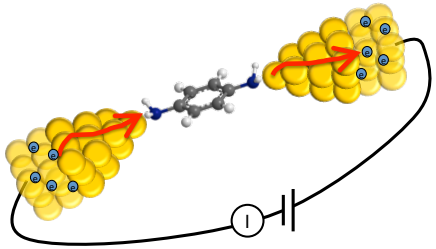
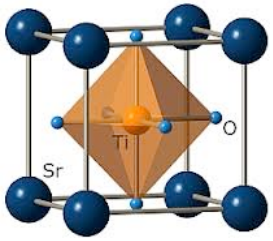
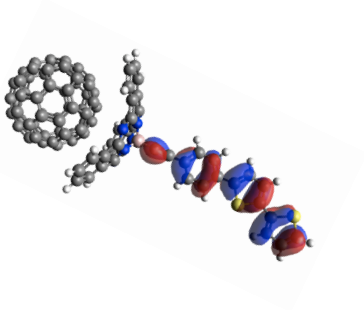
Molecular Foundry

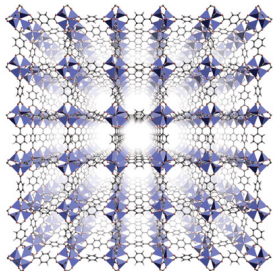
BERKELEY LAB

Complex Energy Materials with GW/BSE Approaches at the Molecular Foundry









Jeffrey B. Neaton
Director, Molecular Foundry
Lawrence Berkeley National Laboratory

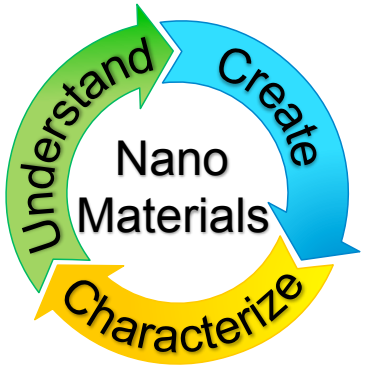
The Molecular Foundry:

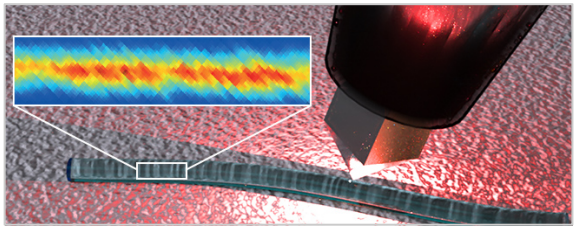
Knowledge-Based User Facility for Nanoscale Science @ LBNL

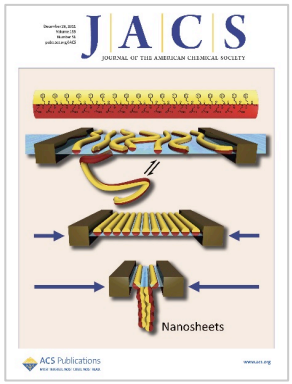
Molecular Foundry | BERKELEY LAB | U.S. DEPARTMENT OF ENERGY | Office of Science

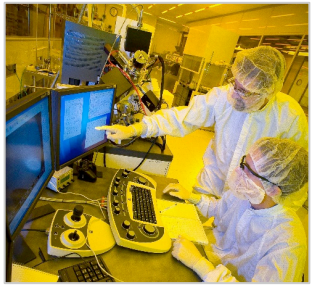
Use • Learn • Collaborate

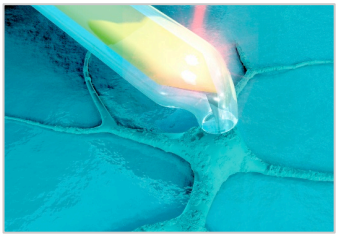
- Multidisciplinary expertise & culture
- State of the art equipment and labs
- 22 scientific staff; 14 technical staff
- Access: peer reviewed; free of charge
- Web: **foundry.lbl.gov**
- Proposal deadline: **March 31, 2014**

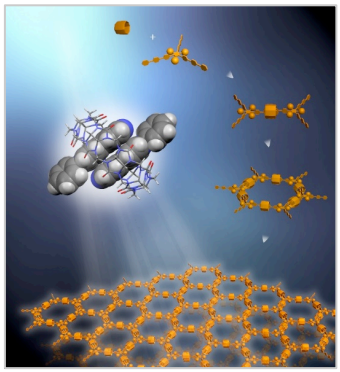


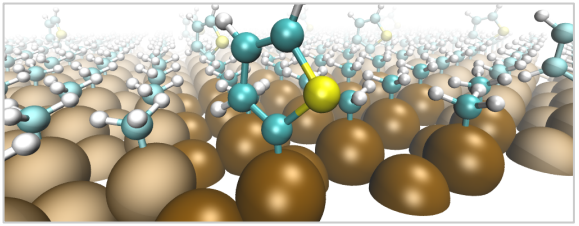




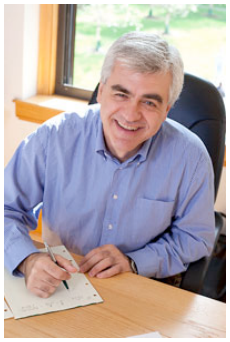








Foundry Users of BerkeleyGW



Tim Kaxiras,
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Per Hyldegaard
Chalmers

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Patrick Rinke
FHI-Berlin

Ferdinand Evers
KIT

Alberto Morgante
U of Trieste

Norbert Koch
Humboldt
University

Leeor Kronik,
Weizmann Institute of
Science

Latha Venkataraman
Columbia

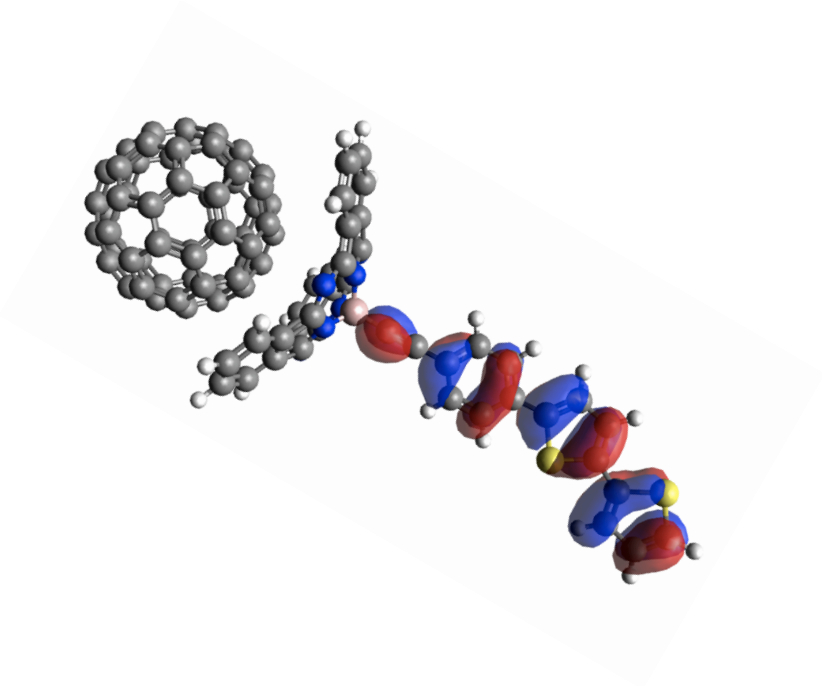
Stanimir Bonev,
LLNL

MATERIALS PROJECT

JCAP
JOINT CENTER FOR ARTIFICIAL PHOTOSYNTHESIS

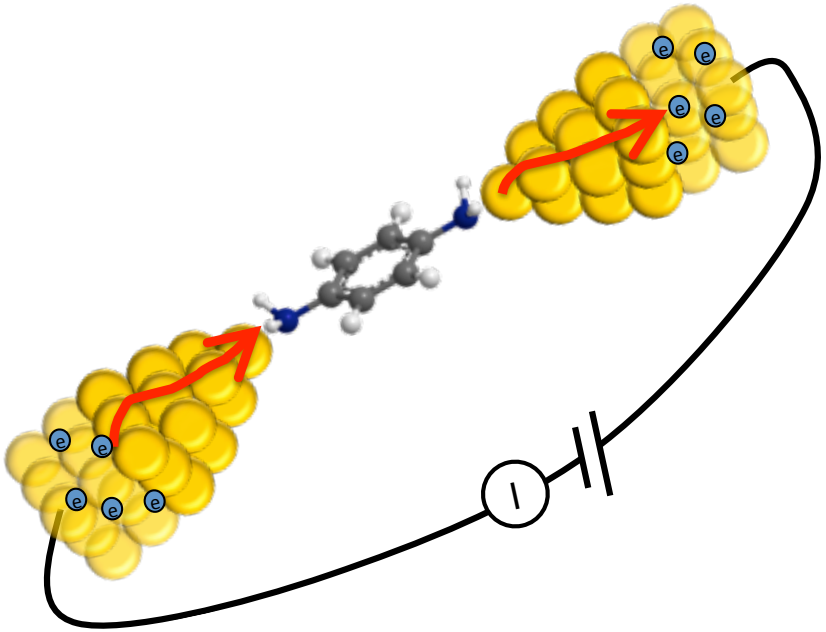
Ab Initio Studies of Organic-Based Interfaces

Organic Semiconductors



Excited states

Molecular Junctions



Charge Transport

Motivation: Organic Semiconductors in PV

- Organics → light, flexible, inexpensive, chemically-diverse
- Low efficiencies (~10%), prone to degradation
- Excited states & transport → critical to efficiency, stability

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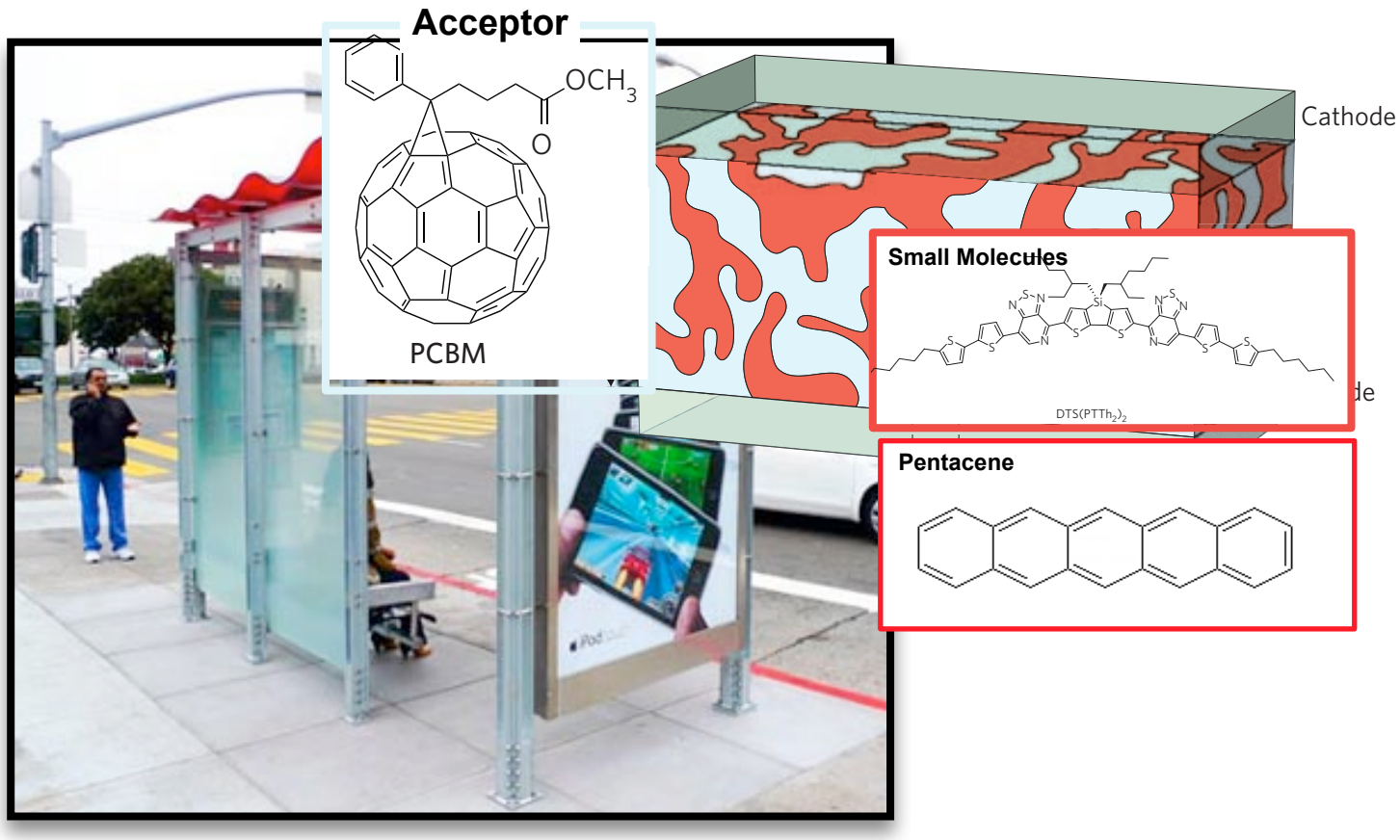

- Organics → light, flexible, inexpensive, chemically-diverse
- Low efficiencies (~10%), prone to degradation
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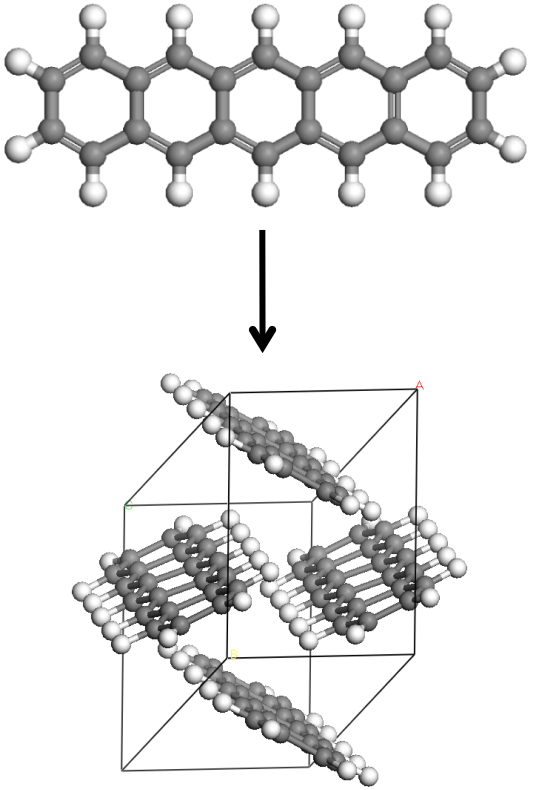
Solid-Phase Pentacene and PTCDA

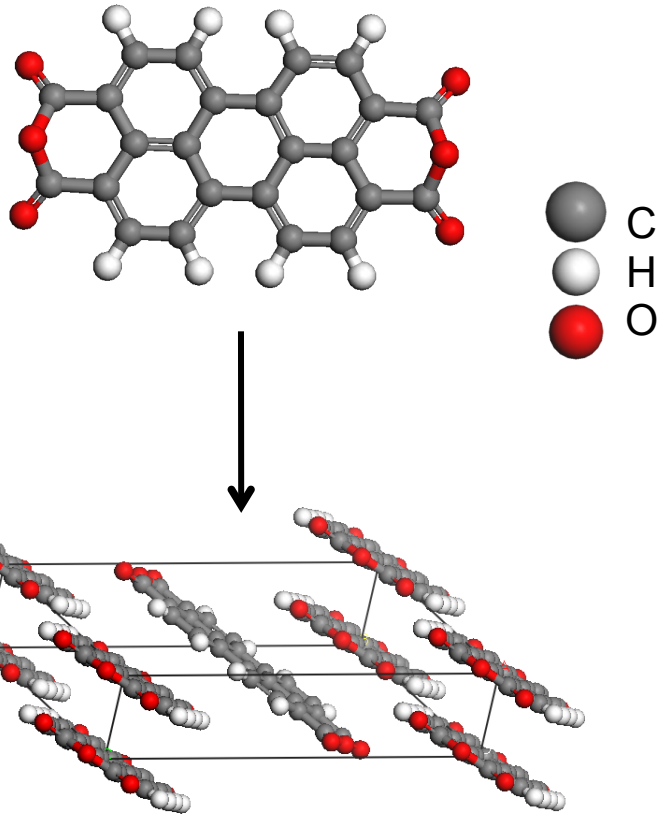
Pentacene ($C_{22}H_{14}$)

- Triclinic, $P\bar{1}$ space group
- 2 molecules/unit cell



PTCDA ($C_{24}H_8O_6$)

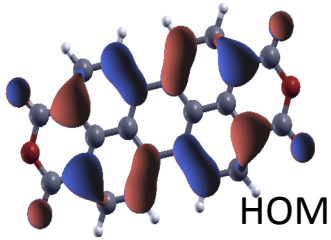
- Monoclinic, P2/m space group
- 2 molecules/unit cell

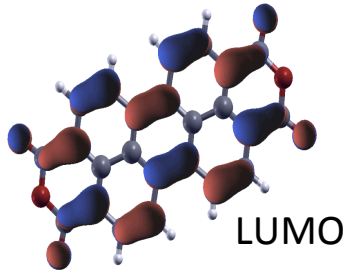


Systems optimized with lattice parameters fixed to experiment

PTCDA Ionization Potential with DFT & GW

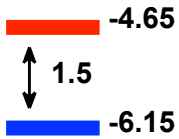
PTCDA





$E_{vac} = 0$

Vertical energies



PBE DFT

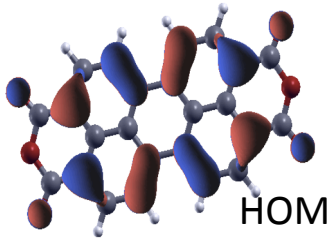
xpt.

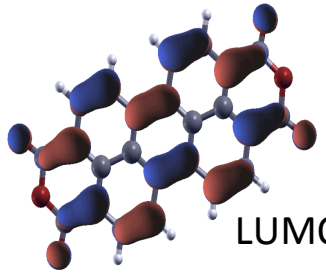
RMS error (100 molecules) for G_0W_0: 0.31 eV

Refaely-Abramson, Sharifzadeh, Govind, Autschbach, Neaton, Baer, Kronik PRL **109** 226405 (2012)
Sharifzadeh, Biller, Kronik, Neaton, PRB **85**, 125307(2012)
Sharifzadeh, Tamblyn, Doak, Darancet, Neaton, Europhys. J B **85**, 323 (2012)

PTCDA Ionization Potential with DFT & GW

PTCDA





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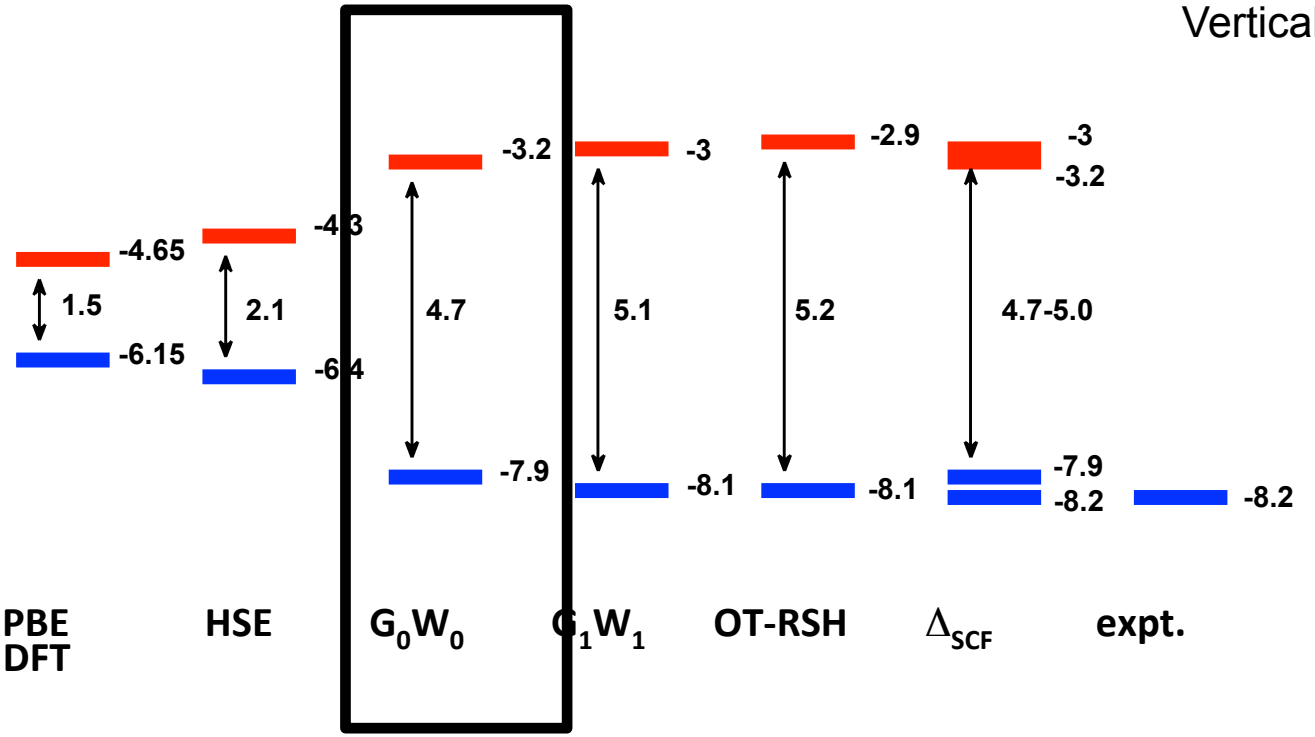

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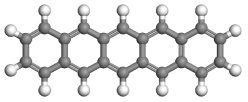
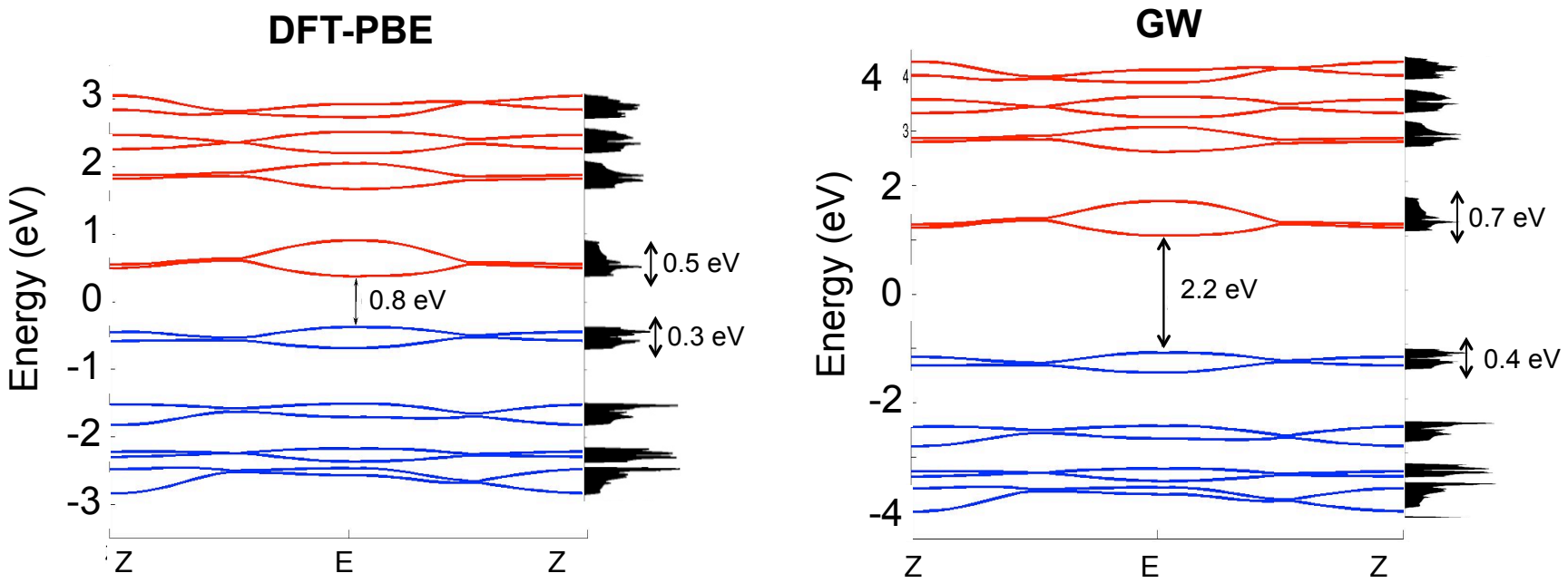
Band Structure and Densities of States: DFT vs GW

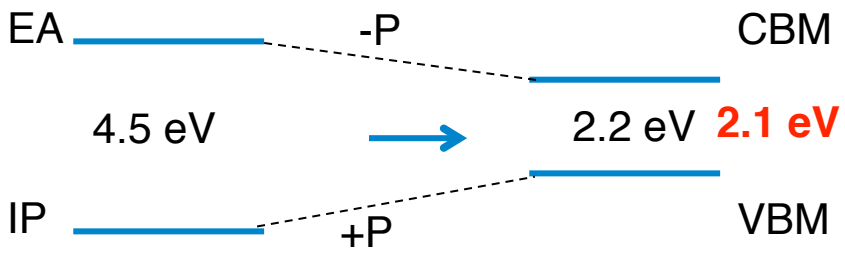
Pentacene



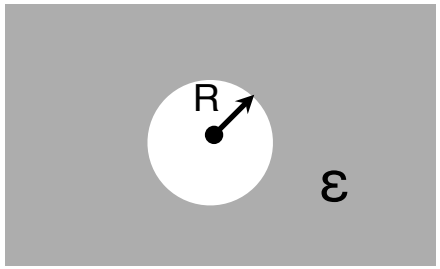


• Bulk gap of 2.2 eV rationalizes photoemission experiments

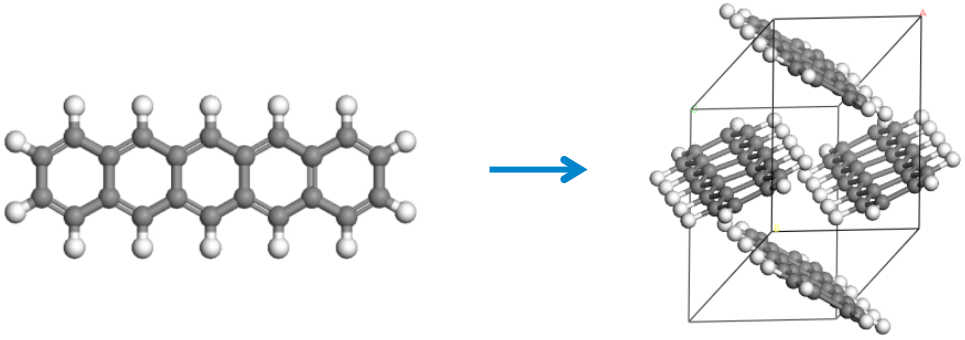
Quasiparticle Gaps and Polarization



Simple electrostatic model



Gap(solid) = Gap(molecule) – 2*P

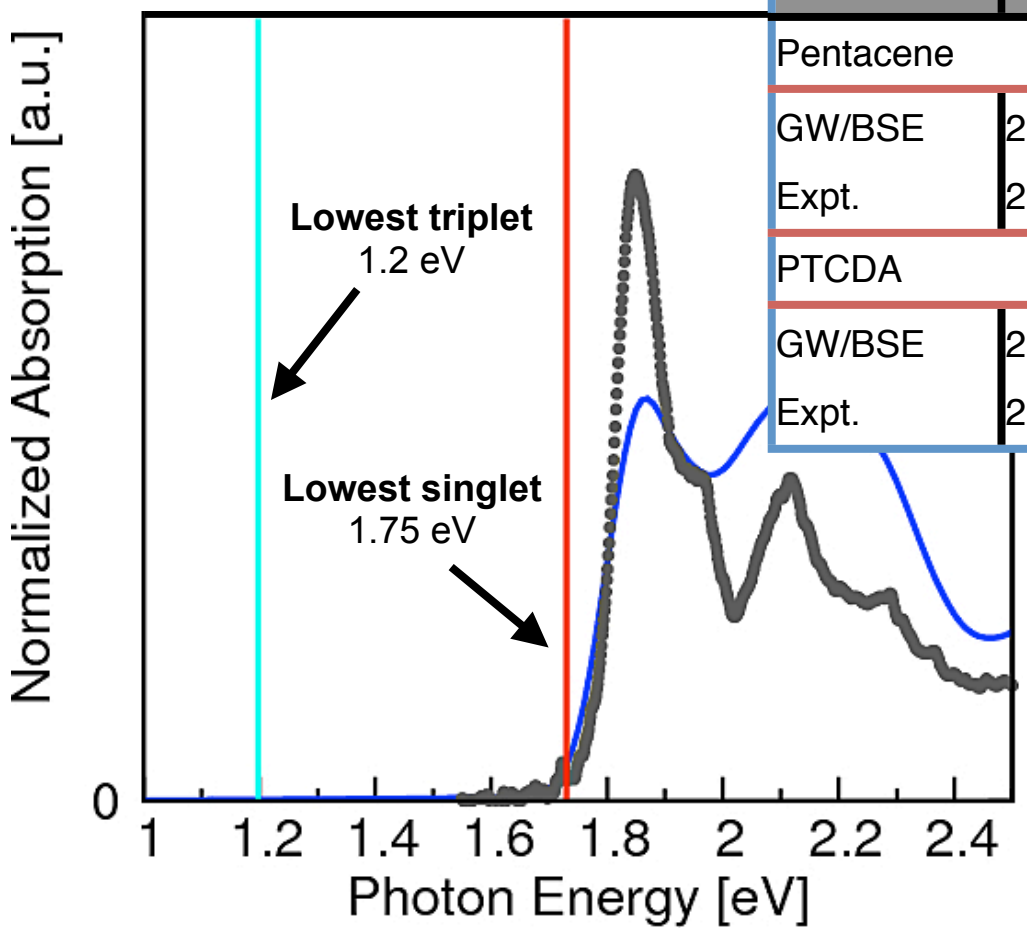


$$P = -\frac{q^2(\varepsilon - 1)}{2R\varepsilon}$$

P = 1.2 eV for pentacene

$$R = \left[\frac{3}{4\pi}\frac{V_{unit\_cell}}{2}\right]^{1/3}$$

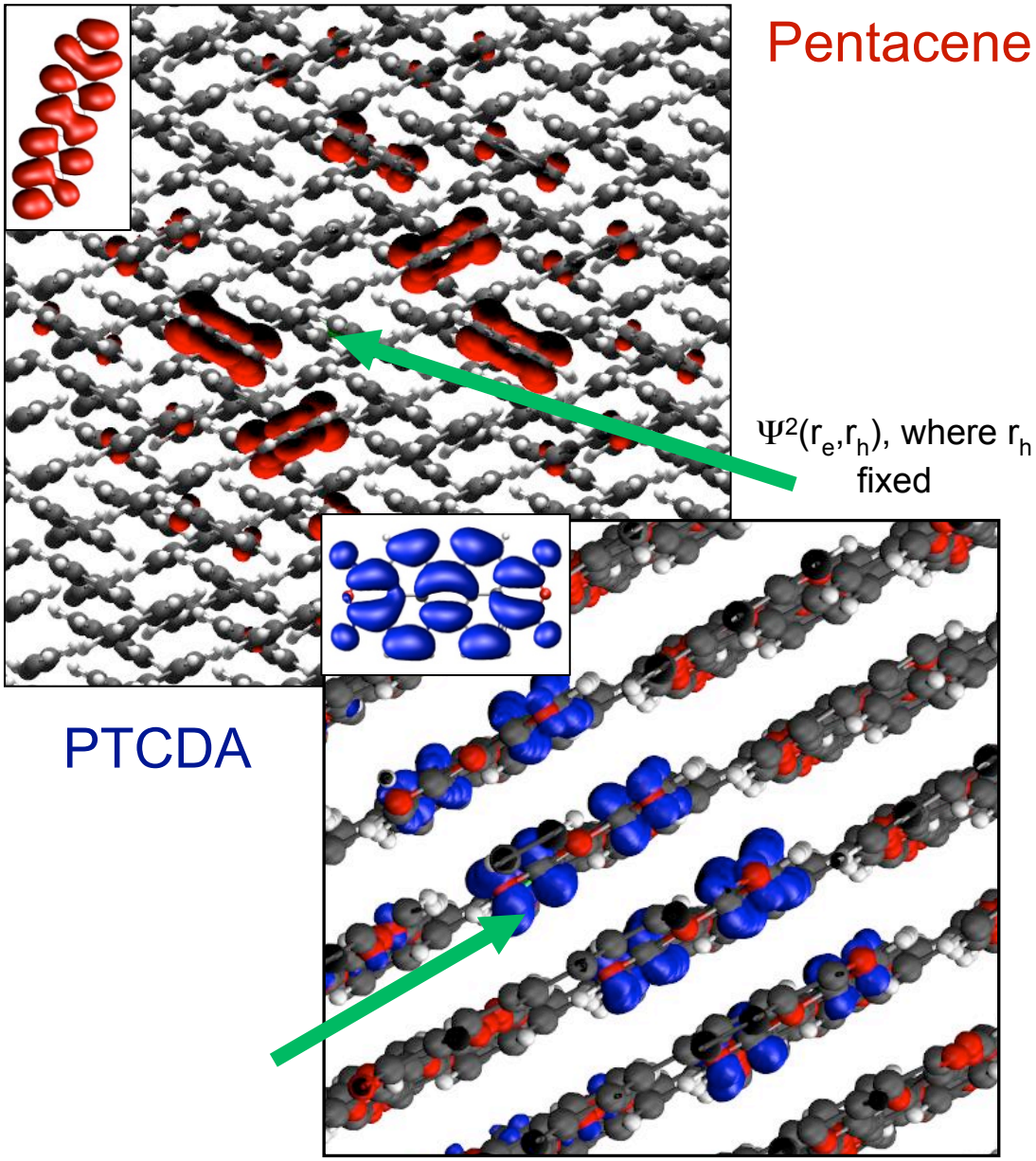
Pentacene Optical Absorption Spectrum



Optical Gap	Molecule	Crystal
Pentacene		
GW/BSE	2.2 eV	1.75 eV
Expt.	2.3 eV	1.8 eV
PTCDA		
GW/BSE	2.6 eV	2.1 eV
Expt.	2.6 eV	2.2 eV

Onset energies agree well with previous work:
Tiago,et al. *PRB* **67** (2003); Amborsch-Draxl,et al. New J. Phys.(2009);
Sharifzadeh, et al. *PRB* **85** (2012); Cudazzo, et al. *PRB* **86** (2012)

Low-Energy Excitons in PEN and PTCDA

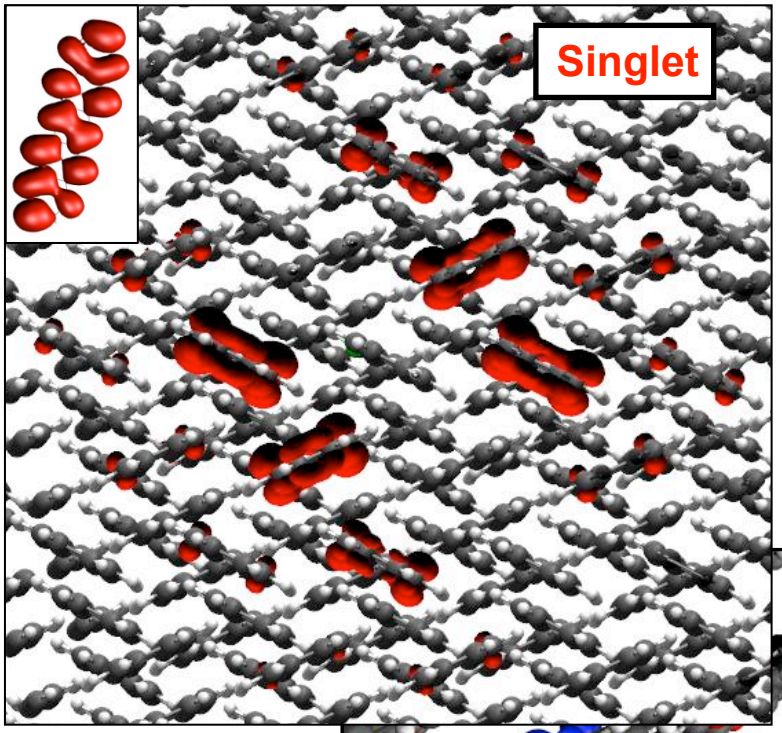


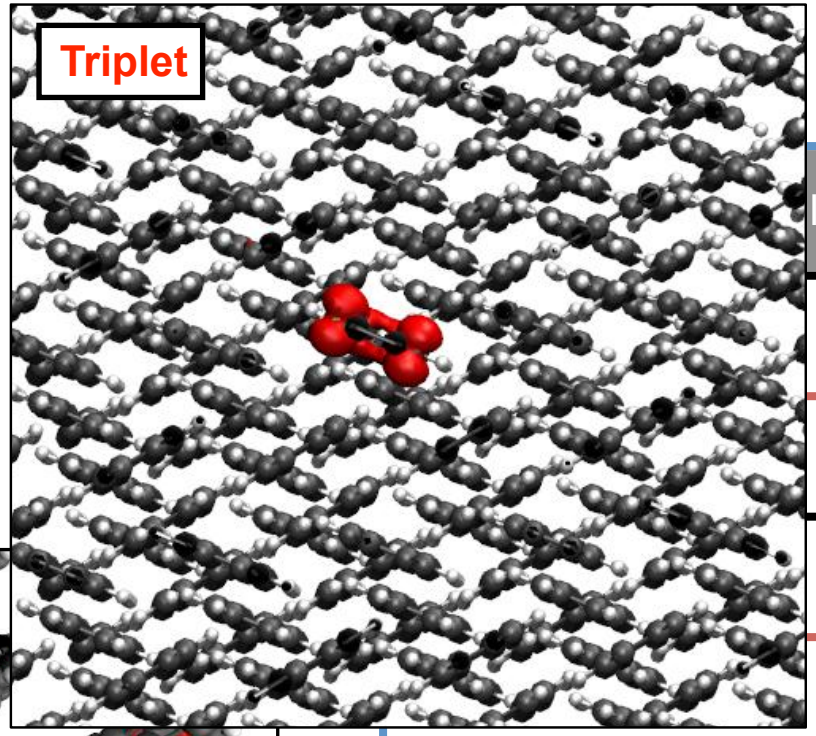
Δ(eV)	Molecule	X'tal
Pentacene		
GW/BSE	2.3	0.45
PTCDA		
GW/BSE	2.1	0.6

Simple screening provides good estimate of binding energy!

$$\Delta_{bulk} \sim 1/\varepsilon * \Delta_{mol}$$

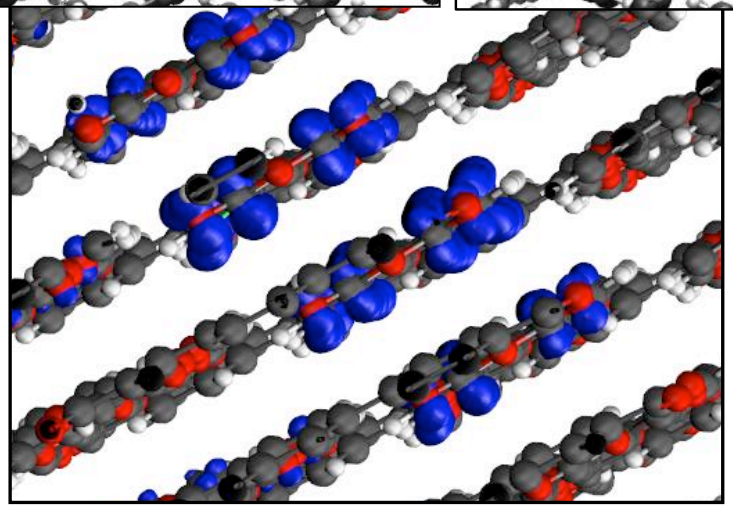
Low-Energy Excitons in PEN and PTCDA





le	X'tal
	0.45
	0.6

PTCDA



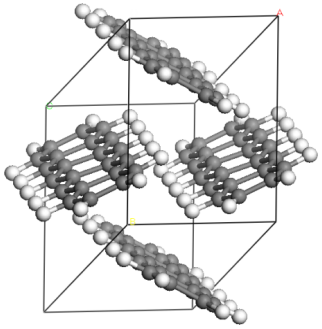
Electrostatics dominate binding energy!

$\Delta_{bulk} \sim 1/\varepsilon * \Delta_{mol}$

Are Low-Energy Excitons in Pentacene of Charge-Transfer Character?

Experimental disagreement

- Exciton dispersion: Schuster, et al Phys Rev. Lett (2007)
- Electroabsorption: Haas, et al PRB (2010); Sebastien, et al (1981)



Inversion symmetry:

no net dipole

Theoretical disagreement

- Semi-empirical studies: Yamagata, et al., JCP (2011)
- Many-body perturbation theory studies:

  Tiago, et al. *PRB* **67** (2003); Sharifzadeh,et al. *PRB* **85** (2012); Cudazzo, et al *PRB* **86** (2012)
- TDDFT calculations on clusters: Zimmerman, et al *JACS* **133** (2011)

Our approach

- Electron-hole correlation function to quantify charge transfer character
- Future → relate to observables (fission, transport, matrix elements ...)

Quantifying Charge Transfer

Probability that electron and hole are a distance r apart

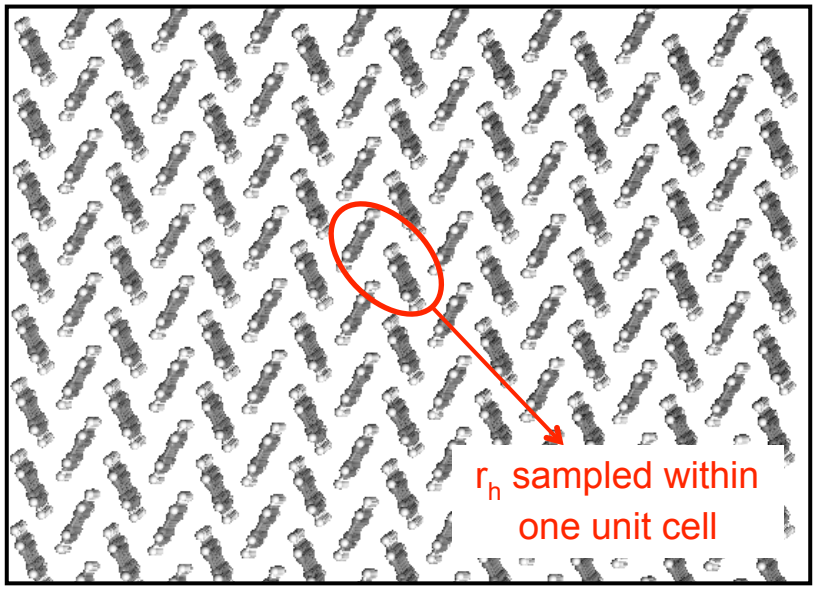
$$F(\mathbf{r}) = \int |\Psi(\mathbf{r}_e = \mathbf{r} - \mathbf{r}_h, \mathbf{r}_h)|^2 d^3\mathbf{r}_h$$

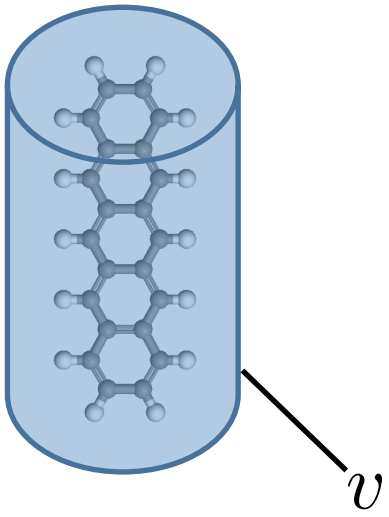
Average electron-hole distance

$$\langle \mathbf{r} \rangle = \int \mathbf{r} F(\mathbf{r}) d^3\mathbf{r}$$

Percent charge-transfer character

$$\eta = 1 - \int_v F(\mathbf{r}) d^3\mathbf{r}$$

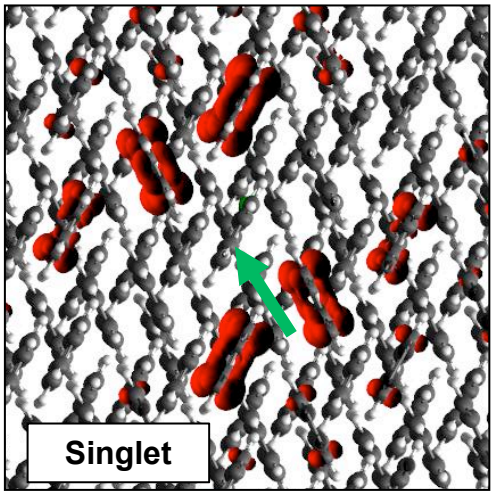


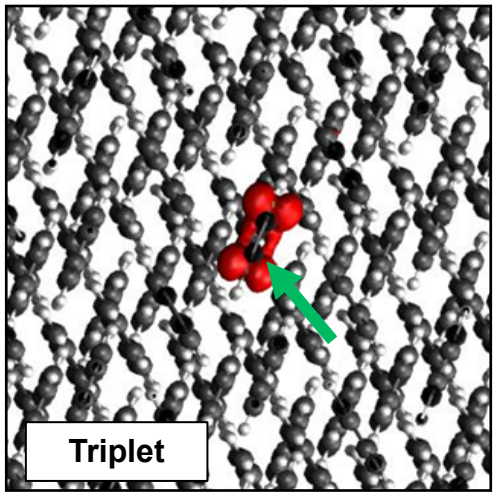


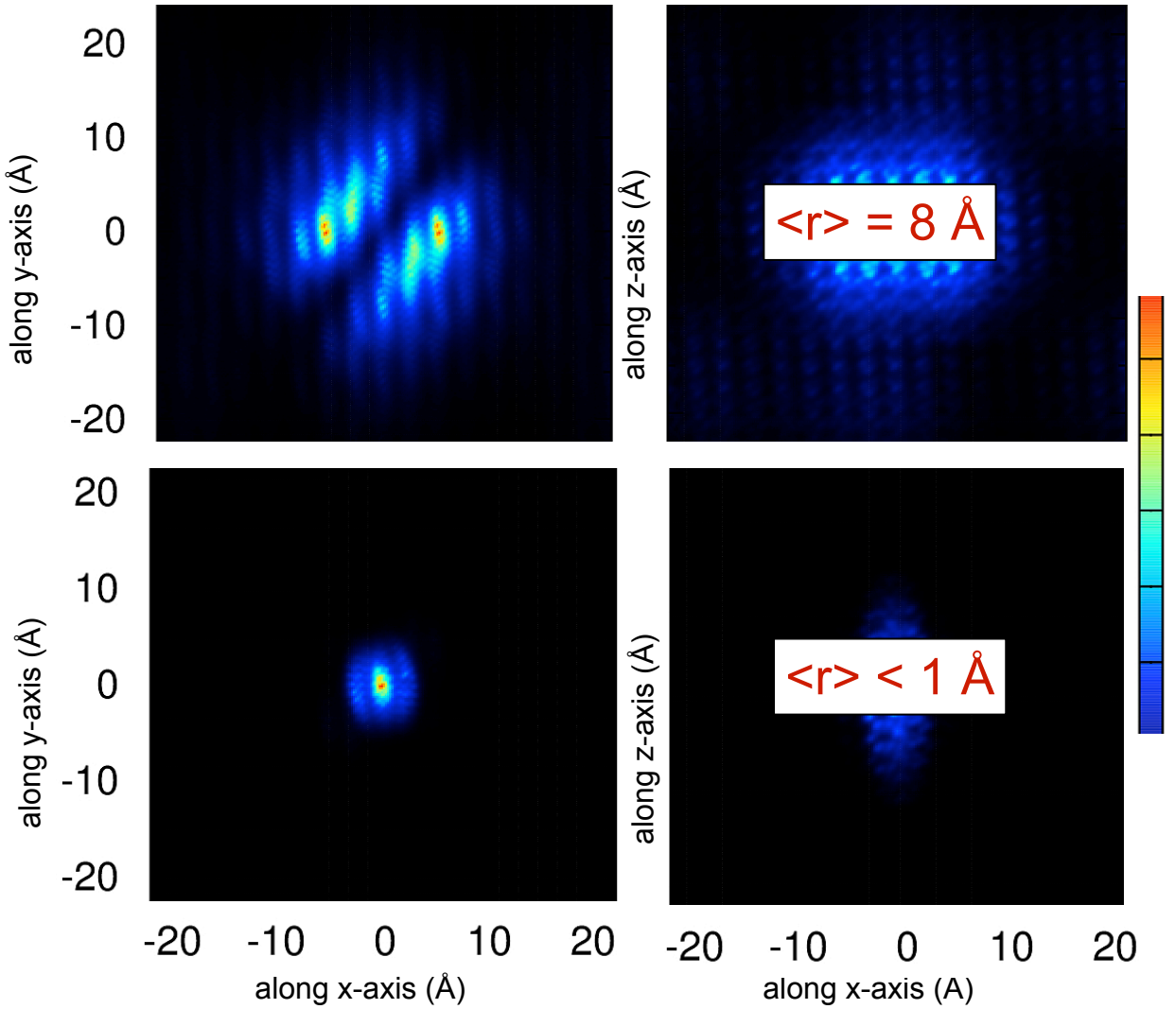
Lowest Energy Singlet and Triplet States in Pentacene

$\Psi^2(r_e,r_h)$, where r_h fixed

$$F(\mathbf{r}) = \int |\Psi(\mathbf{r}_e = \mathbf{r} - \mathbf{r}_h, \mathbf{r}_h)|^2 d^3\mathbf{r}_h$$

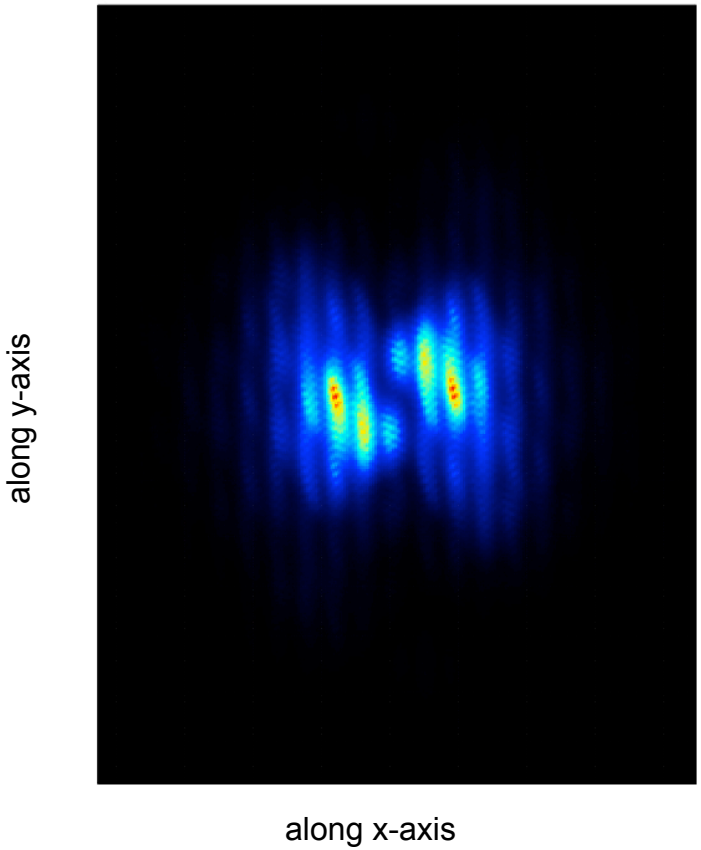


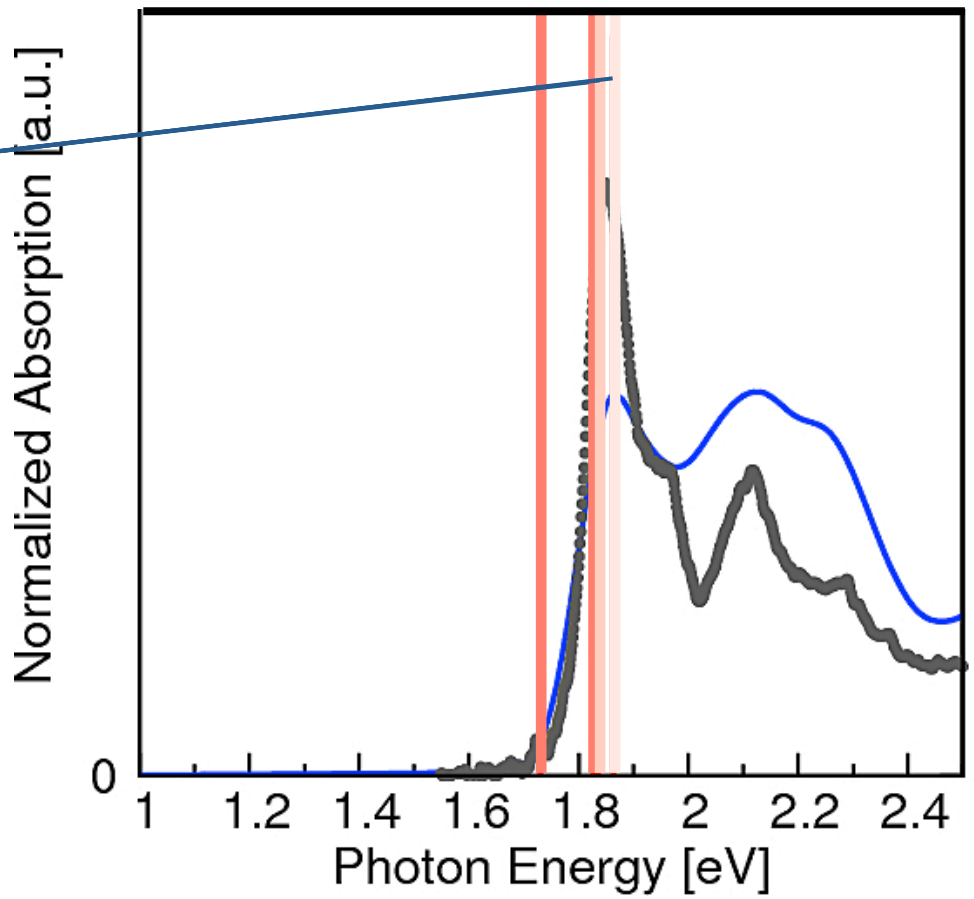




Charge-Transfer States at Higher Energies in Pentacene

$$F(\mathbf{r}) = \int |\Psi(\mathbf{r}_e = \mathbf{r} - \mathbf{r}_h, \mathbf{r}_h)|^2 d^3\mathbf{r}_h$$



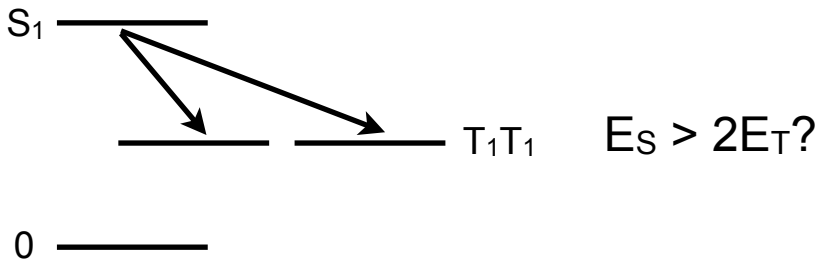


Percent CT Character:

82%

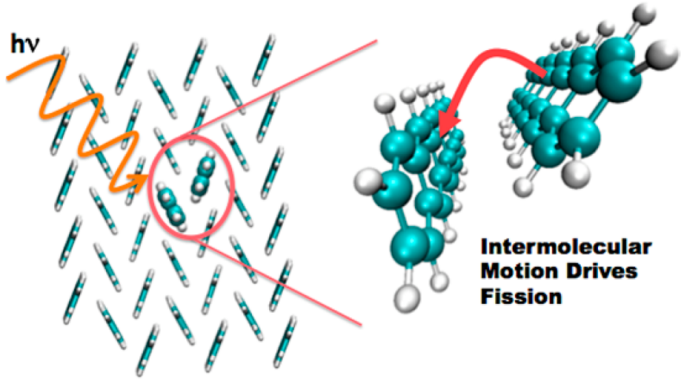
Sharifzadeh, Darancet, Kronik, Neaton, J. Phys. Chem. Lett. **4**, 2197 (2013)

Singlet fission in acene crystals & the role of charge transfer excited states



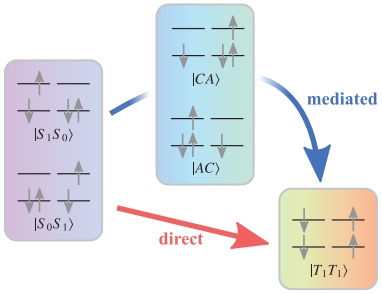
$E_S > 2E_T$?

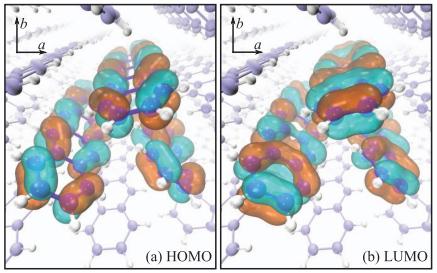
Fission via non-adiabatic vibrational coupling



Head-Gordon et al,
J. Am. Chem. Soc. **138**, 114103 (2013)

Fission via charge-transfer states

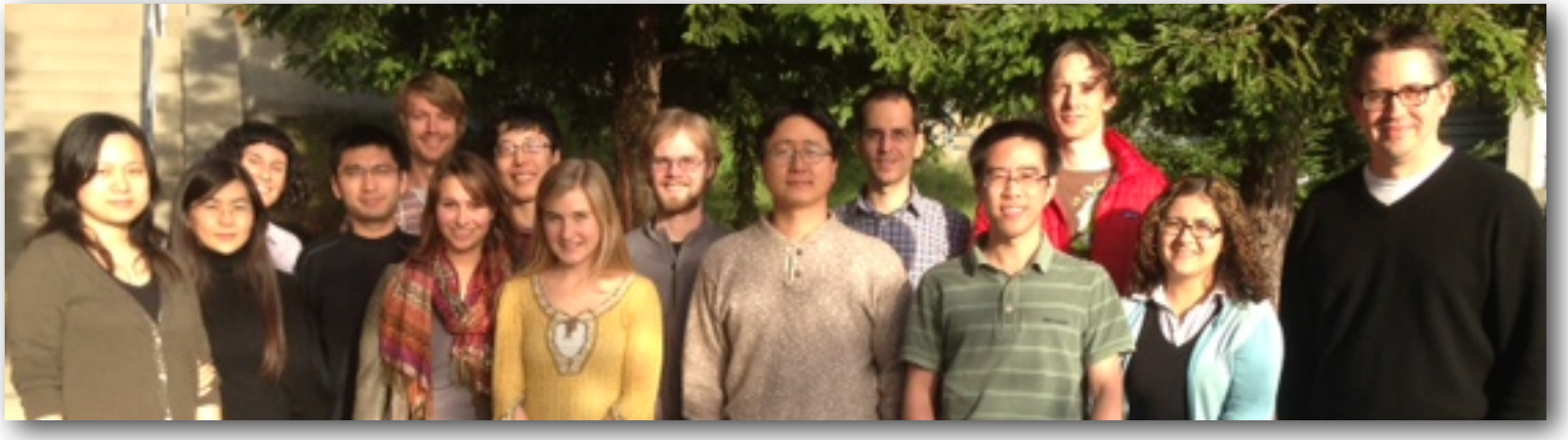




Reichmann et al, J. Chem. Phys. **138**, 114103 (2013)

Singlet fission: our solid-state calculations indicate that the singlet is “charge-transfer like”, suggesting a direct transfer mechanism is possible

Acknowledgements



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