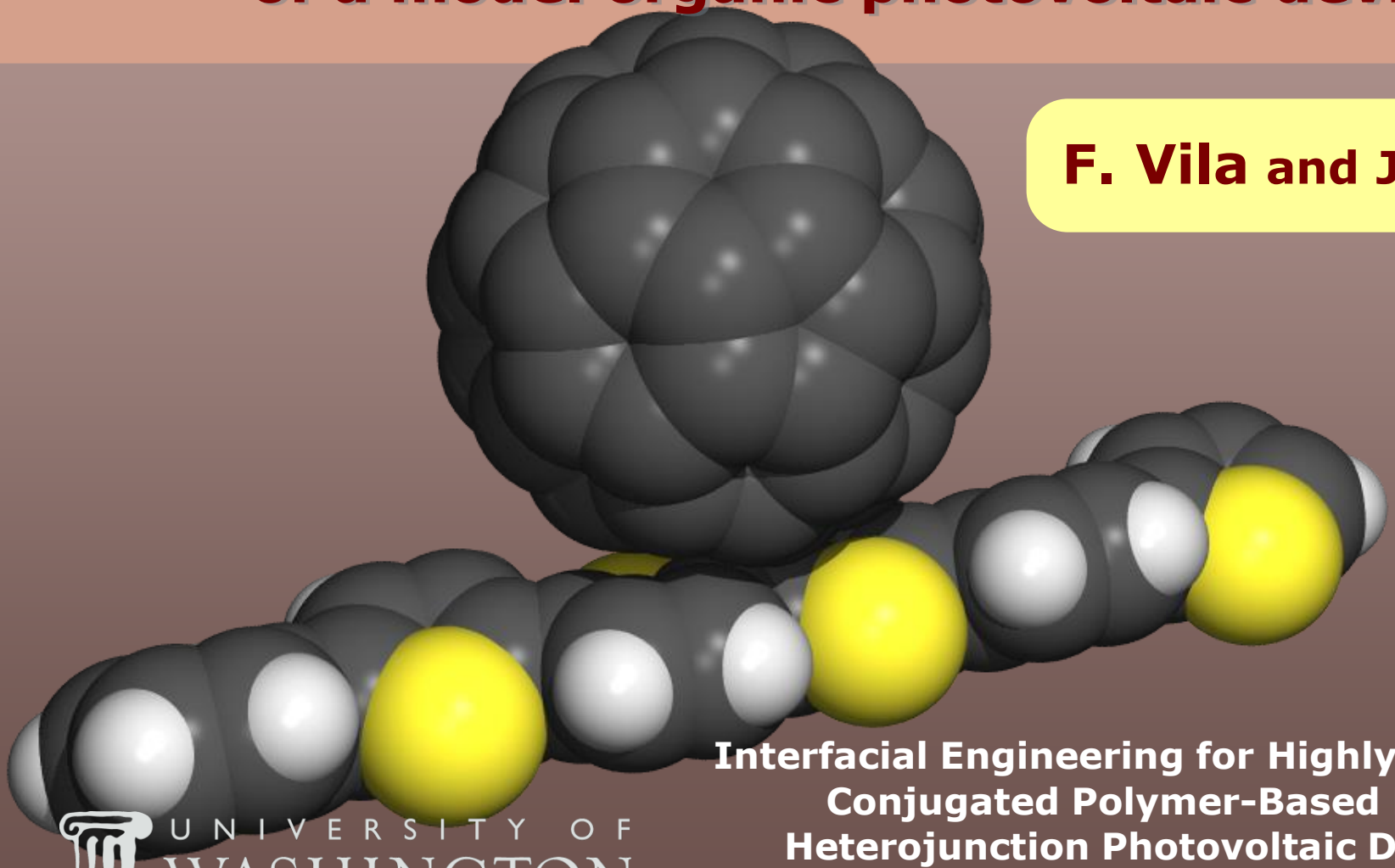
RT-TDDFT simulation of the optical properties of a model organic photovoltaic device

F. Vila and J. J Rehr



UNIVERSITY OF WASHINGTON

Interfacial Engineering for Highly Efficient-Conjugated Polymer-Based Bulk Heterojunction Photovoltaic Devices

DOE Grant DE-FG35-08G018024

Why Solar?

"Sunlight provides by far the largest of all carbon-neutral energy sources."

"Sunlight is a compelling solution to our need for clean, abundant sources of energy in the future."

Why Organic?

""Plastic" solar cells made from molecular, polymeric, or nanoparticle-based structures could provide flexible, inexpensive, conformal, low-cost solar electricity systems."

Why Theory?

"... new theoretical tools are required to guide and interpret experiment and assist in the design of molecules, materials, and systems."

BASIC RESEARCH NEEDS FOR SOLAR ENERGY UTILIZATION.
(Report on the Basic Energy Sciences Workshop on Solar Energy Utilization, DOE, 2005)

Aims

Theoretically study the initial process of light harvesting in organic photovoltaic devices:

Optical Absorption

1. **Develop simple structural models of organic photovoltaic devices**
2. **Calculate the optical absorption of photovoltaic components using RT-TDDFT**
3. **Explore spectral trends induced by changes in the structure of the components**

Real-Time Time Dependent DFT

Direct numerical integration of the time-dependent Kohn-Sham equations in a time-dependent external electric field:

$$i\frac{\partial \Psi}{\partial t} = H(t)\,\Psi \qquad \Psi(t) = T\,\exp\left(-i\int_0^t H(t')dt'\right)\Psi(0)$$

$$H = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r},t) + V_H[\rho](\mathbf{r},t) + V_{xc}[\rho](\mathbf{r},t)$$

Optical properties are determined from the total dipole moment:

$$\mathbf{p}(t) = \int \rho(\mathbf{r},t)\,\mathbf{r}\,d^3\mathbf{r}$$

$$\underbrace{\chi^{(1)}_{ij}(\omega) = \delta p_i(\omega)/E_j(\omega) = \alpha_{ij}(\omega)}_{\text{Linear Response}} \qquad \underbrace{\sigma(\omega) \sim \omega\,\mathbf{Im}\,\langle\alpha(\omega)\rangle}_{\text{Absorption}}$$

Yabana and Bertsch, Phys. Rev. B 54, 4484 (1996)

Numerical Real-Time Evolution

The ground state density ρ_0, overlap matrix S and Hamiltonian matrix $H(t)$ are evaluated at each time-step using SIESTA:

$$i\frac{\partial c(t)}{\partial t} = S^{-1}H(t)\underbrace{c(t)}_{\text{Orbital coefficients}}$$

Soler *et al.* J. Phys.: Condens. Matter 14, 2745 (2002)

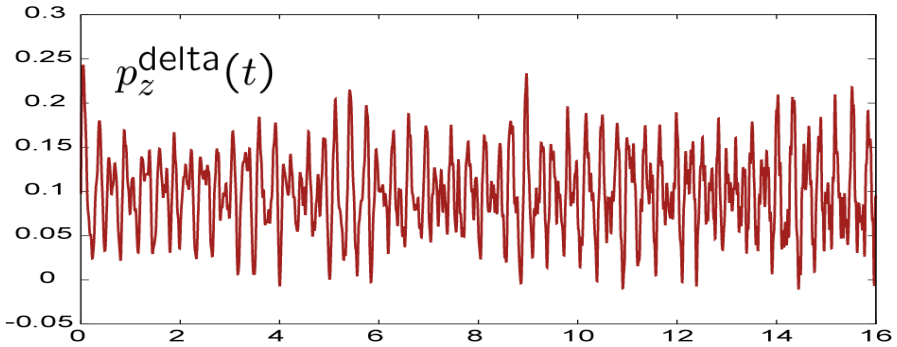
Accurate and stable time evolution achieved using the Crank-Nicholson approximation:

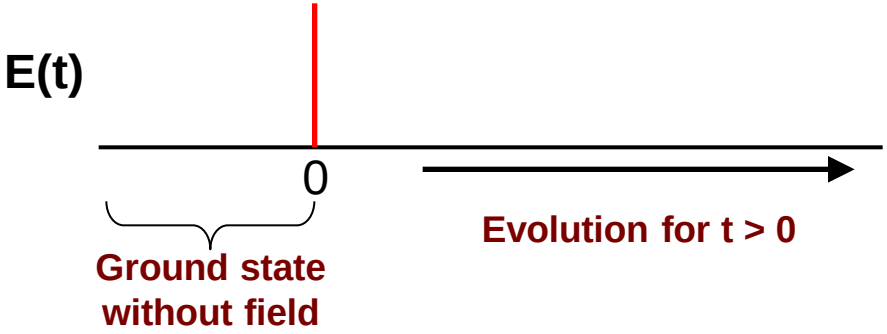
$$c(t+\Delta t) = \frac{1 - iS^{-1}H(t)\Delta t/2}{1 + iS^{-1}H(t)\Delta t/2}c(t) + \mathcal{O}(\Delta t^2)$$

Tsolakidis *et al*. Phys. Rev. B 66, 235416 (2002)

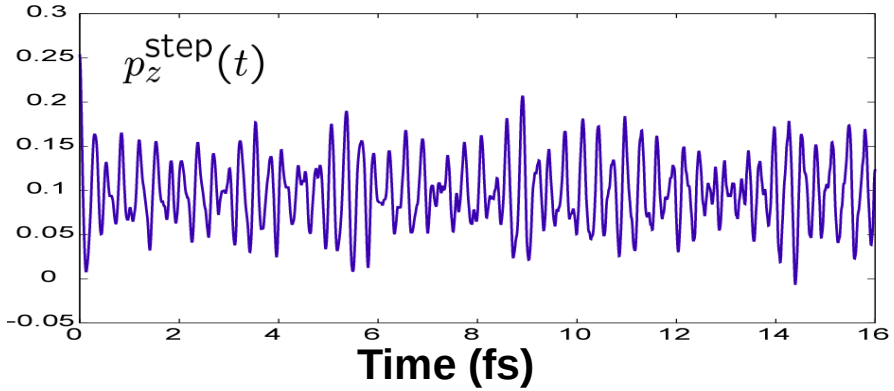
Optical Absorption in CO (Y. Takimoto)

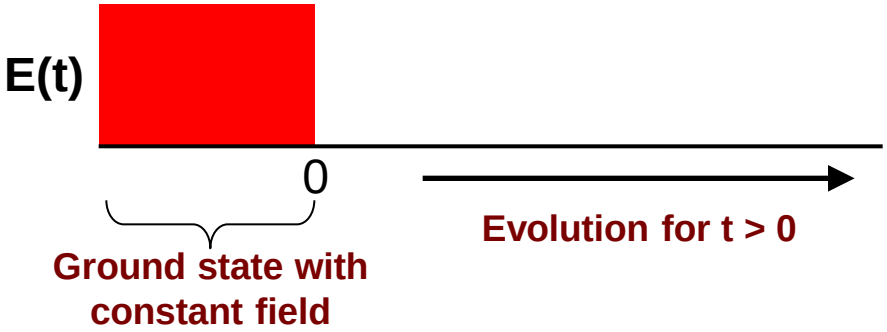
Delta Function (Unit Impulse at t=0)





Step Function (Turn-off Constant E at t=0)

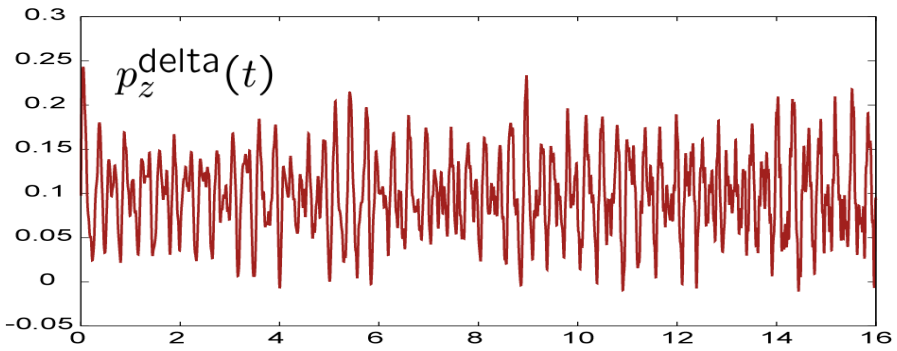


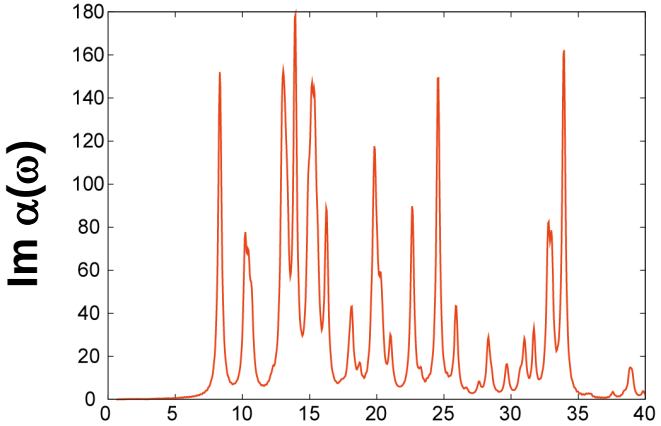


Takimoto *et al.* J. Chem. Phys. 127, 154114 (2007)

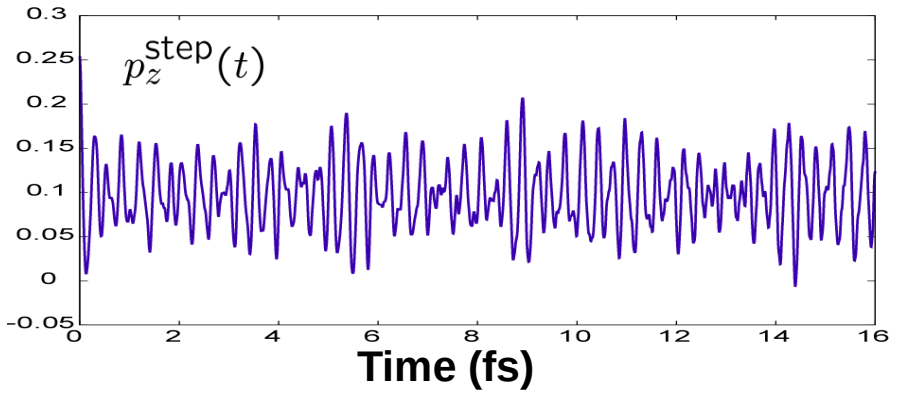
Optical Absorption in CO (Y. Takimoto)

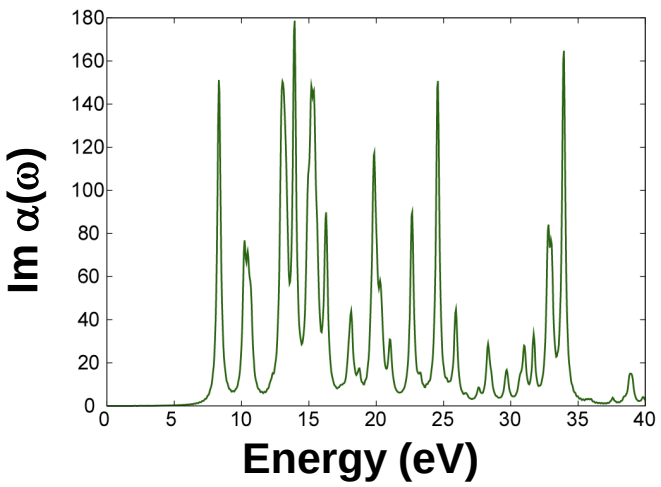
Delta Function (Unit Impulse at t=0)





Step Function (Turn-off Constant E at t=0)

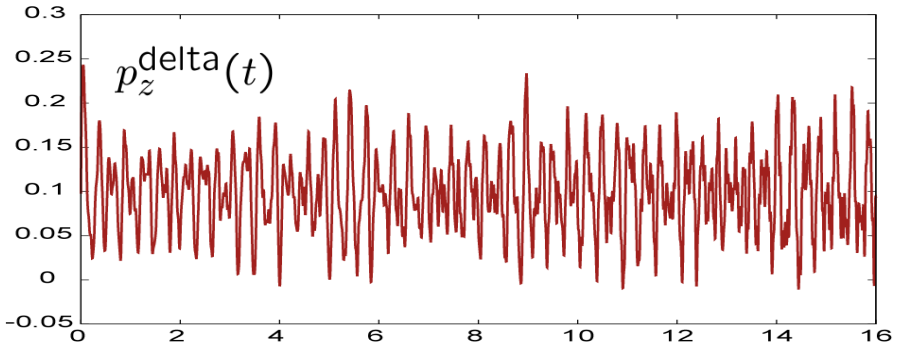




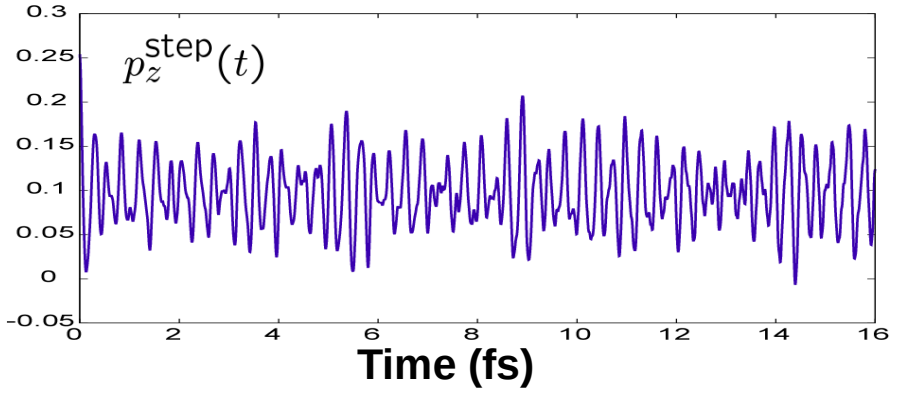
Takimoto *et al.* J. Chem. Phys. 127, 154114 (2007)

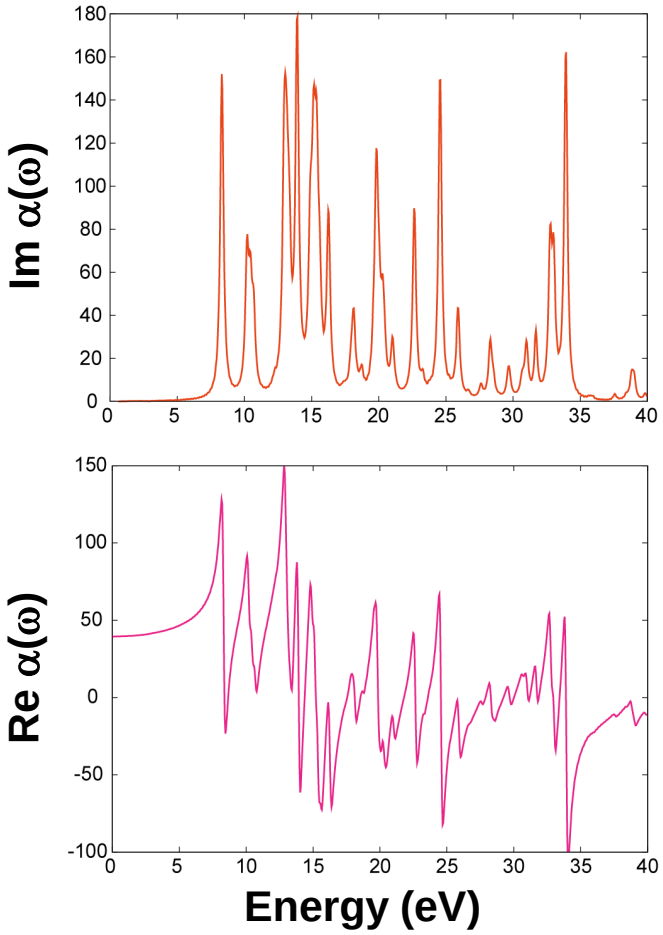
Optical Absorption in CO (Y. Takimoto)

Delta Function (Unit Impulse at t=0)



Step Function (Turn-off Constant E at t=0)



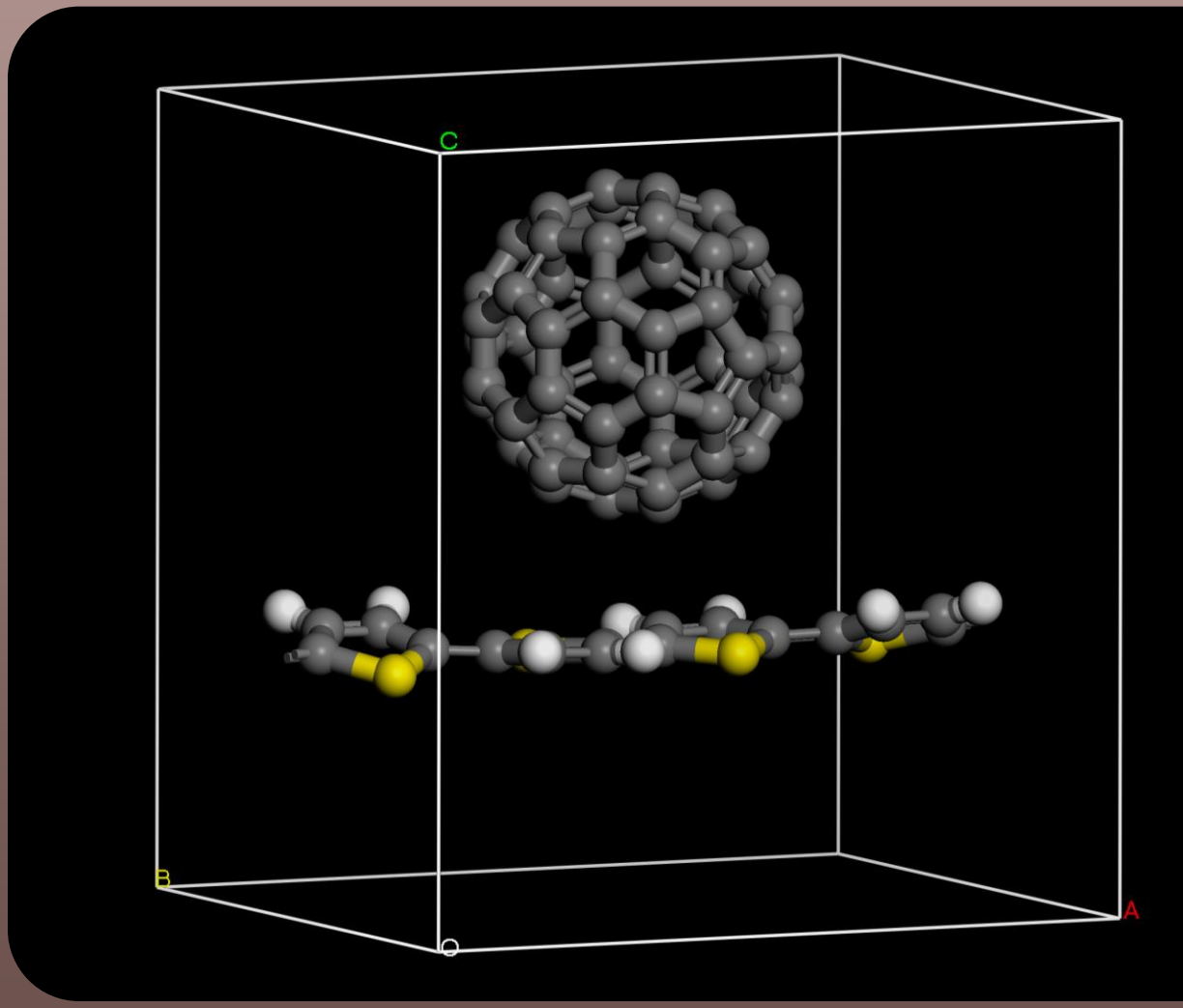


Takimoto *et al.* J. Chem. Phys. 127, 154114 (2007)

Computational Details: RT-Siesta

- Energy Resolution: 0.2 eV
- Time Step: 0.01 fs
- # of Time Steps: 1068
- XC Functional: PBE
- Basis Set: Double Zeta + Polarization
- Energy Shift: 1 meV (Radii ~ 9 au)
- Mesh Cutoff: 120 Ry
- Pseudopotentials: Troullier-Martins

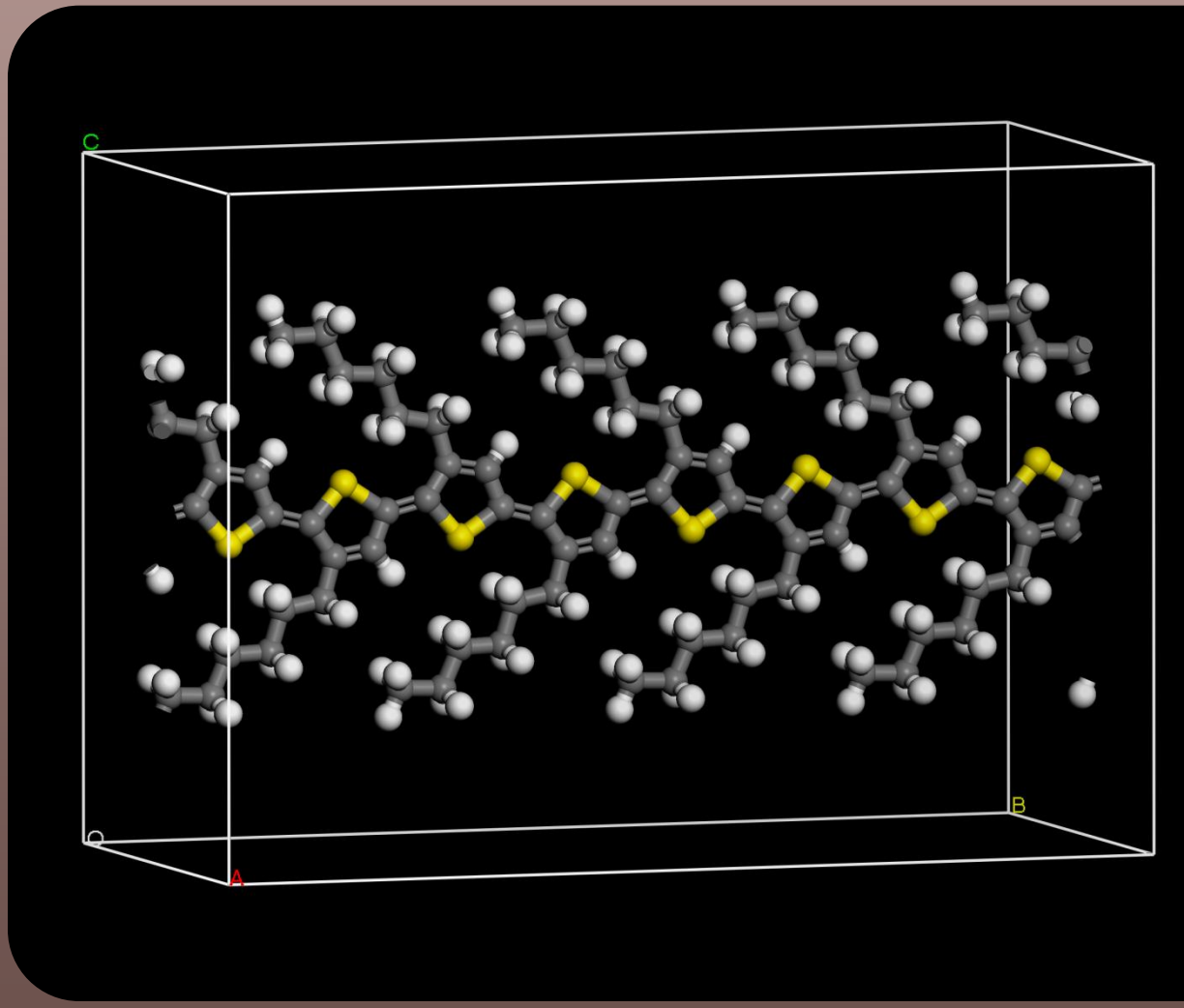
Model Structures (VASP, PBC)



C_{60} on poly-Thiophene (pT)

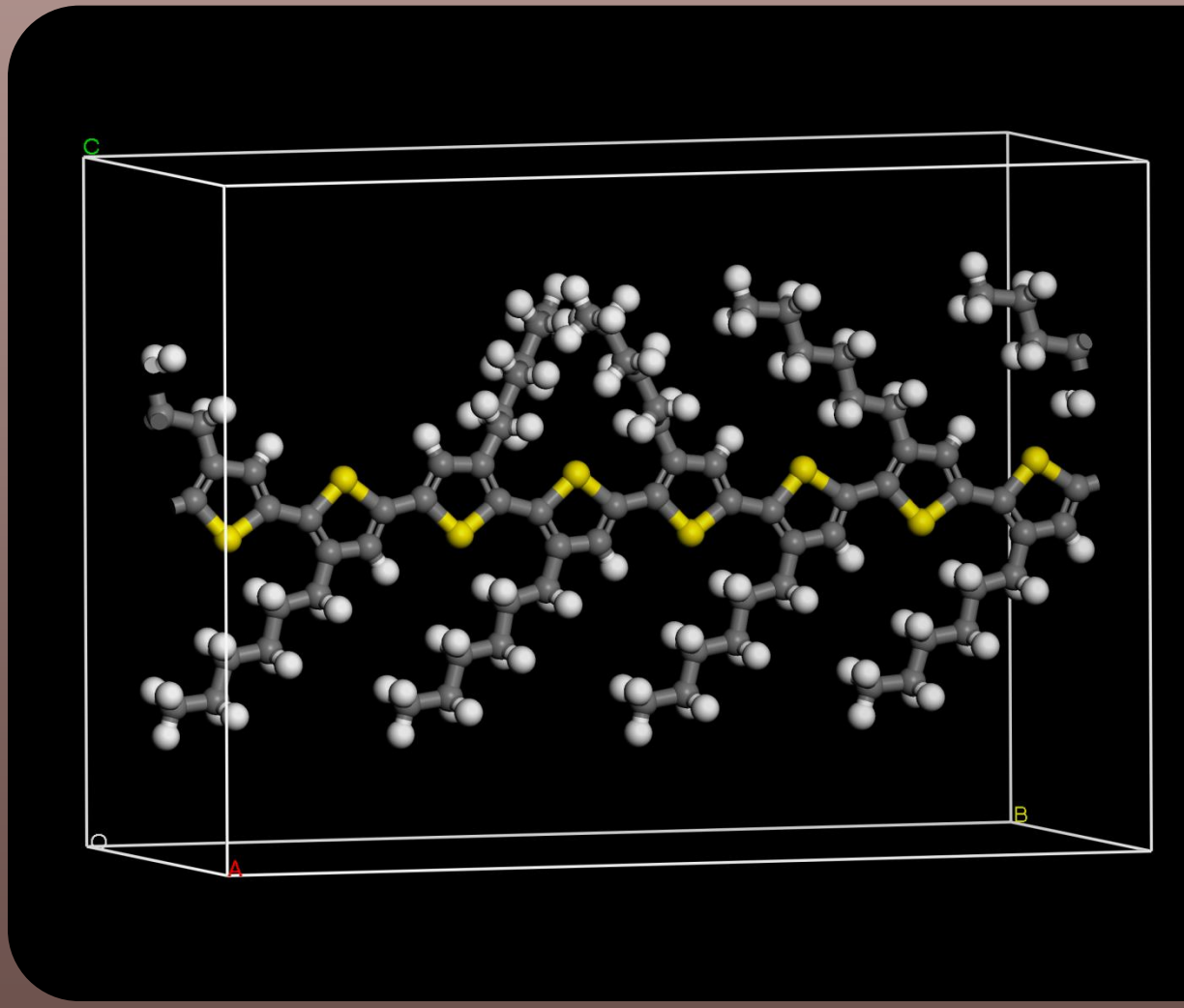
A model for a PCBM-p3TH heterojunction device

Model Structures (VASP, PBC)



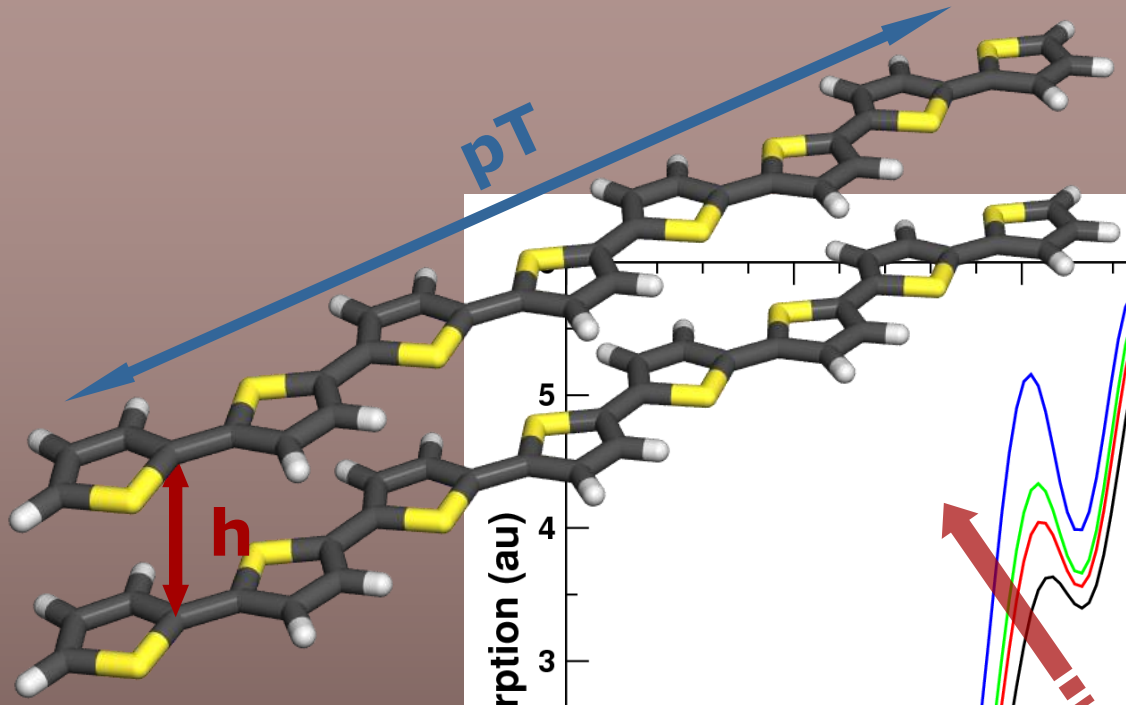
A model for a regioregular (rr) p3TH

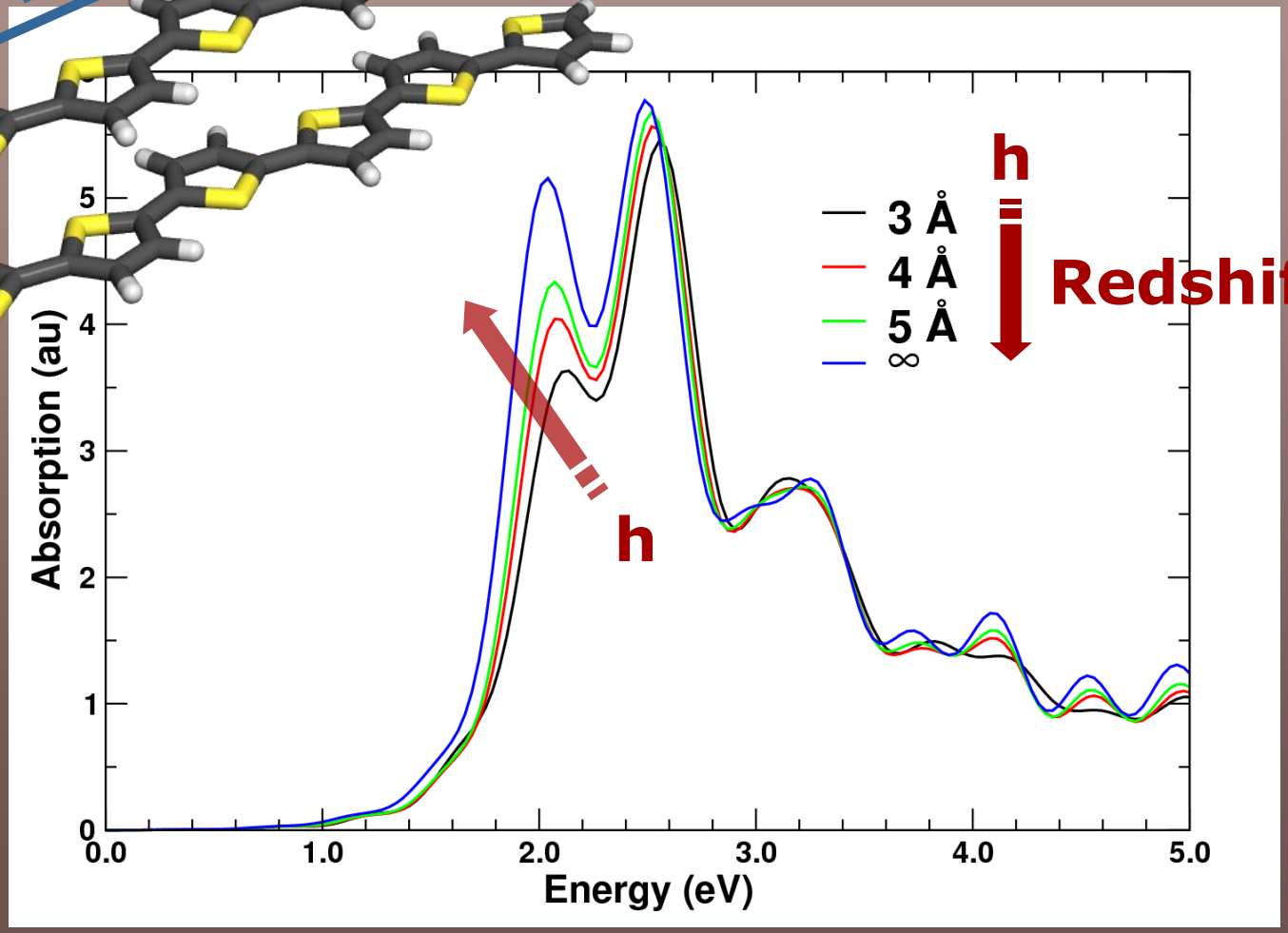
Model Structures (VASP, PBC)



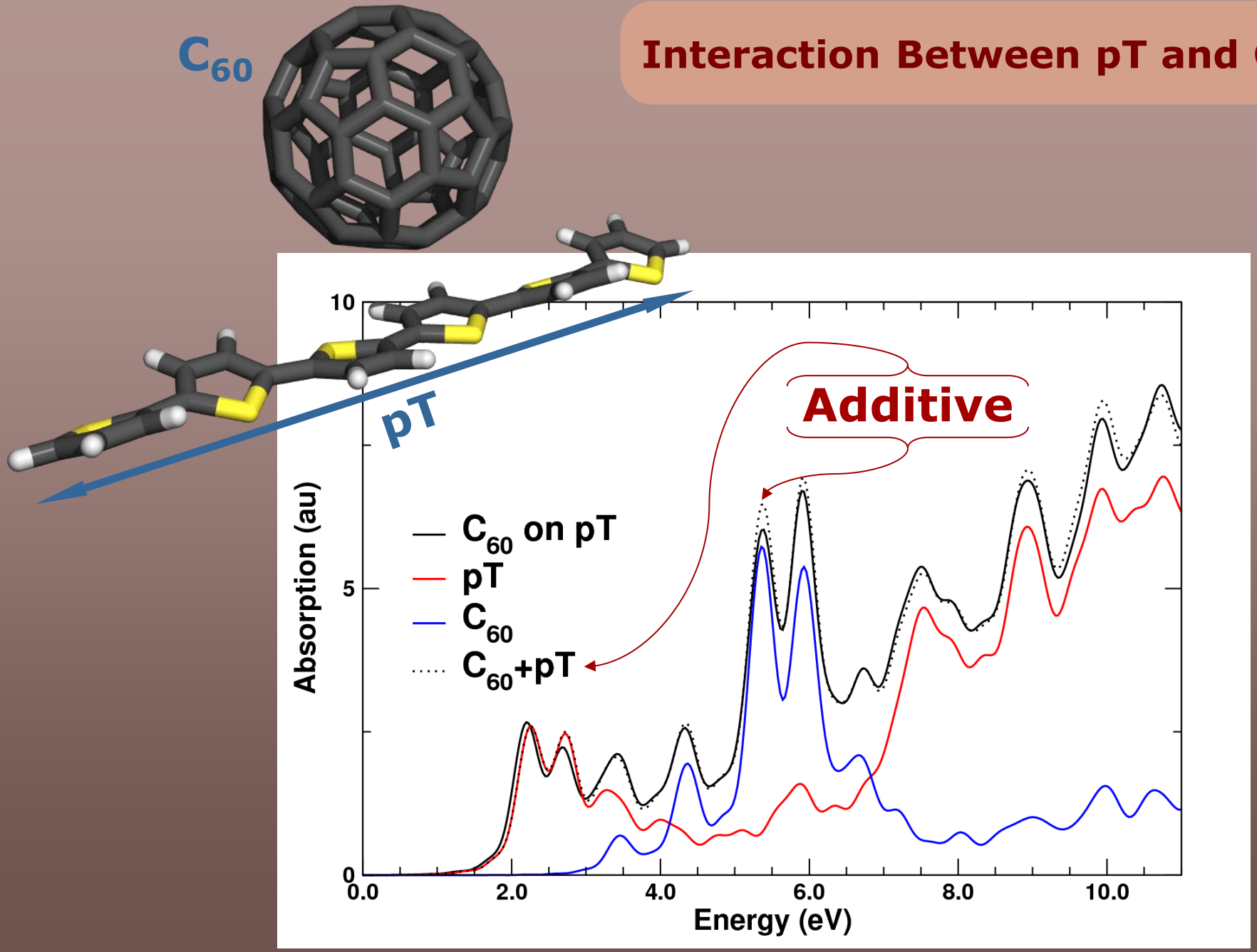
A model for a regiorandom (ra) p3TH

Interaction Between pT Chains

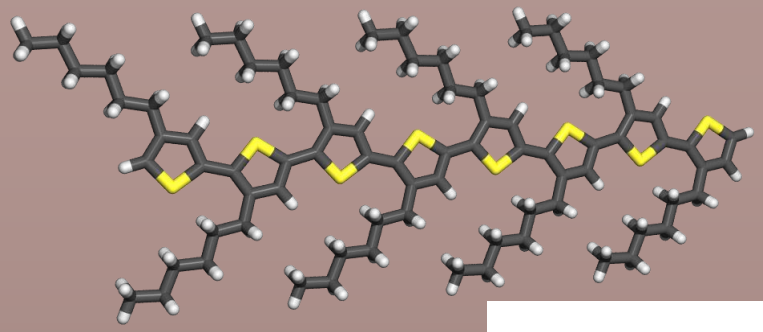




Interaction Between pT and C_{60}



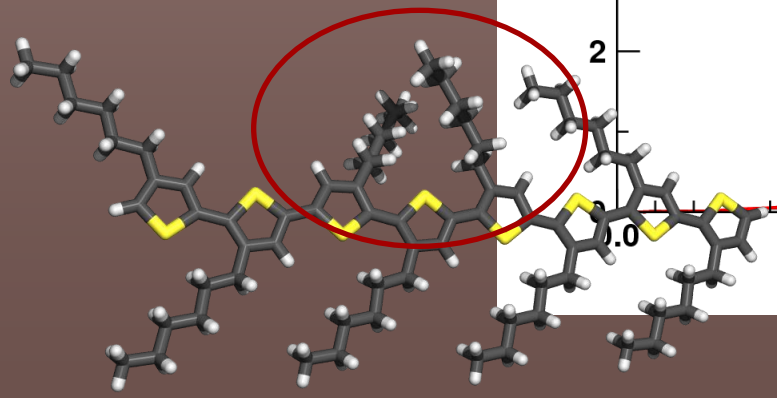
Effect of Hexyl Chains in p3HT

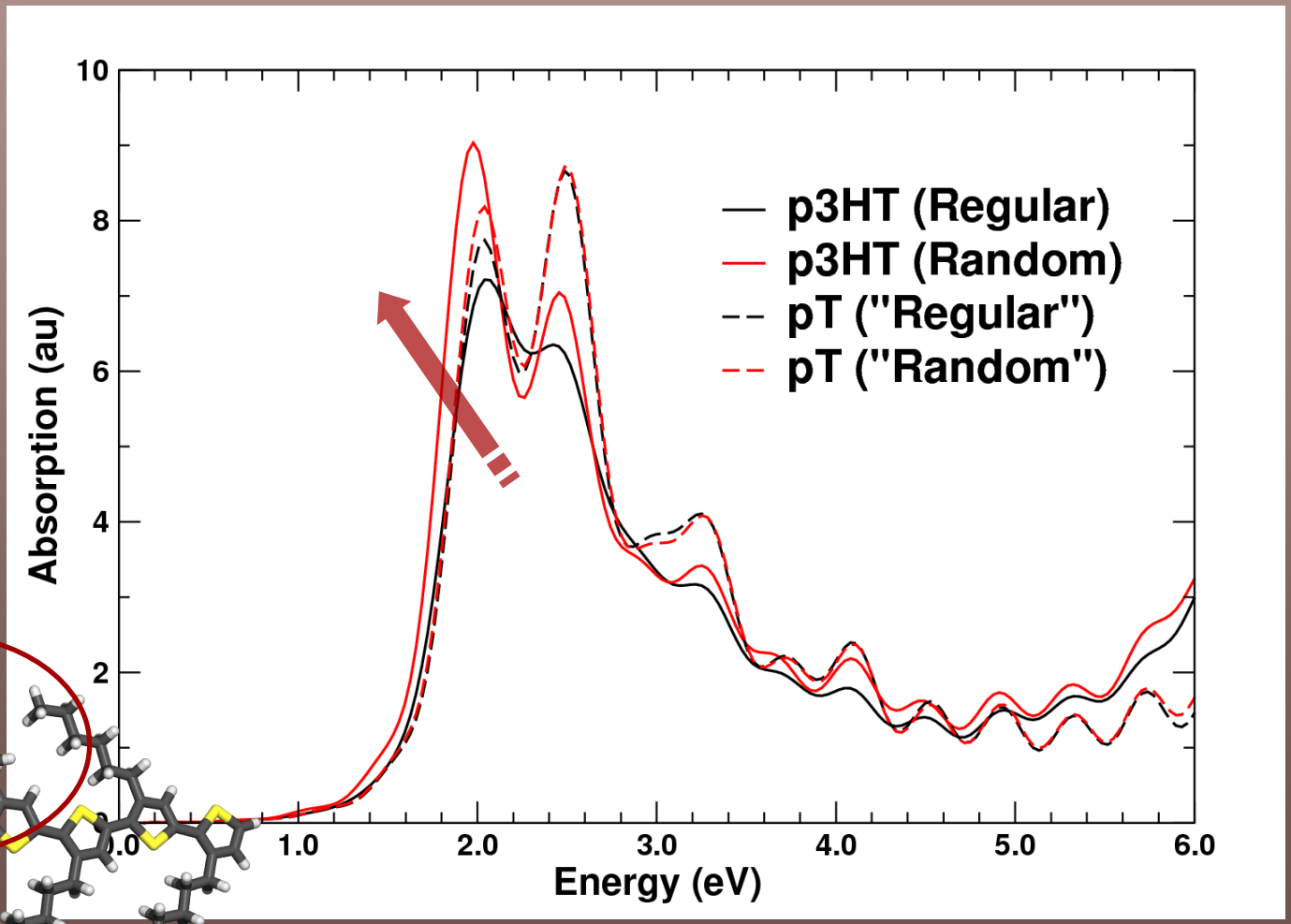


p3HT (Regular)

Redshift

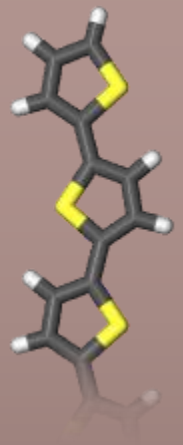
p3HT (Random)





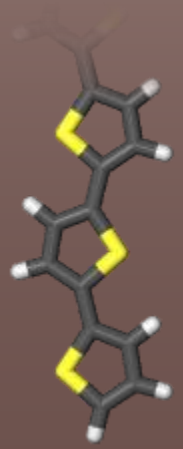
Effect of pT Chain Length

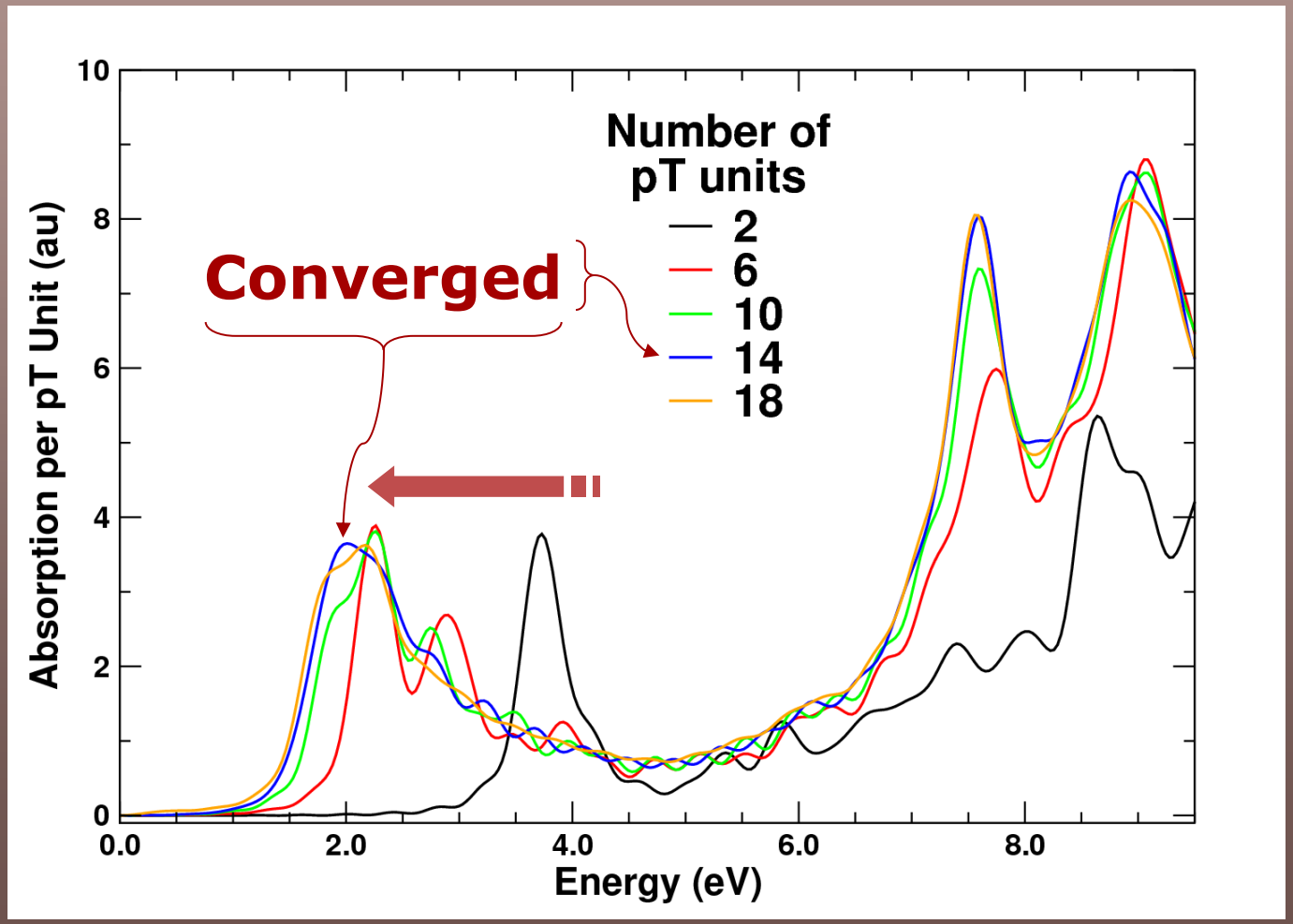
pT



18

2

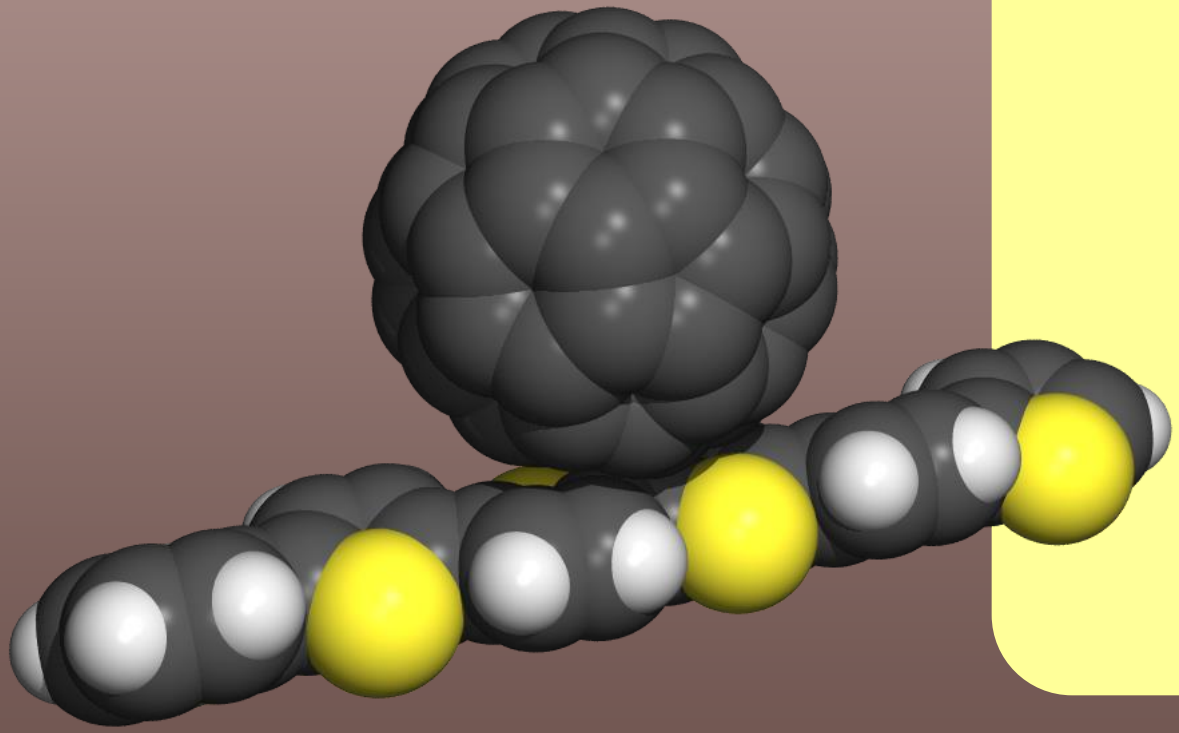




Conclusions

1. Interaction between pT chains blueshifts the absorption onset
2. C_{60} affects the pT absorption only through structural changes
3. Effect of p3HT regioregularity can be clearly observed in the simulated absorption spectrum
4. Simple device models give insights into the nature of light harvesting
5. RT-TDDFT is very efficient, making possible routine studies of device atomic morphology

RT-TDDFT simulation of the optical properties of a model organic photovoltaic device



Our Collaborators:

Y. Takimoto

T. Ahmed

C. Luscombe

A. Jen

D. Ginger

UNIVERSITY OF WASHINGTON

... and Thank You