omega^2$$

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)]

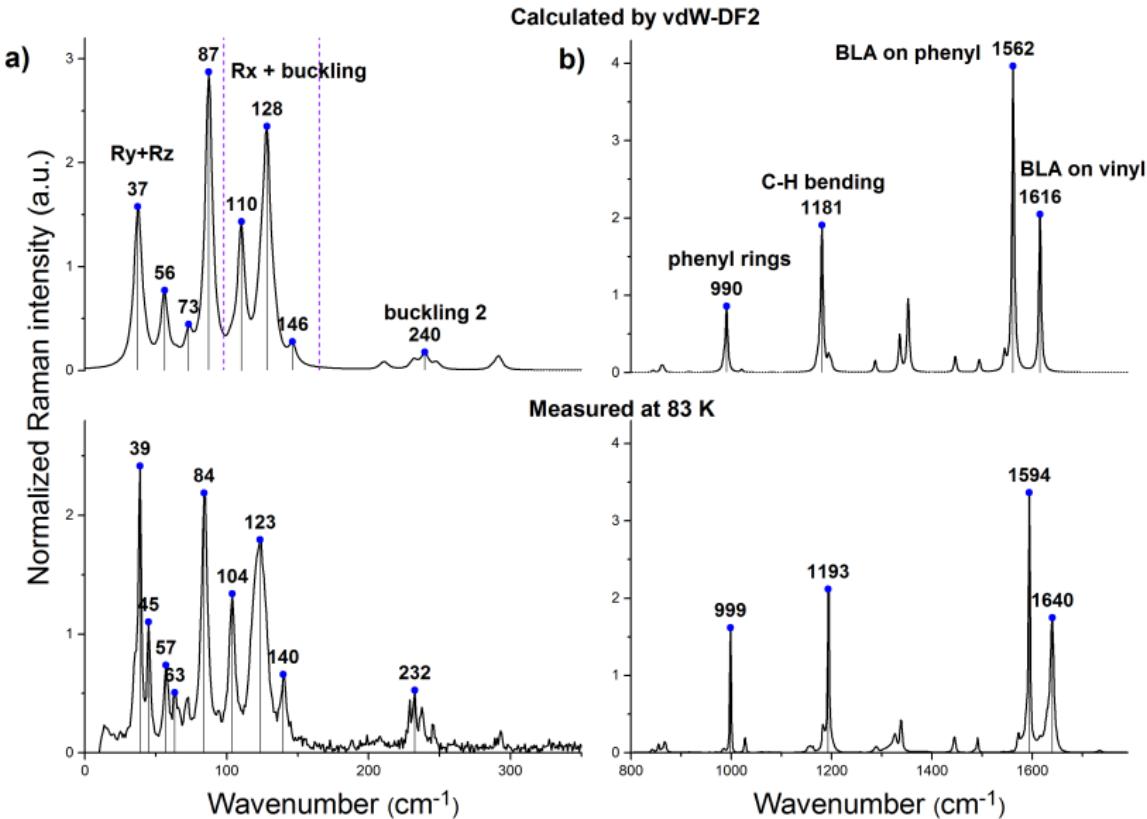
- The main challenge is to calculate vibronic couplings to higher excitations

# Raman spectra of stilbene molecule



# Raman spectra of stilbene crystal

J Phys Chem Lett 10, 3232 (2019)



## 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

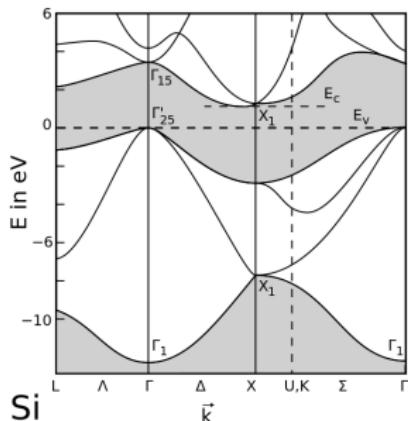
| Scale                                     | Method          | Electronic processes   |
|---|-----------------|--|
| molecular complex<br>(1000 atoms)         | NAMD            | intramolecular relaxation<br>internal conversion<br>intermolecular transfer<br>redox reactions |
| single bulk phase<br>(crystal,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

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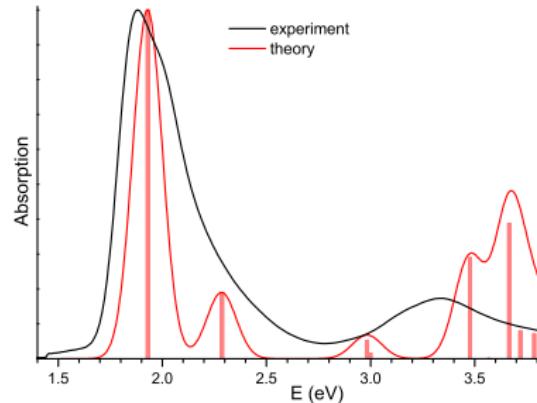
NAMD=nonadiabatic MD, MF=mean field, KMC=kinetic Monte Carlo,  
MD=molecular dynamics, PDE=partial differential equations

# Some definitions: electronic and vibronic bandwidth



Electronic bandwidth

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



Vibronic bandwidth

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

---

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

## Electron-phonon couplings: organic vs inorganic

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

“Inorganic electronics”

$$W_{\text{el}} \gg W_{\text{vib}}$$

(weak el-ph correlations)

⇒ model of free charge carriers scattered by phonons

“Organic electronics”

$$W_{\text{el}} \sim W_{\text{vib}}$$

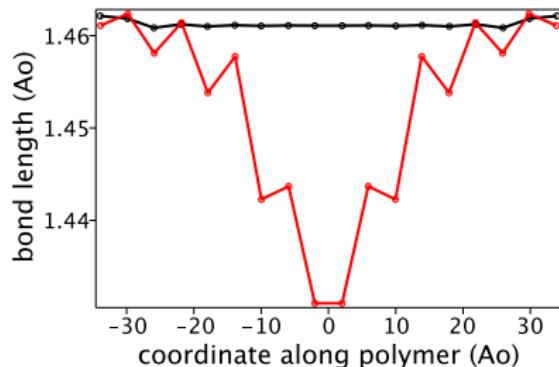
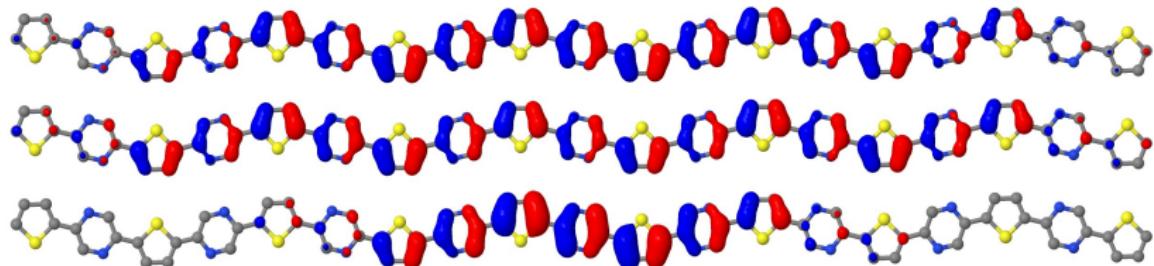
(strong el-ph correlations)

⇒ more complicated models

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

# Polaron formation

(HOMO, cation NO, polaron NO)



# Charge carrier mobility

Basic equations in homogeneous medium

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

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

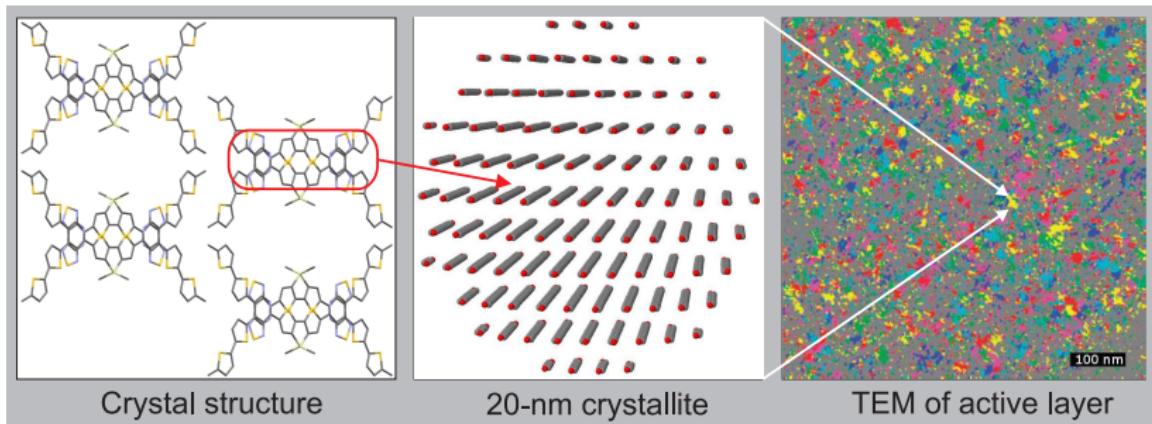
\* Purely electronic and electron-phonon interaction terms are factorized

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

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

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

# 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,  $b_\alpha$  – normal modes or phonons,

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

$\varepsilon_i$  – 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<br>$n_h = 2$<br>$n_e = 0$                  |      |      |
| cation/anion<br>$n_{h/e} = 1$<br>$\Delta n_2 = .07/.06$ |      |      |
| singlet exciton<br>$n_h = 1 + .12$<br>$n_e = 1 - .12$   |      |      |
| triplet exciton<br>$n_h = 1 + .17$<br>$n_e = 1 - .18$   |      |      |

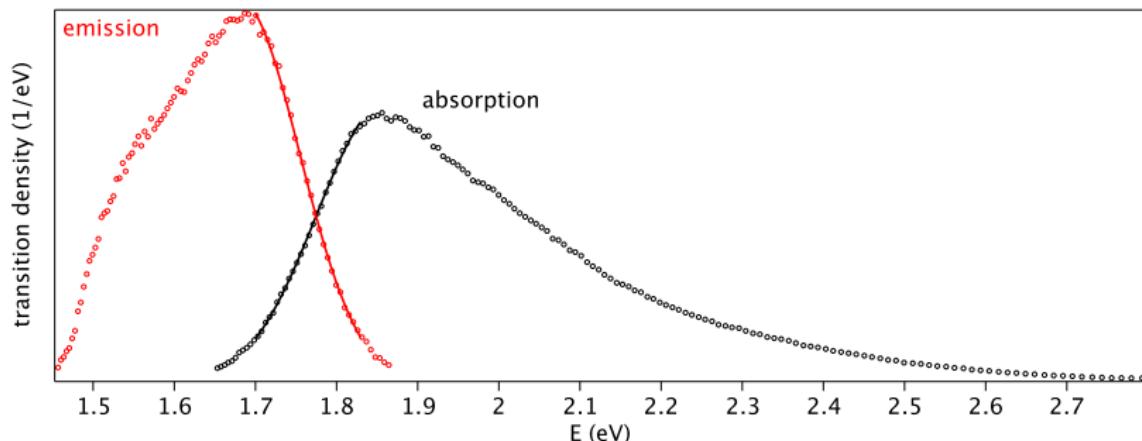
## Excitation=exciton

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

# Solving Holstein–Peierls Hamiltonian: hopping regime

Calculate hopping rates using Fermi's golden rule:

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



## Details: charge/energy transfer in donor-acceptor model

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

Fermi's golden rule:

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

where  $\rho_n$  is initial population and  $\delta$  is spectral lineshape function.

For local electron-phonon couplings (Holstein model)

$$H_{nn'}^{\text{int}} = t \langle n_D | n'_D \rangle \langle n_A | n'_A \rangle, \quad \rho_n = \rho_{n_D}^D \rho_{n_A}^A, \quad E_n = E_{n_D} + E_{n_A},$$

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

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

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

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

whose Fourier transform is correlator between initial and final states.

# Spectral overlap via phonon correlator

$$J_{ij} = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \left\langle e^{itH_i^{\text{vib}}/\hbar} e^{-itH_j^{\text{vib}}/\hbar} \right\rangle dt$$

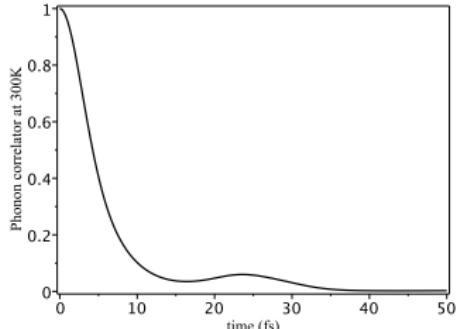
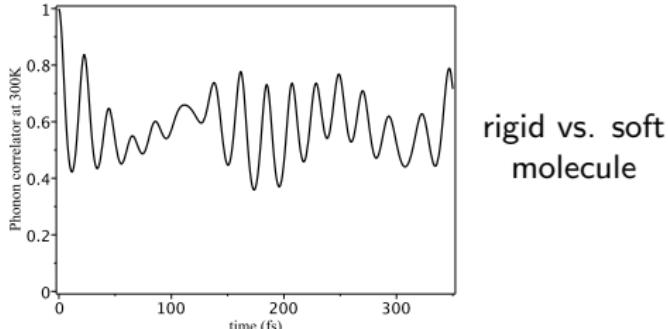
Independent boson model (displaced harmonic oscillator):

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

where  $C_{\alpha}(t) = \exp \left[ g_{\alpha}^2 \left( \coth \frac{\hbar\omega_{\alpha}}{2T} (\cos \omega_{\alpha} t - 1) - i \sin \omega_{\alpha} t \right) \right]$ ,

$\hbar\omega_{00}$  is 0-0 transition energy,

$\hat{\delta}$  is line shape function (inhomogeneous broadening) e.g.  $e^{-\sigma^2 t^2 / 2\hbar^2}$

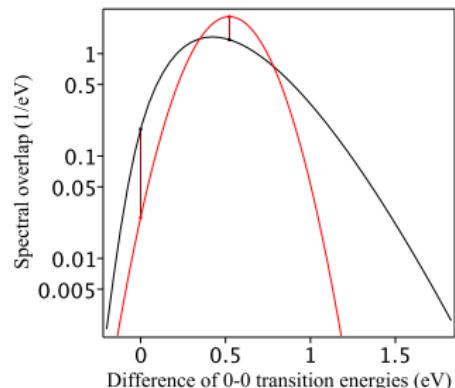
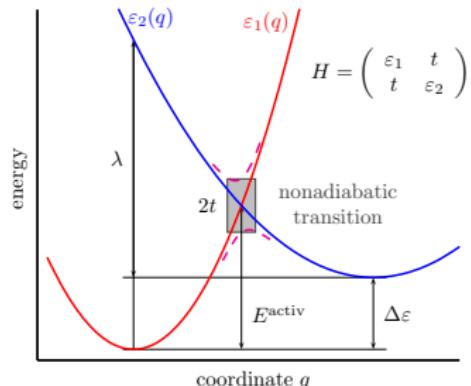


# Spectral overlap in high temperature limit: Marcus formula

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



— independent bozon model — Marcus formula

## Final step: solving master equation for hopping

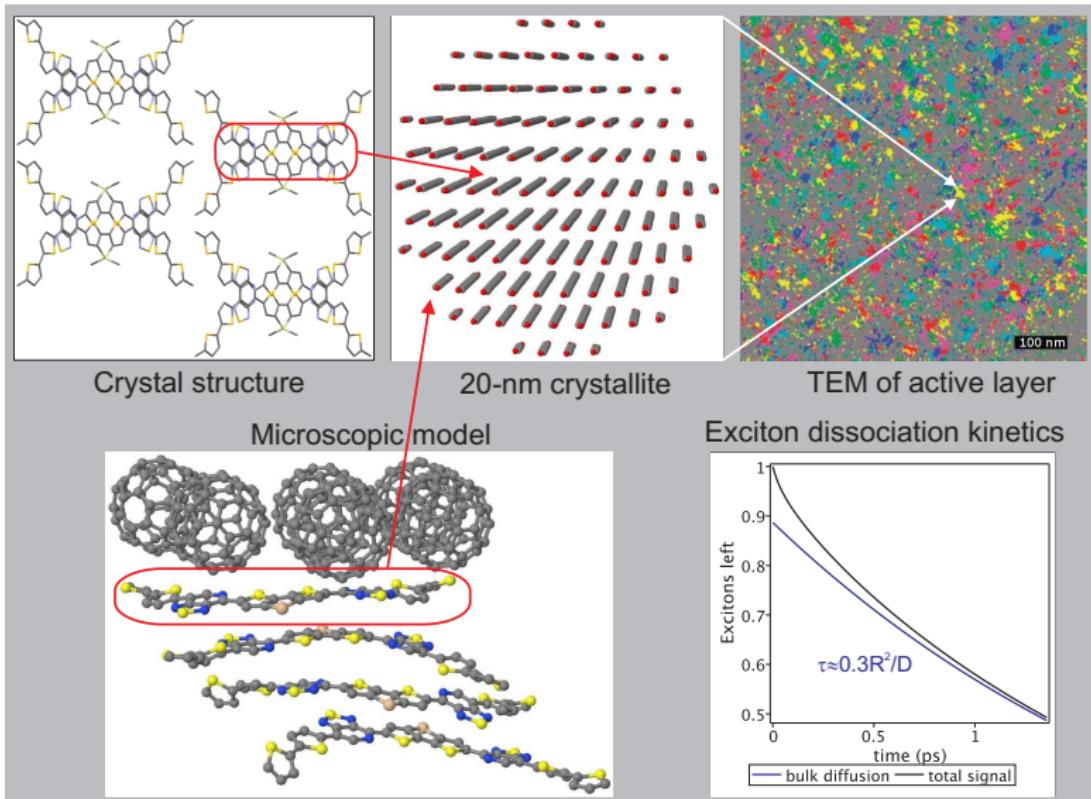
Master equation for average site occupation  $n_i(t)$ :

$$\frac{dn_i}{dt} = \sum_j (n_j w_{ji} - n_i w_{ij})$$

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*

## Resources

- Lab
- The WSPC Reference on Organic Electronics, ed J L Bredas, S R Marder (WSPC, 2016)
- Computational Chemistry and Materials Modeling course