Computational Chemistry and Materials Modeling

Lecture
Computational Chemistry of Molecules: part 2

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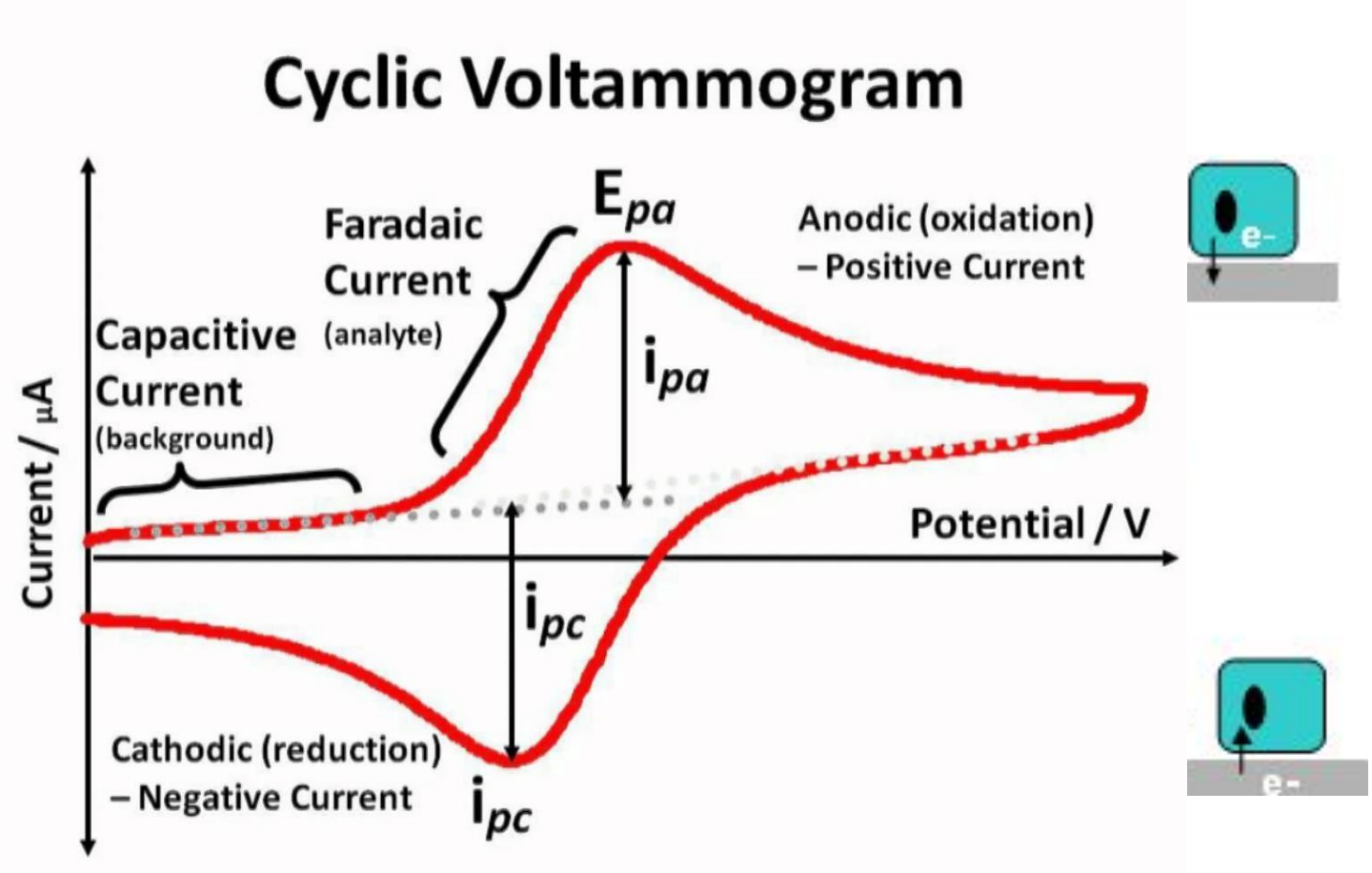
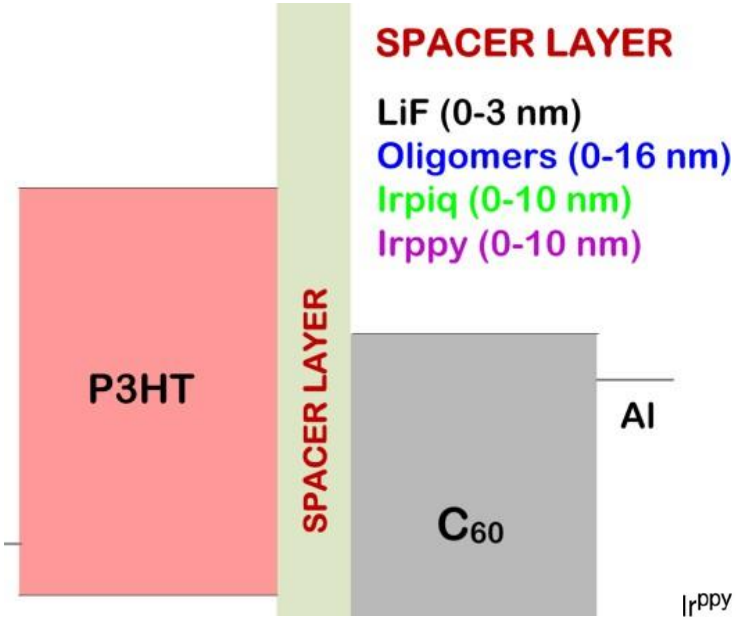
IP and EA

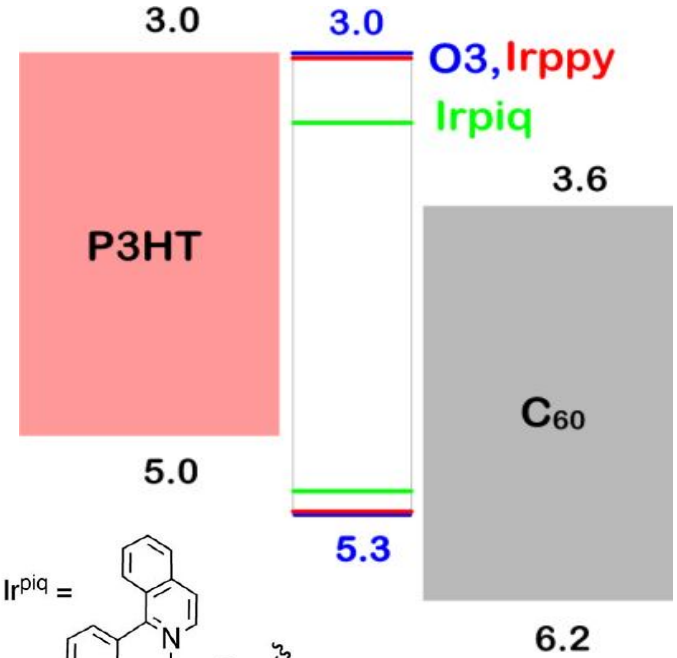


Cyclic Voltammetry: experimental characterization technique using a reversible electron transfer allowing evaluation of Electron Affinity (EA) and Ionization potential (IP) - although quite inaccurate

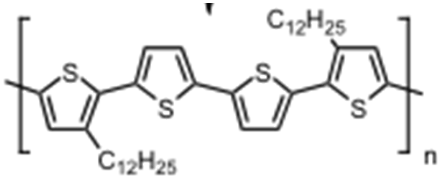
Example: organic semiconductors

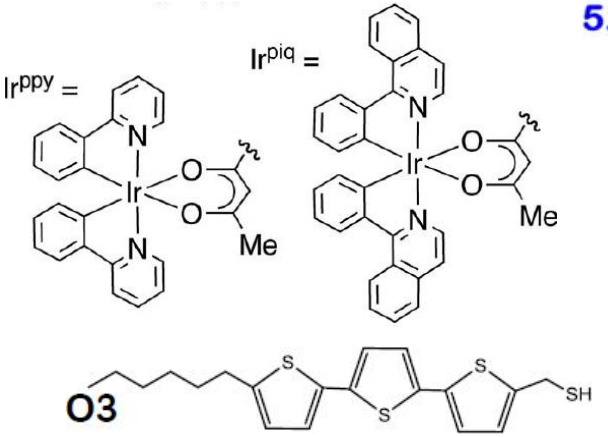
Experimentalist: I have prepared a prototype device and trying to understand how electron and hole energies are lining up in different materials. Cyclovoltammetry gives me the following numbers. Does it make sense?



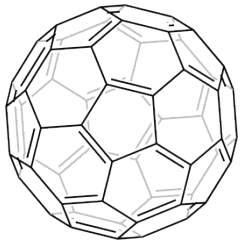


P3HT





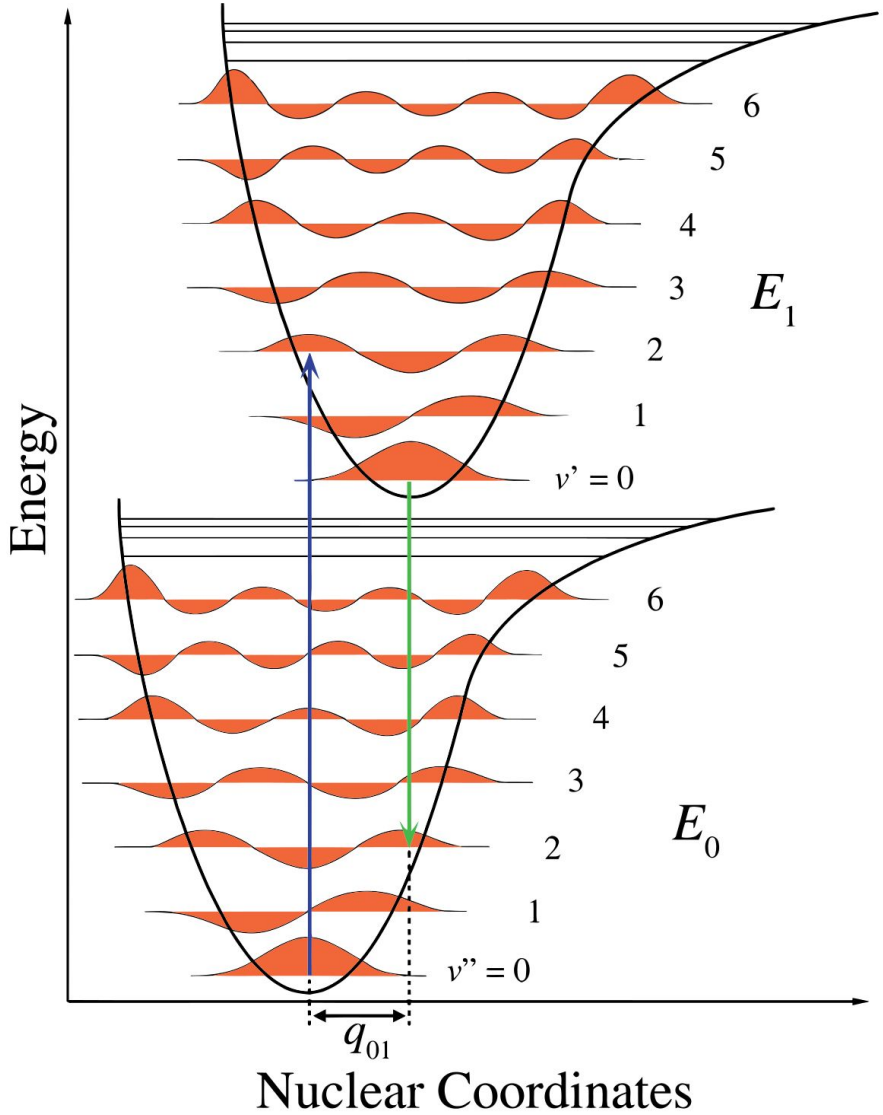
C60



Vertical and adiabatic IP

- IP=E(Q=+1)-E(Q=0)
- Koopman's theorem:

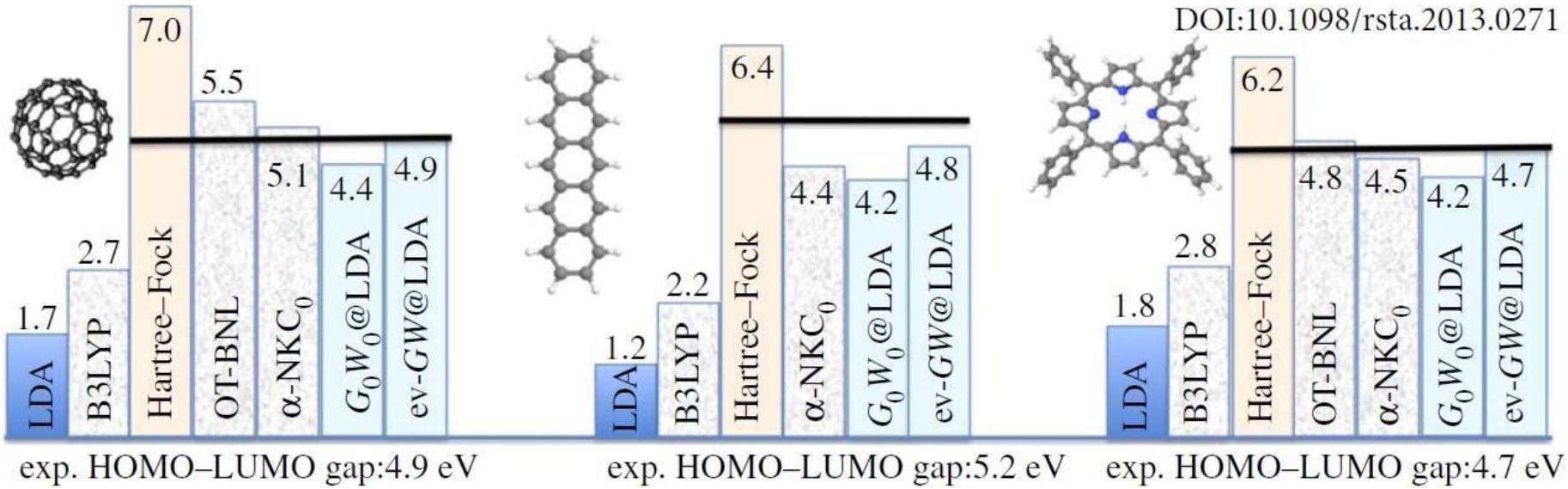
  IP_{vert}=-E(HOMO)



IP-tuning of density functionals

Idea: tune density functional (in the example below, range separation parameter) by requiring IP+E(HOMO)=0

$$\frac{1}{r_{12}} = \frac{1}{r_{12}}\left\{1-\left[\operatorname{erf}\left(\mu r_{12}\right)\right]\right\} + \frac{1}{r_{12}}\left[\operatorname{erf}\left(\mu r_{12}\right)\right]$$

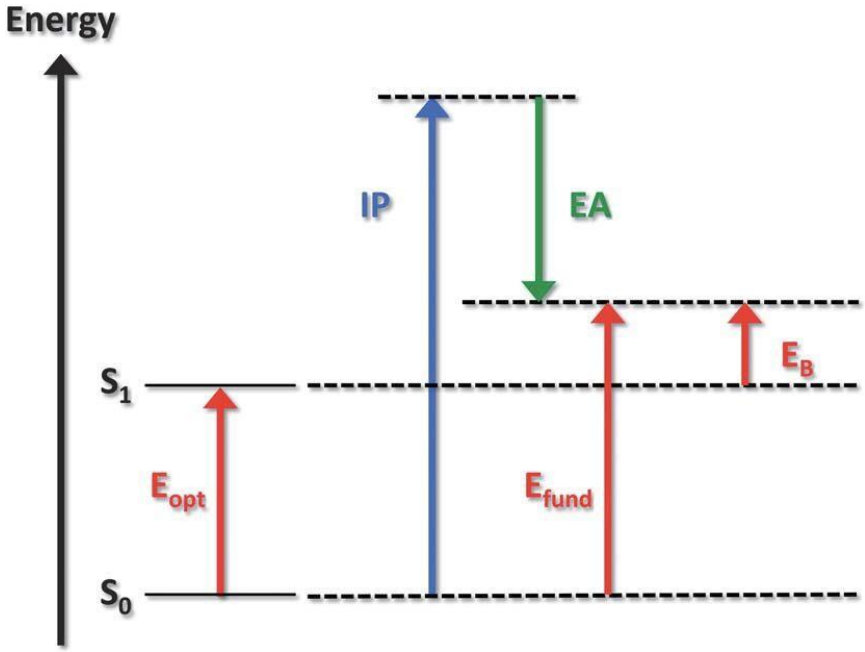


While excellent results were achieved for medium sized molecules, the limiting case to the bulk falls back to the GGA limit due to lack of proper treatment of dielectric effects

Mind the gap

J Bredas, Mind the gap, Mater Horiz 1, 17 (2014)

- Charge gap (IP-EA)
  (fundamental or transport gap)
- Optical gap (S1-S0)
  (absorption edge)
- Spin gap (T1-S0)
- HOMO-LUMO gap
  (!experimentalists interpret it either as optical or charge gap!)
- Band gap center (-IP-EA)/2
  (minus Mulliken electronegativity)



- For closed shell systems charge gap > optical gap > spin gap
- For strong correlations one of the gaps approaches zero
- By default all gaps are vertical (only electronic relaxation), but adiabatic gaps (also nuclei relaxation) are also meaningful

Vibronic couplings

Used in spectroscopy and charge transport studies

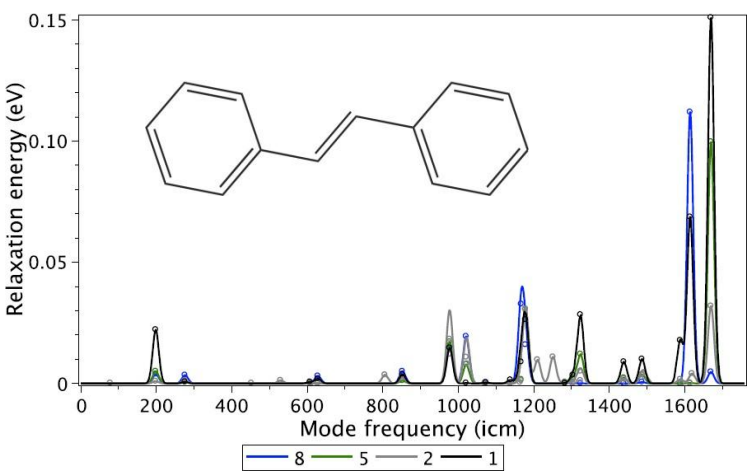
Simplest electron-phonon Hamiltonian

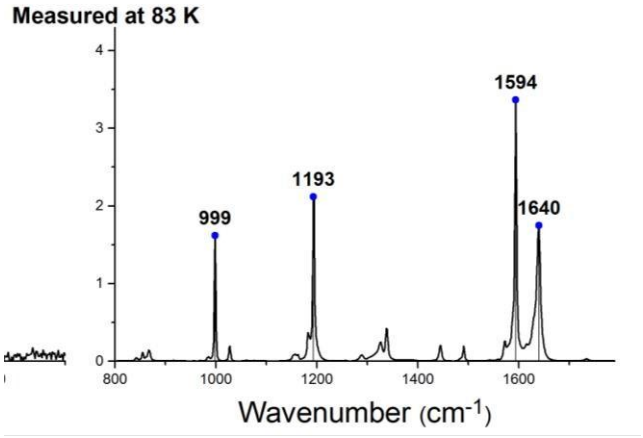
$$\left(\sum_{ij} H_{ij}^{1p} c_i^\dagger c_j + \sum_\alpha \hbar\omega_\alpha \left(b_\alpha^\dagger b_\alpha + \frac{1}{2} \right) + \sum_{ij\alpha} \hbar\omega_\alpha g_{ij\alpha} \left(b_\alpha^\dagger + b_\alpha \right) c_i^\dagger c_j \right.$$

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)





Batch calculations and benchmarking

- Batch calculations
- Benchmarking (as side task)

Batch calculations

- Before starting batch calculations
  - Document computational protocol
  - Assess demands vs resources
  - If variation of runtimes in your set is large think about efficient processing
  - Maybe run a small subset
- During calculations
  - Check if everything goes smoothly
- After calculations
  - Identify failed jobs and decide what to do with them
  - Keep results in a well-maintained database to avoid repeated calculations
- If you use shared facilities
  - Remember that there are other users
  - Clean up after finishing or failures

Complex calculations

- Intermolecular interactions
- Solvent effects: implicit solvation and QM/MM
- Embedding and fragmentation methods
- Photoelectron spectroscopy (PES)
- Pump-probe spectroscopy
- X-ray Free-Electron Laser (XFEL)
- Nuclear magnetic resonance (NMR) spectroscopy

Intermolecular interactions

- Use ‘plain’ DFT only if dispersion forces are small
- MP/CC can be used for fragment benchmarking
- Use Symmetry-Adapted Perturbation Theory (SAPT) for in-depth study, see also DOI:10.1063/5.0005093
- Dispersion-corrected DFT (DFT-D) such as D3/D4 is the best “universal” approach for organic molecules
- Many-Body Dispersion (MBD) is one of the most reliable “post-DFT” methods
- Use nonlocal van der Waals density functional vdW-DF2 if analytic derivatives are needed

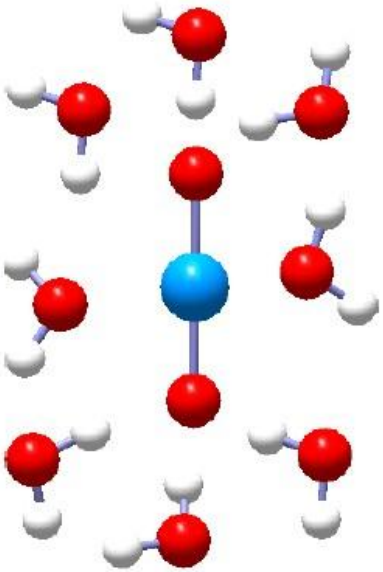
See also Review by Hermann&Tkachenko

Solvent effects (from Jensen)

- Non-specific (long-range) solvation
  - Polarization
  - Dipole orientation
- Specific (short-range) solvation
  - Hydrogen bonds
  - van der Waals interaction
  - Solvent shell structure
  - Solvent–solute dynamics
  - Charge transfer effects
  - Hydrophobic effects (entropy effects).

Solvation energies and models

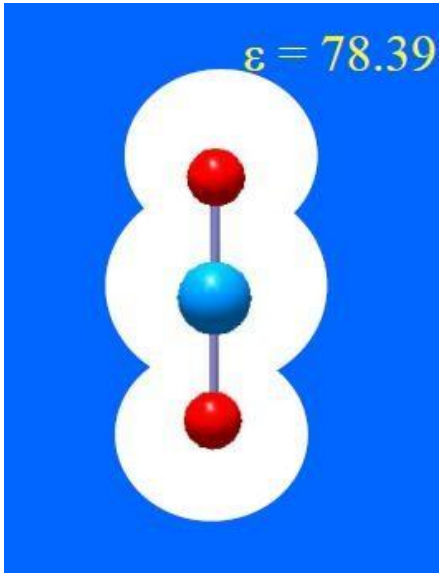
- $\Delta G_{sol} \Rightarrow$ the free energy change to transfer a molecule from vacuum to solvent.
- $\Delta G_{sol} = \Delta G_{elec} + \Delta G_{vdw} + \Delta G_{cav}$



Electrostatic component

Van der Waals interaction between solute and solvent

Free energy required to form the solute cavity. Is due to the entropic penalty due to the reorganization of the solvent molecules around the solute and the work done in creating the cavity



- Explicit solvent models
- Implicit solvent models

Solvent effects – explicit solvation

- **Quantum Mechanics/Molecular Mechanics (QM/MM)**

- **Aslo Morokuma's ONIOM (layered structure, complexity reduces when going from the center to periphery)**

- **The simplest case is to add a few 'solvent molecules' around your target system.**

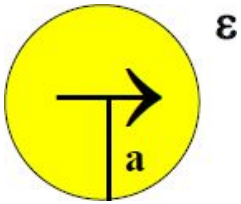
Be careful! The solvent molecules have to be 'intelligently' put around the solute, where interactions matter the most (e.g., hydrogen bonding).

Solvent effects – implicit solvation

- Solvent is treated as a polarizable continuum with a dielectric constant, ε, instead of explicit solvent molecules.
  - The charge distribution of the solute polarizes the solvent producing a reaction potential.
  - The reaction potential of solvent alters the solute.
  - This interaction is represented by a solvent reaction potential introduced into the Hamiltonian.
  - Must be computed self consistently
  - Also known Interactions as self consistent reaction field (SCRF) methods
  - Significantly cheaper than explicit solvent models
  - Cannot model specific interactions such as hydrogen bonds

Example the Onsager model:

Onsager (1936): a polarizable dipole at the center of a sphere. The solute dipole induces a reaction field in the surrounding medium which in turn induces an electric field in the cavity (reaction field), which interacts with the dipole: analytic solution



$$\phi_{RF} = \frac{2(\varepsilon - 1)\mu}{(2\varepsilon + 1)a^3}$$

Energy of a dipole in an $\vec{E}$ field $\phi_{RF} = -\phi_{RF}\mu$

Work done assembling charge distribution $= \frac{\phi_{RF}\mu}{2}$

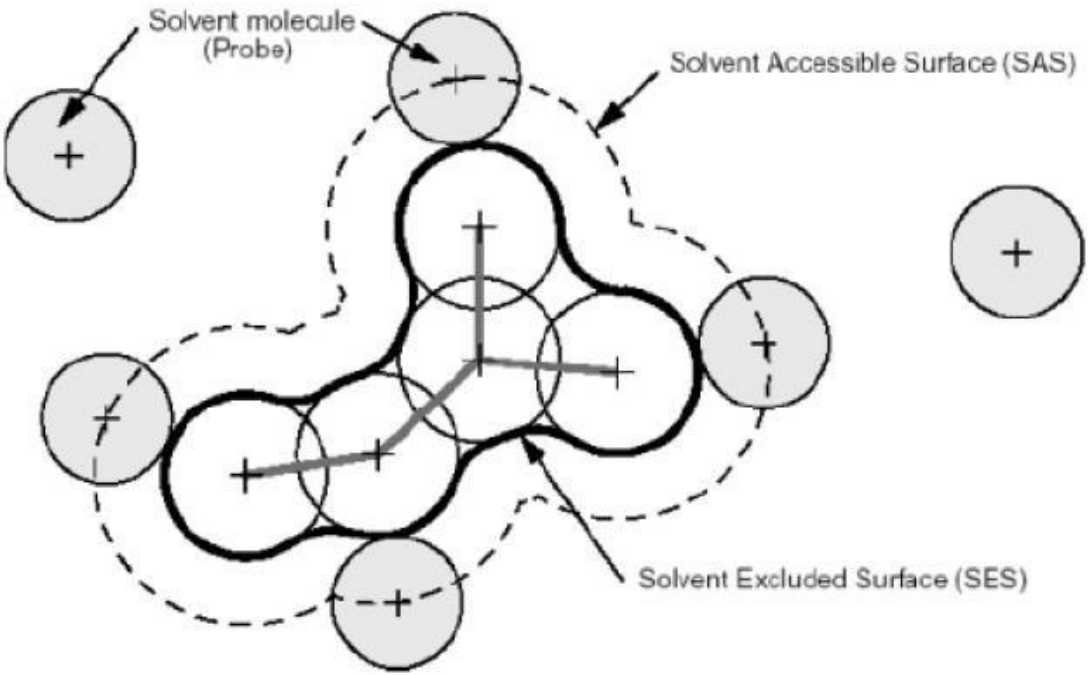
$$\Delta G_{elec} = \frac{-\phi_{RF}\mu}{2} = -\frac{(\varepsilon - 1)\mu^2}{(2\varepsilon + 1)a^3}$$

Implicit solvation: practical models

- ***Realistic molecular cavity;***
- ***Solve Poisson's equation in some approximation numerically:***

$$\nabla \cdot (\varepsilon(\mathbf{r}) \nabla \phi(\mathbf{r})) = -4\pi\rho(\mathbf{r})$$

a second-order differential equation describing the connection between the electrostatic potential φ, the charge distribution ρ and the dielectric constant ε



- The Polarizable Continuum Model (PCM) employs a van der Waals cavity formed by interlocking atomic van der Waals radii scaled by an empirical factor, a detailed description of the electrostatic potential, and parametrizes the cavity/dispersion contributions based on the surface area.
- The COnductor-like Screening MOdel (COSMO) also employs molecular shaped cavities, and represents the electrostatic potential by partial atomic charges.

Bottom line: magic words – SCRF, PCM, COSMO and dielectric constant!

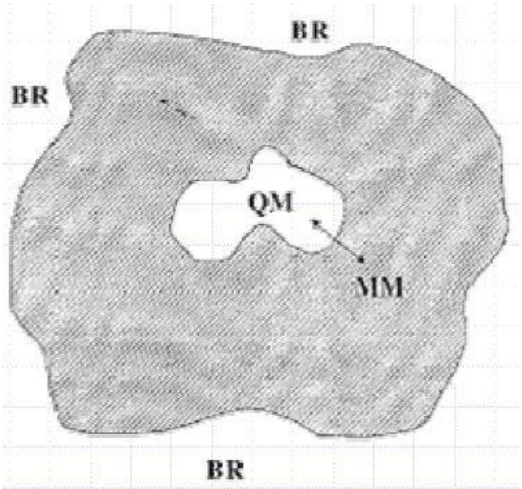
QM/MM – a standard tool

QM/MM Partitioning

$$E = E_{QM} + E_{MM} + E_{QM/MM}$$

- What should be used in the QM region? Ab Initio OR DFT OR Semiempirical
- QM/MM interaction term can be problematic – it is not good to have this boundary close to the chemistry of interest…
- Not clear which force fields to use – much experience with expected accuracy of ab initio methods alone and MM methods alone, but not much with QM/MM
- No direct map from wavefunction to parameters

$$V(\vec{R}) = \sum_{i \in bonds} k_{i,bond}\left(r_{i,bond} - r_{i,bond}^{eq}\right) + \sum_{i \in angles} k_{i,angle}\left(\theta_{i,angle} - \theta_{i,angle}^{eq}\right) + \\ + \frac{1}{2}\sum_{\substack{i \neq j \\ i,j \in atoms}} \frac{q_i q_j}{\left|r_i - r_j\right|} + \frac{1}{2}\sum_{\substack{i \neq j \\ i,j \in atoms}} V_{LJ}^{ij}\left(\left|r_i - r_j\right|\right)$$



- Mechanical Embedding: Include only Van der Waals in $E_{QM/MM}$
- Electrostatic Embedding: Include electrostatic interaction in $H_{QM/MM}$
- Covalent Embedding: Breaking the bond at the QM/MM borderline. Most difficult scheme. Need to assure continuity of the energy. Electronegativity idea (Thiel). Frozen orbital idea.

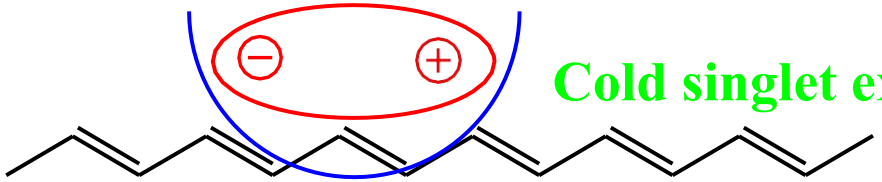
Benchmarking (as side task)

- Required for a new combination of system and method

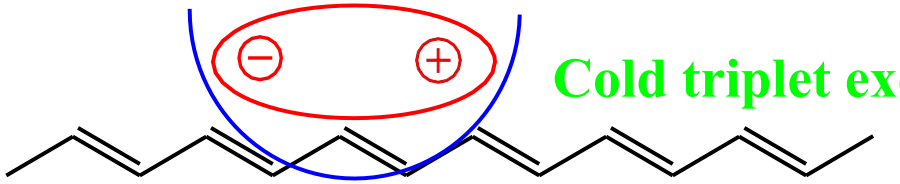
1. Benchmarking against experiment:
   - Use training and validation sets
     (e.g. geometry for training – spectra for validation)
   - Use only reliable data for training
   - In most cases you can avoid training by experiment
     (e.g. use Koopman's theorem or options 2,3)
   - Always compare (validate) your calculations with experiment
1. Benchmarking against higher-level theory:
   - Make sure that you use relevant property for comparison
     (e.g. it can be smallest molecule in series or easier-to-calculate property)
3. Compare several reasonably good methods:
   - Always check sensitivity of your results to method
   - Use range of methods expected to get lower and upper bounds
     (e.g. B3LYP and ωB97X for band gap of large π-conjugated molecules)

Example: spatial extent of relaxed excitations

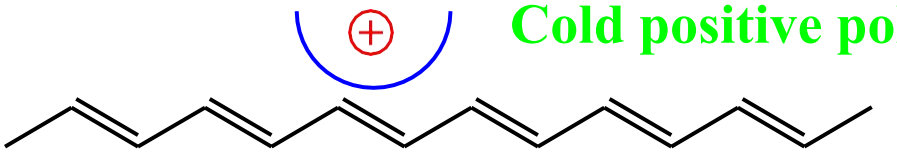
I. H. Nayyar, E.R. Batista, A. Saxena, D. L. Smith, R. L. Martin, S. Tretiak, J Phys Chem Lett 2, 566 (2011)



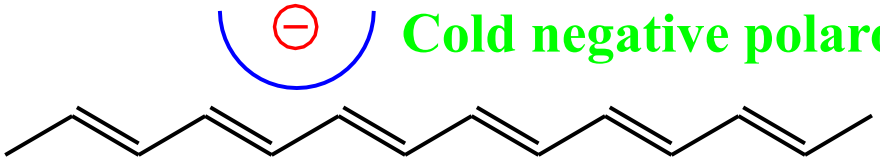
Cold singlet exciton S_1



Cold triplet exciton T_1



Cold positive polaron P+ (hole)



Cold negative polaron P- (electron)

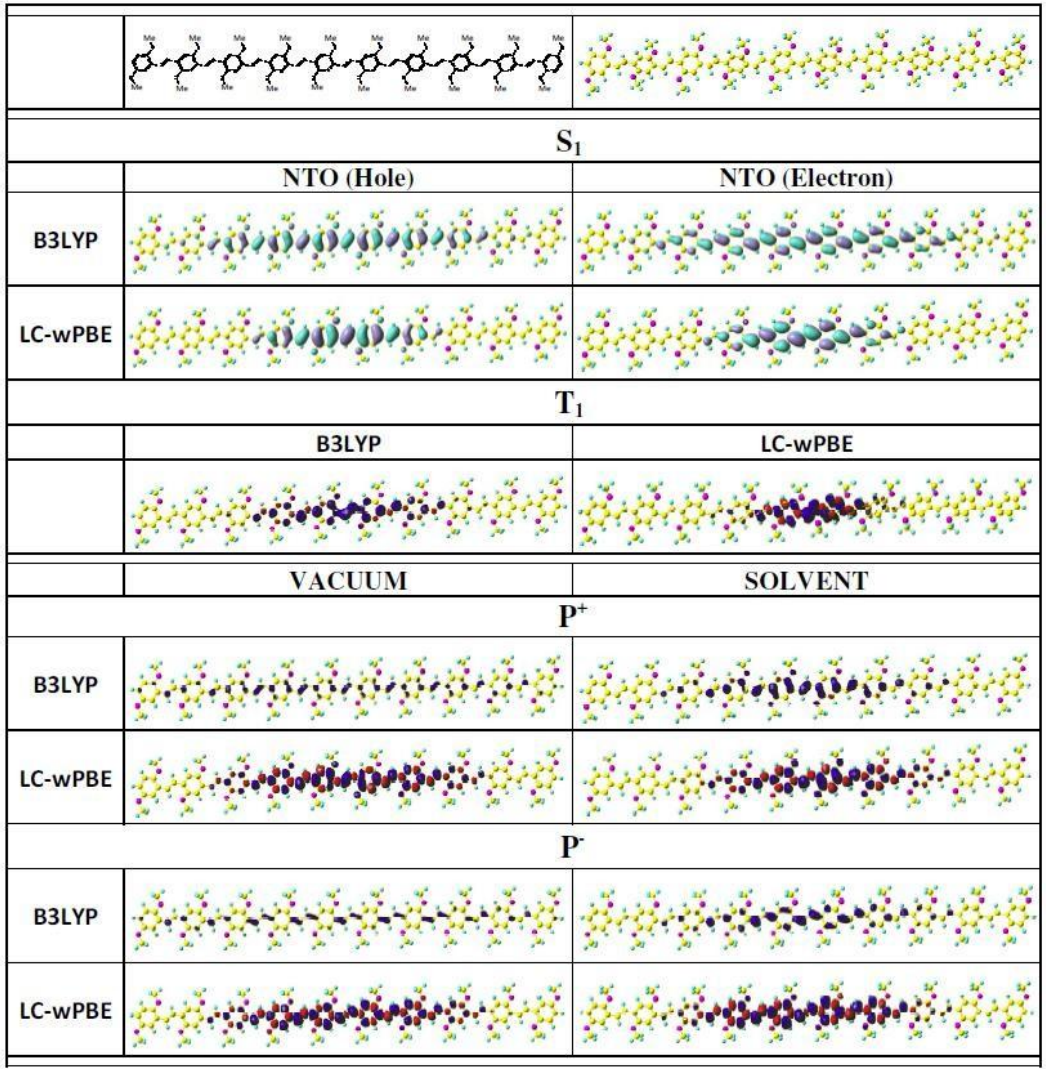
Main questions:

a) Dependence on the DFT model

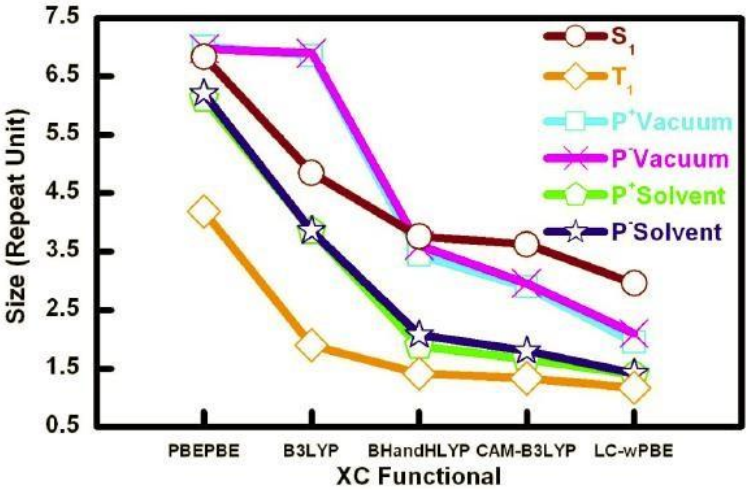
b) The role of the dielectric medium

Experimental determination of polaronic size in MEH-PPV : ~10 C-H units ~ 2-3 repeat units

… all excitations are localized

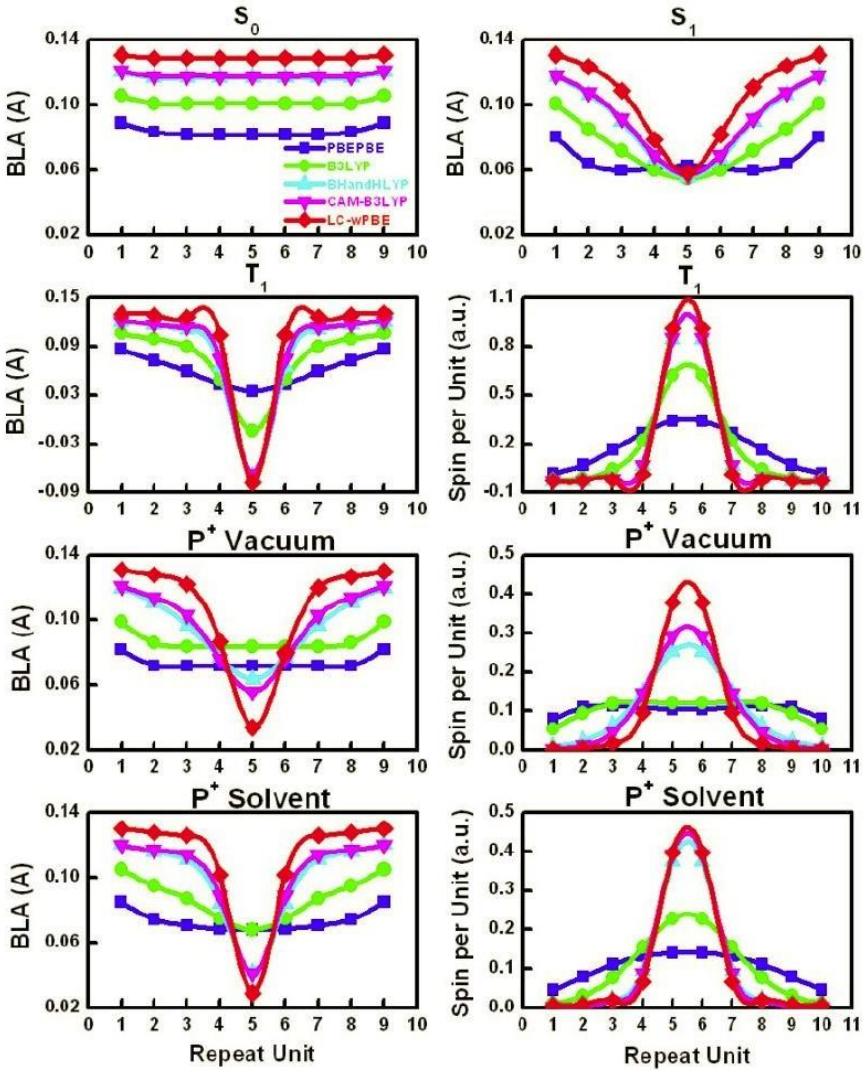


Orbital plots show natural transition orbitals (NTOs) for hole and electron for S_1 and Mulliken atomic spin density distribution for T_1, P^+ and P^- calculated at B3LYP/6-31G* and LC-wPBE/6-31G* optimized levels.



Characteristic size of the electronic excitation defined as full width at half maximum (in terms of repeat units).

… variations of bond lengths and spin densities



Orbital exchange in the DFT models

a) PBE (0%)
b) B3LYP (20%)
c) BHandHLYP (50%)
d) CAM-B3LYP (20-65%)
e) LC-wPBE (0-100%)

Moderate polarity solvent (COSMO model)

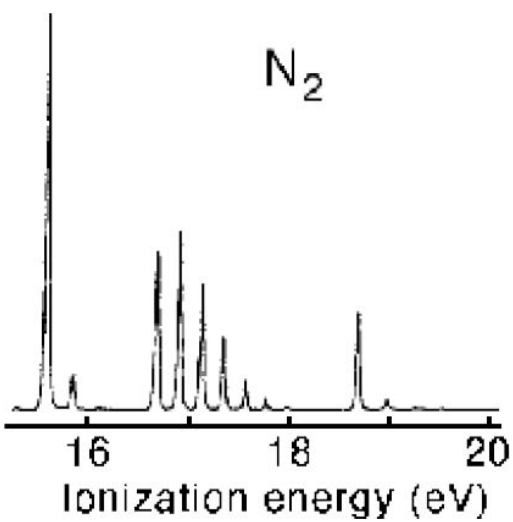
Bond length alternation (BLA) (Å) and Mulliken atomic spin densities (a.u.) per repeat unit of MEH-PPV oligomer computed with 6-31G* basis set.

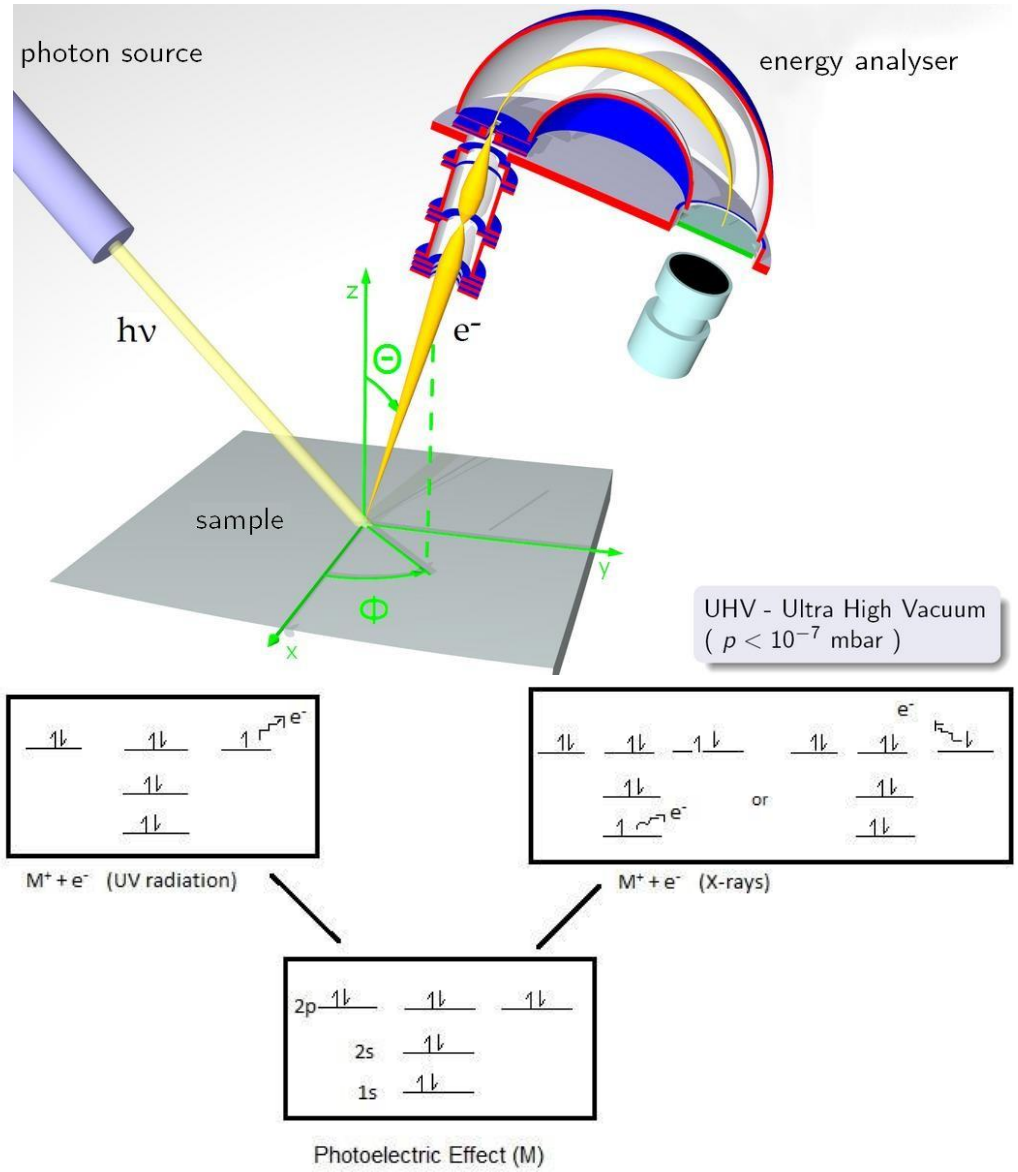
Photoelectron spectroscopy (PES)

Come in variations:
Ultraviolet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS)

$E_k = h\nu - IP\ (i)$

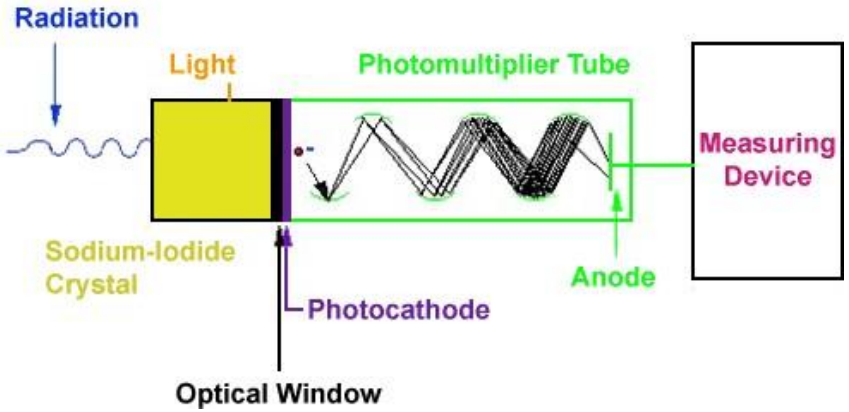
To calculate PES peaks one needs to evaluate energy levels occupied by electrons

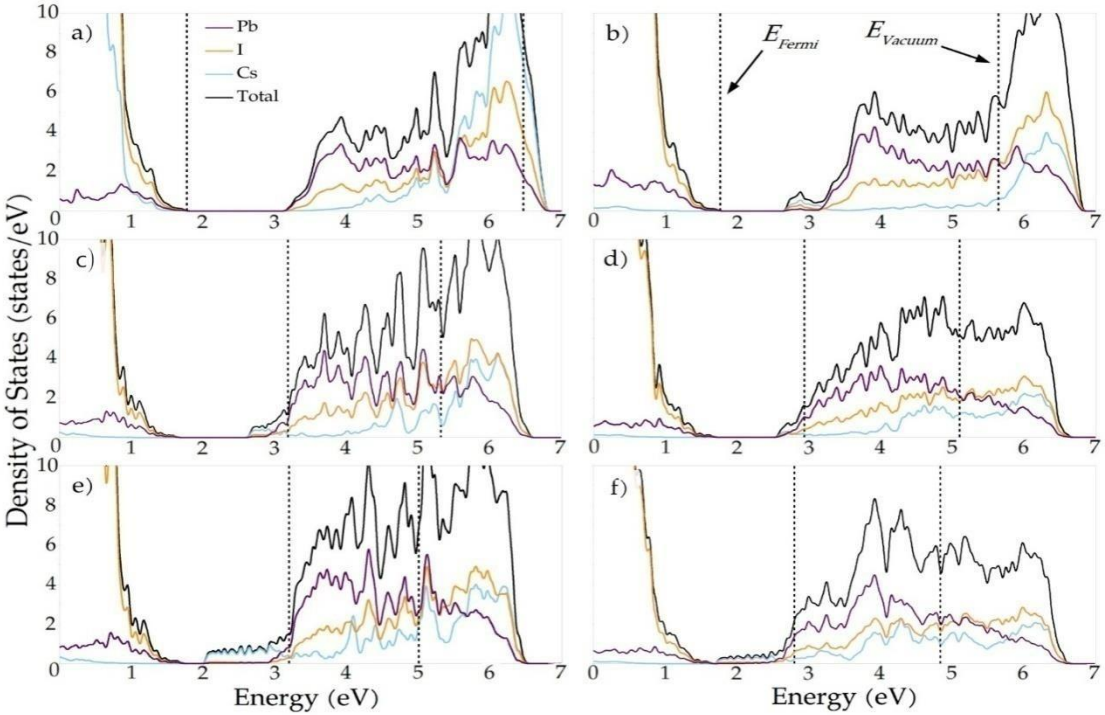


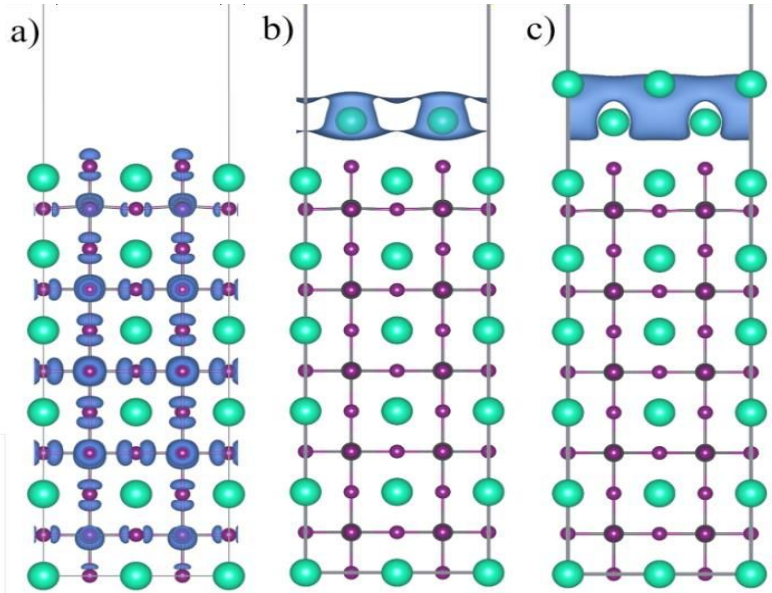


Case study: photocathodes

Requirements: low work-function and high yield



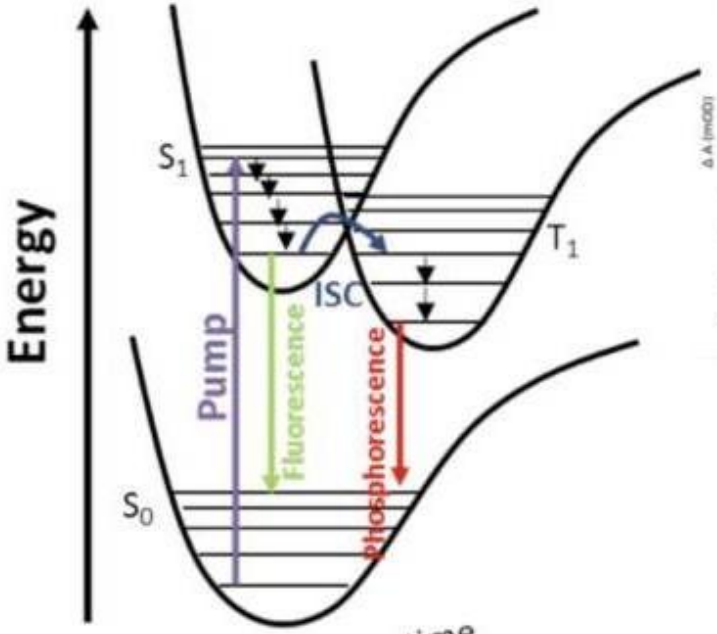


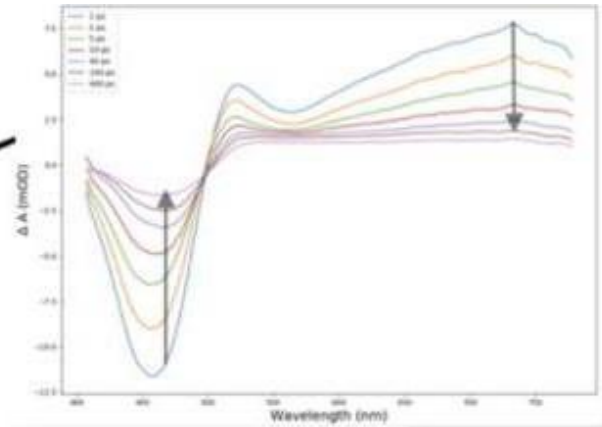


Halide perovskite materials (such CsPbBr3) coated with Cs have lower work functions (from 4.5 eV to ~2 eV, theory) and a high yield of photoelectrons (unpublished)

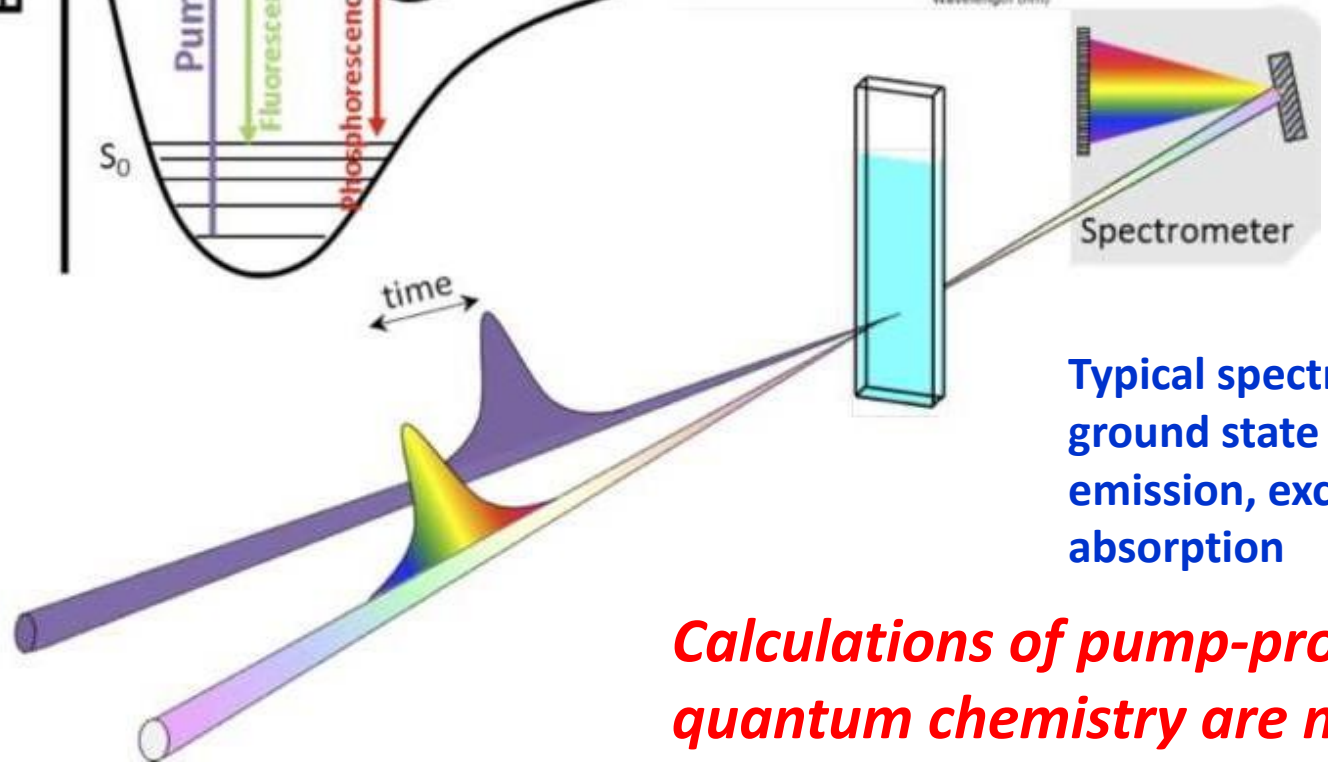
Pump-probe (transient absorption) spectroscopy

A major tool to probe an electronic dynamics in materials





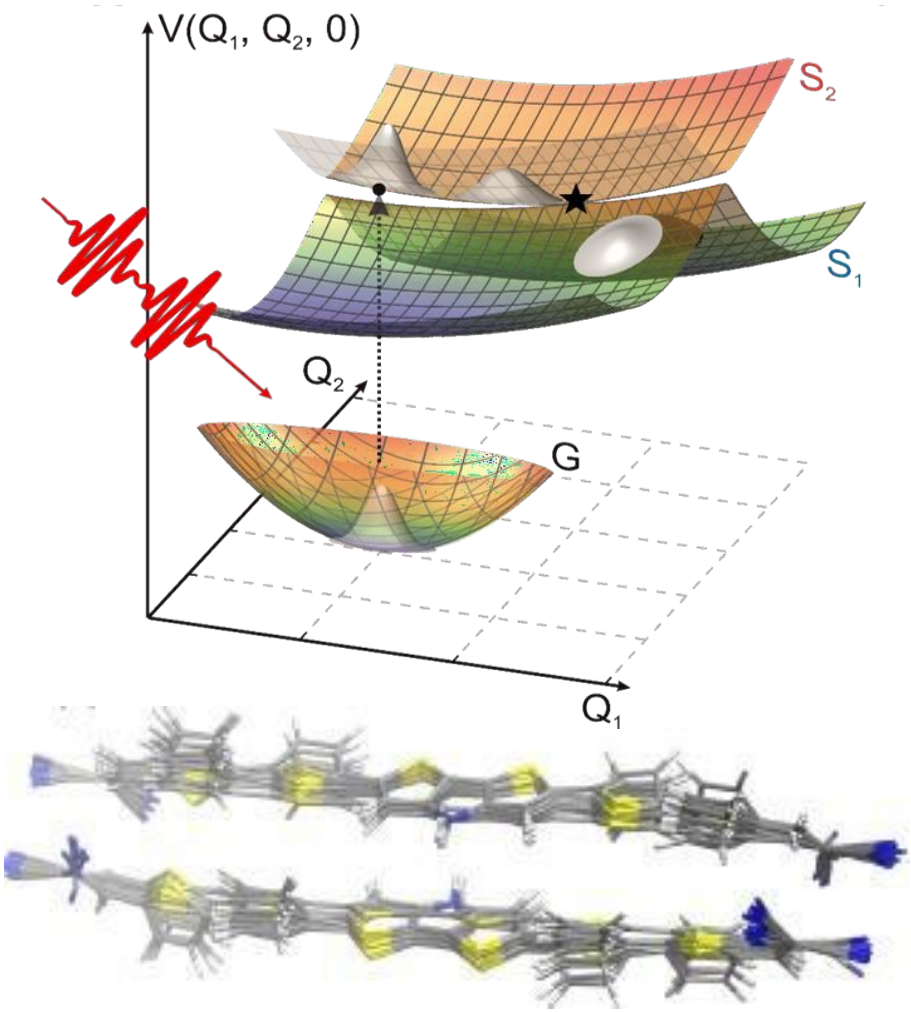
Dynamical information is extracted from time-evolution of various peaks in transient absorption spectra



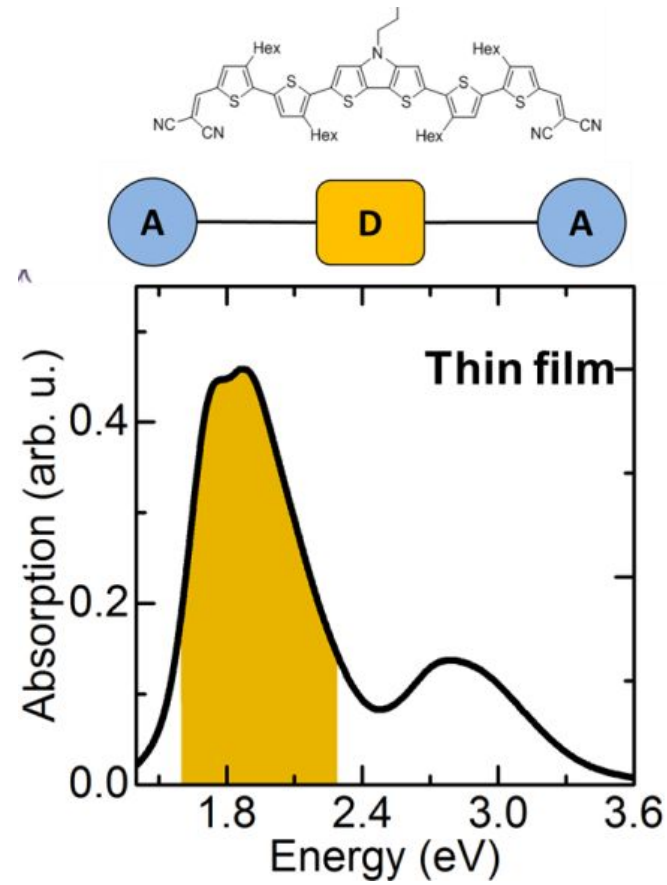
Typical spectroscopic features: ground state bleach, stimulated emission, excited state absorption

Calculations of pump-probe spectra using quantum chemistry are non-trivial

Case study: Intermolecular energy transfer through intermolecular conical intersection in organic photovoltaics

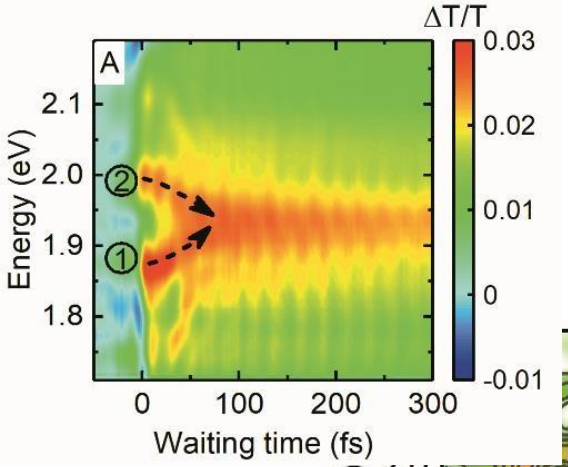


Experimental observation of coherent vibrational dynamics in thin film

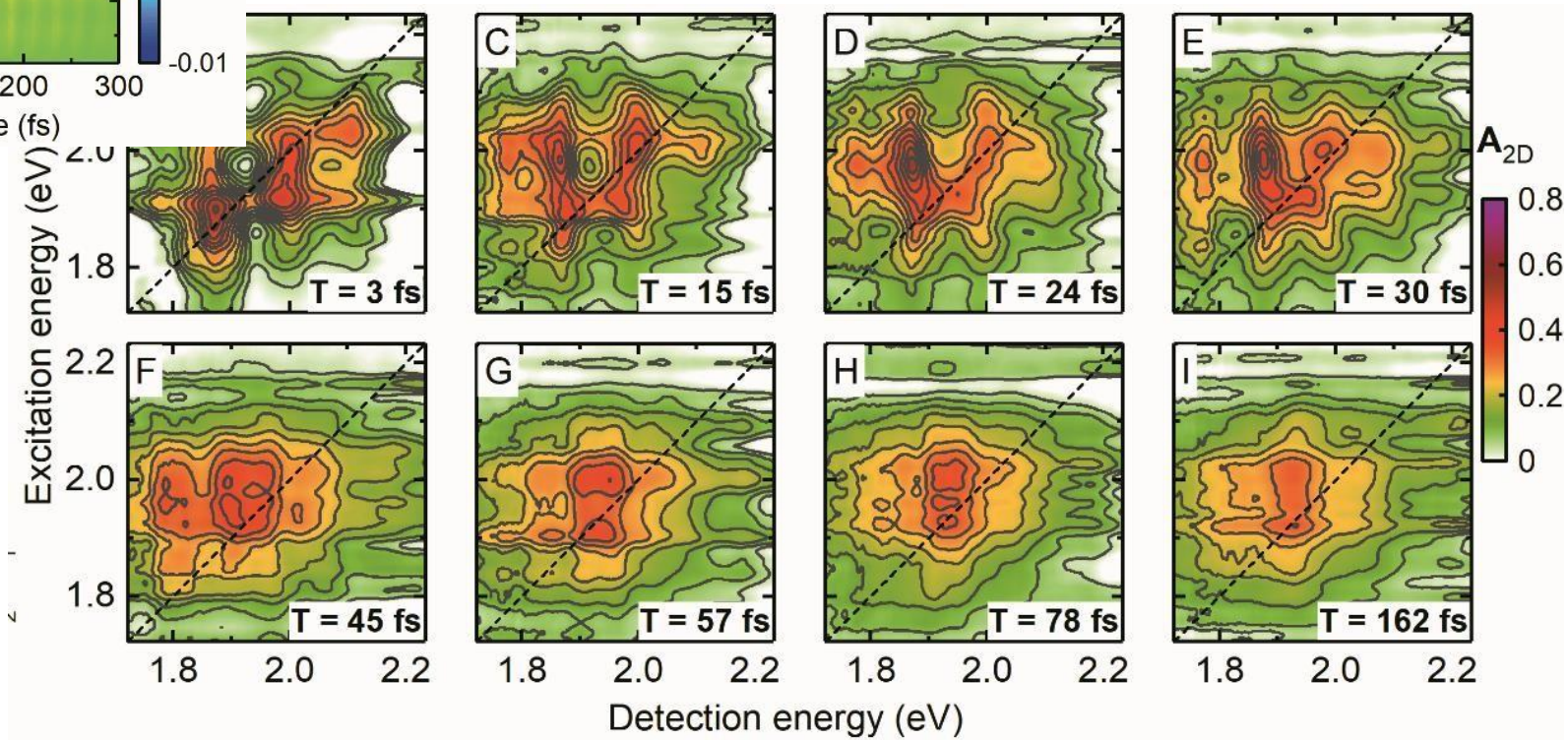


A. De Sio, E. Sommer, X. T. Nguyen, L. Gross, D. Popović, B. Nebgen, S. Fernandez-Alberti, S. Pittalis, C. A.
Rozzi, E. Molinari, E. Mena-Osteritz, P. Bäuerle, T. Frauenheim, S. Tretiak, C. Lienau, Nature Nanotech.

Case study: Two-dimensional electronic spectra suggest coherent passing of intermolecular CoIns



Conical intersection is reached within ~40 fs followed by active coherent vibronic excitations



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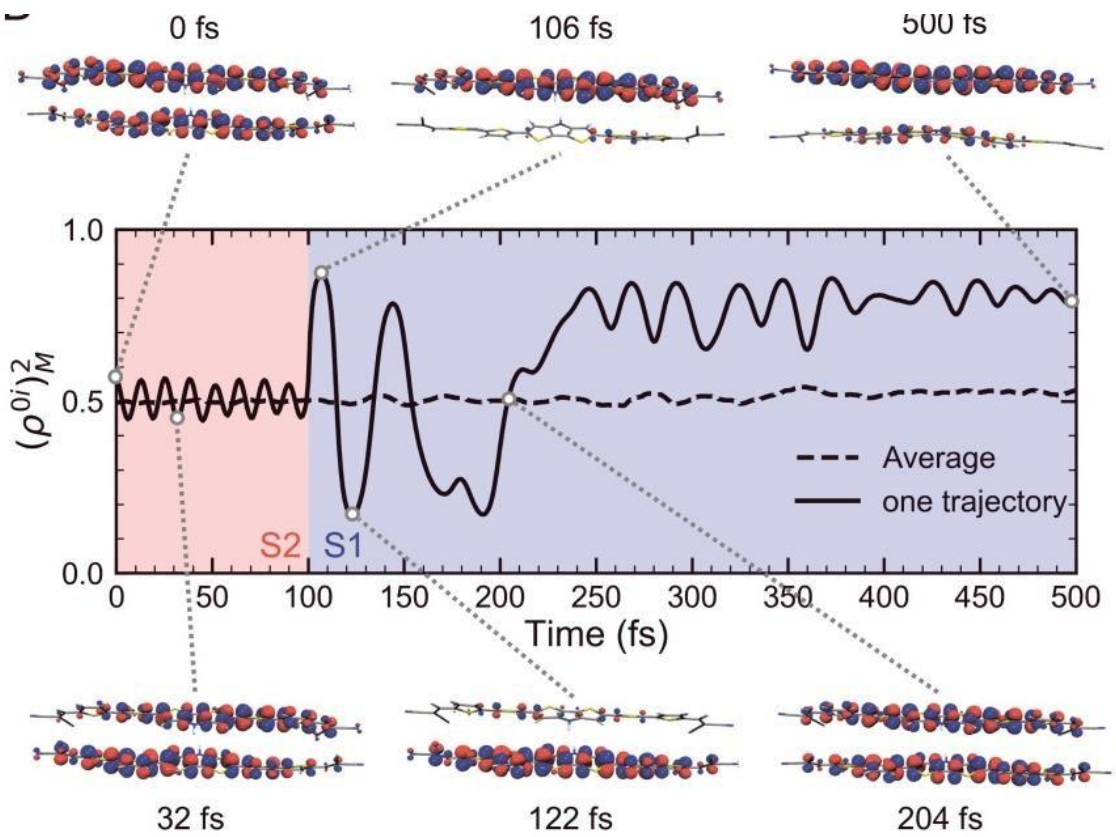
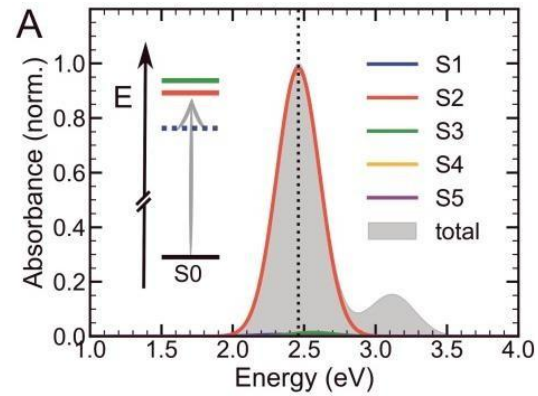
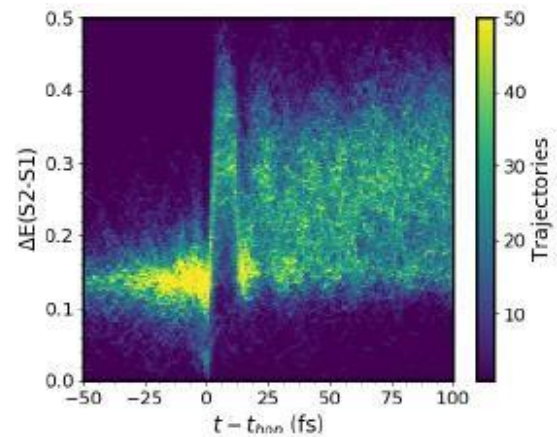
Rozzi, E. Molinari, E. Mena-Osteritz, P. Bäuerle, T. Frauenheim, S. Tretiak, C. Lienau, Nature Nanotech.

Case study: Modeling of coherent non-adiabatic dynamics in a molecular dimer (H-aggregate)

Intermolecular conical intersection is reached within 100 fs. Excess of electronic energy excites vibrational modes coupled on upper and lower surfaces (modulation of dynamics), the wavefunction "collapses" (self-trapping).



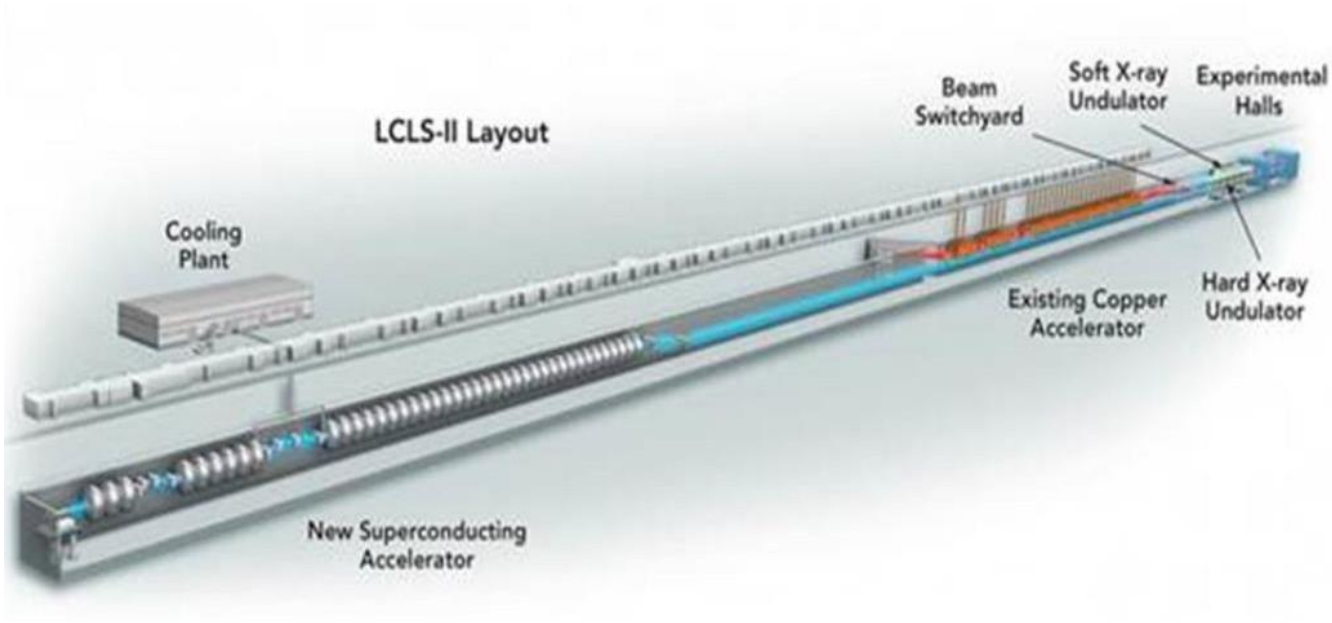


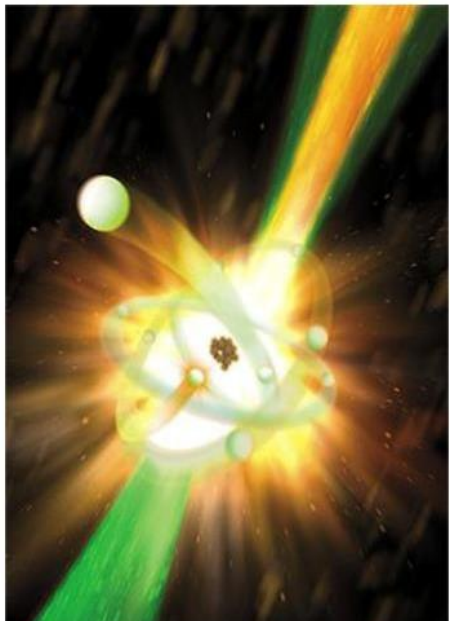


A. De Sio, E. Sommer, X. T. Nguyen, L. Gross, D. Popović, B. Nebgen, S. Fernandez-Alberti, S. Pittalis, C. A.
Rozzi, E. Molinari, E. Mena-Osteritz, P. Bäuerle, T. Frauenheim, S. Tretiak, C. Lienau, Nature Nanotech.

X-ray Free-Electron Laser (XFEL)

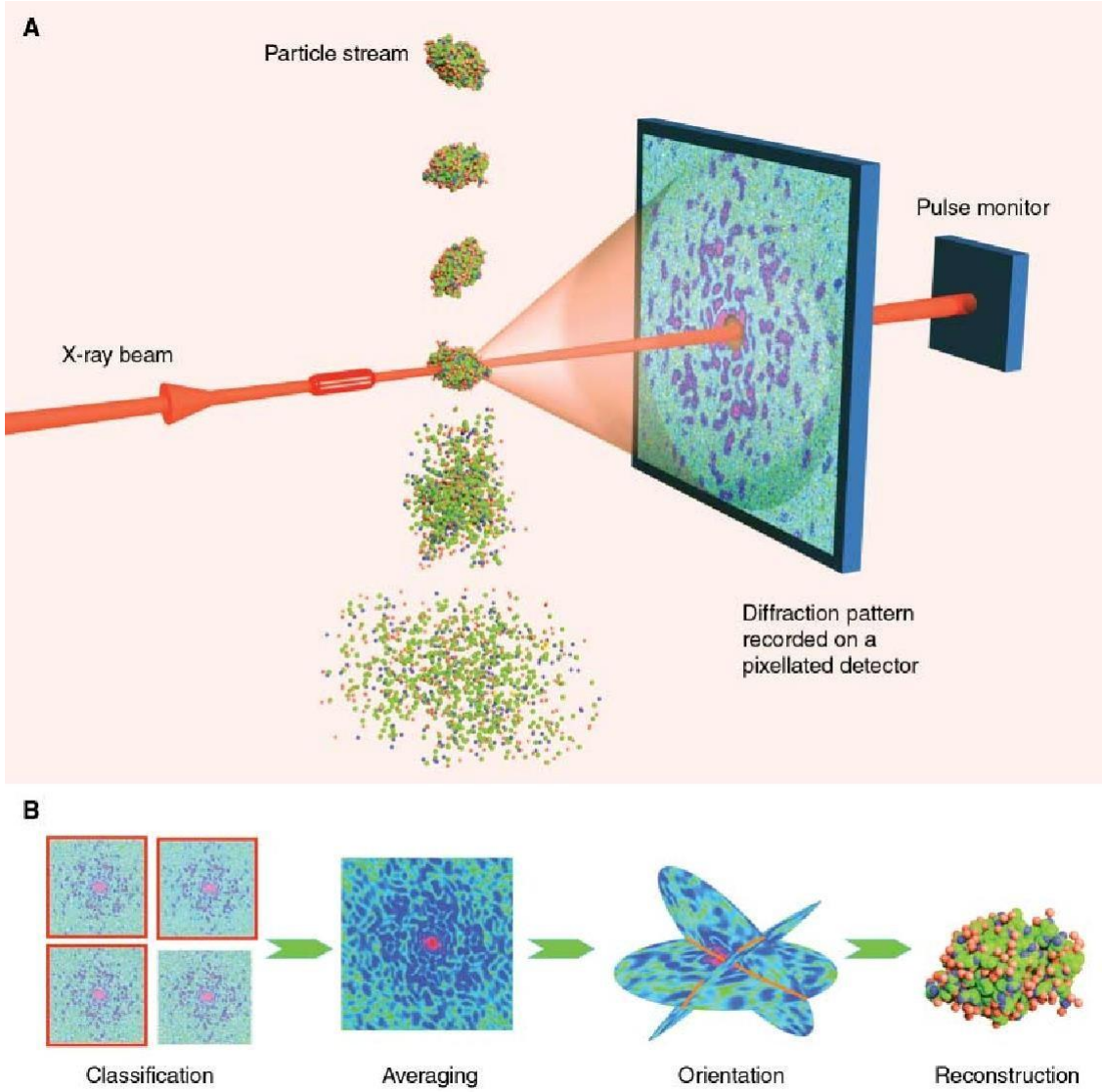
Current and planned XFEL capabilities for LCLS (Stanford)





XFELs (shown for LCLS-II) generate intense x-ray pulses using electrons accelerated to highly relativistic speeds. LCLS operates, for example, at an energy of 15 billion electron volts, producing electrons traveling at 99.999999% of the speed of light. These electrons are passed through periodically modulated magnetic fields, the so-called undulators. The undulators accelerate the electrons and induce them to emit x-ray photons. At the same time, interactions between electrons, the undulator's magnetic fields, and emitted x-ray photons cause the electrons to bunch together in periodic structures. The electrons then radiate coherently in phase with one another, corresponding to laser emission. This coherent emission process can lead to extremely intense and short pulses of x-rays. It is possible to produce x-rays with peak brightness more than 10 million times greater than the brightest modern x-ray storage ring facility, as shown interacting with matter.

Single molecule structure resolution with XFEL



XFELs impact:

-Probing and controlling electron motion within a molecule;

-Discovering novel quantum phases through coherent light-matter coupling

-Capturing rare events and intermediate states in the transformation of matter

RF being one of shareholders (and Skoltech) has a priority access to European X-Ray Free-Electron Laser Facility (European XFEL)

Discussion (short)

1. What is the difference between vertical and adiabatic transitions?

2. For which state solvent effects are the strongest: S0 (zero charge), S1, T1, cation?

3. Often only IP is available in cyclic voltammetry, so experimentalists add band gap estimated from UV-Vis absorption spectra to get EA (they call them HOMO and LUMO energies). What is true meaning of thus obtained LUMO energy?

Discussion (less trivial)

1. What HOMO should be taken in Koopman's theorem: of neutral or ionized state? What can we say about EA_{vert}+E(LUMO)?

2. Upon (dis)charging metal-ion electrode some peaks in Raman spectra (dis)appear. Does this mean (dis)appearance of vibrational modes or vibronic couplings?

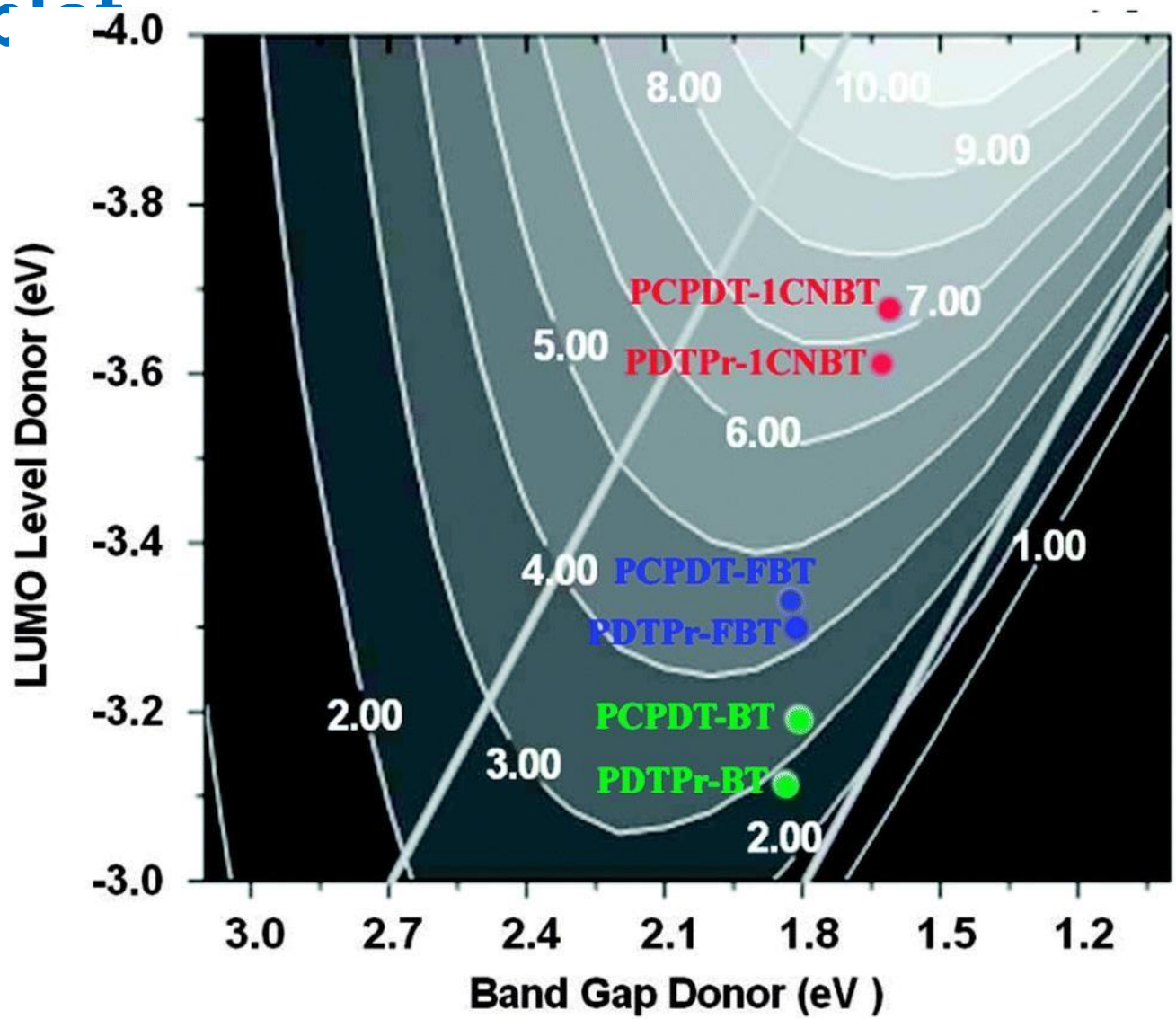
3. Why for PES, e.g. work-function for electrons in photocathodes, the surface dipole matters?

Discussion

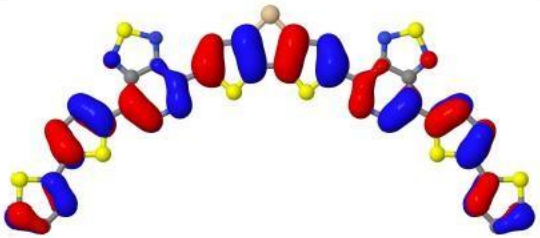
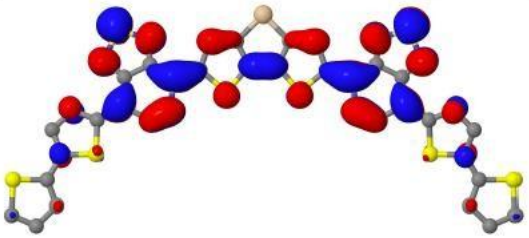
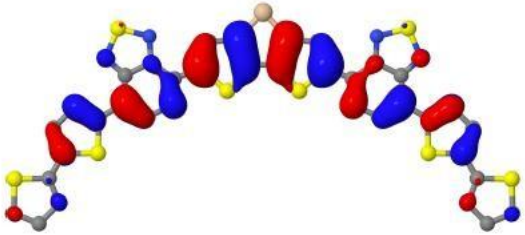
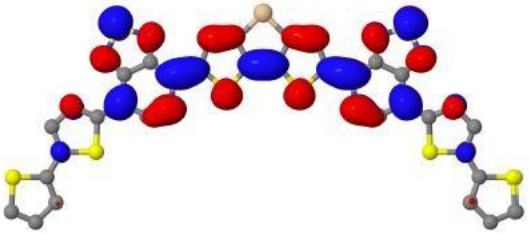
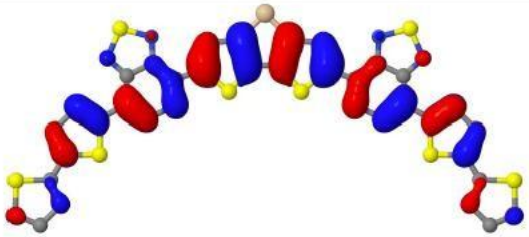
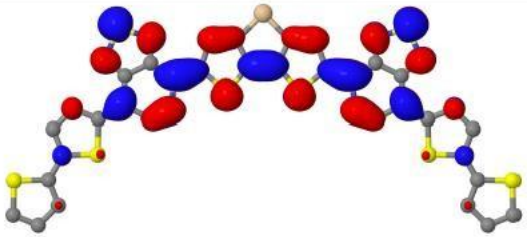
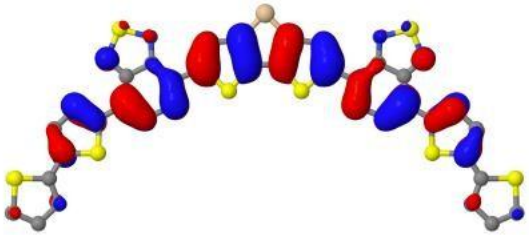
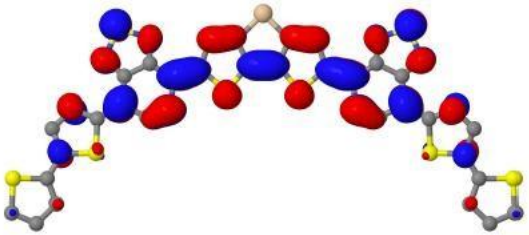
1. You need to calculate alkali ion intercalation potential in a π-conjugated organic material. What is the challenge and how to overcome it?

2. You are calculating a shallow dihedral PES by DF-LCCSD(T)-F12 and get a very strange looking curve. What is wrong?

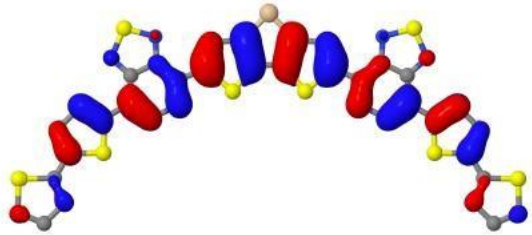
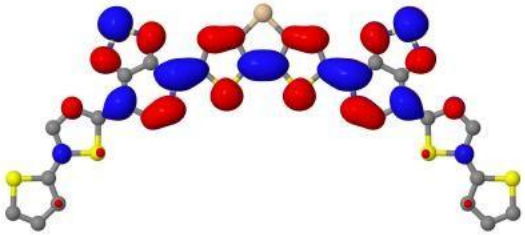
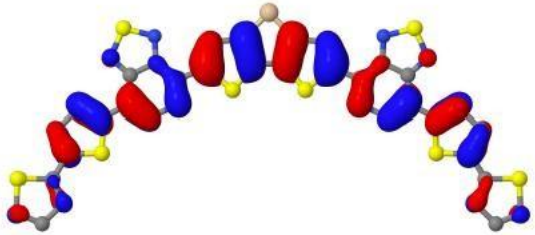
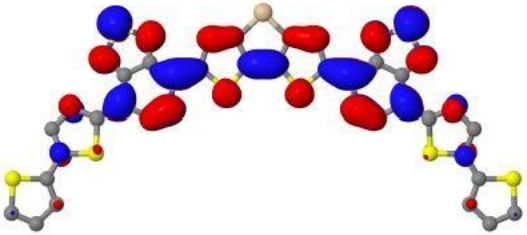
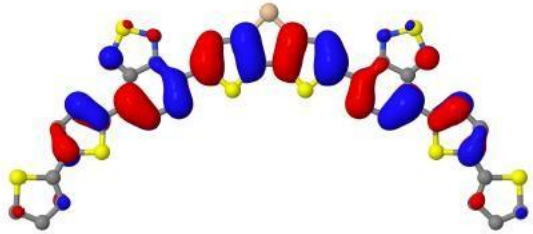
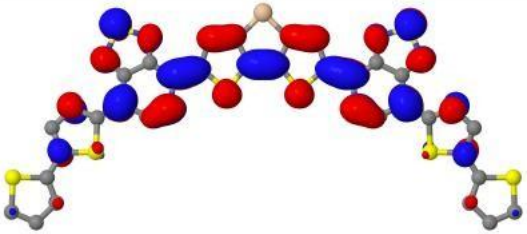
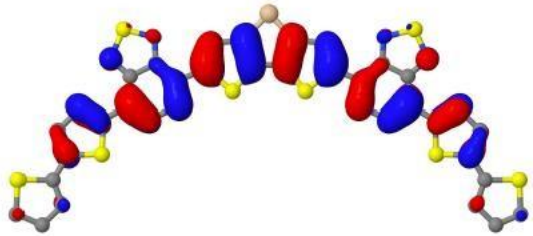
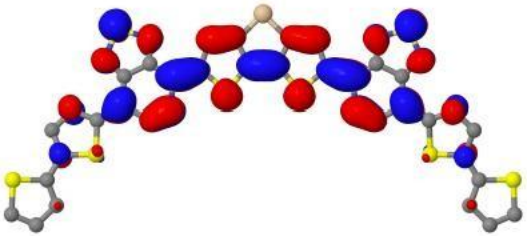
… organic solar cells: Scharber's plot



MO vs NO

	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 $n_h = 1 + .17$ $n_e = 1 - .18$		

NO vs NTO

	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 $n_{h/e} = 1 \pm .25$		

Linear response

- Electric field polarizability, dielectric function
- IR and Raman intensities