Ultrafast Nano-Optics

Excitons + Solar cells

Ultrafast coherent charge and energy transfer in plasmonic and light harvesting systems: Taking movies of electronic motion in nanosystems

Ralf Vogelgesang[1], Sarah M. Falke[1], Antonietta De Sio[1],
Carlo A. Rozzi[3], Elisa Molinari[3], Angel Rubio[4],
Daniele Brida[2], Giulio Cerullo[2], Jens Christoffers[1], Christoph Lienau[1]

Nanolight 2014, Benasque
02.03.2014

(1) Carl von Ossietzky Universität Oldenburg

(2) Politecnico di Milano

(3) CNR NANO Modena S3

(4) Universidad del País Vasco

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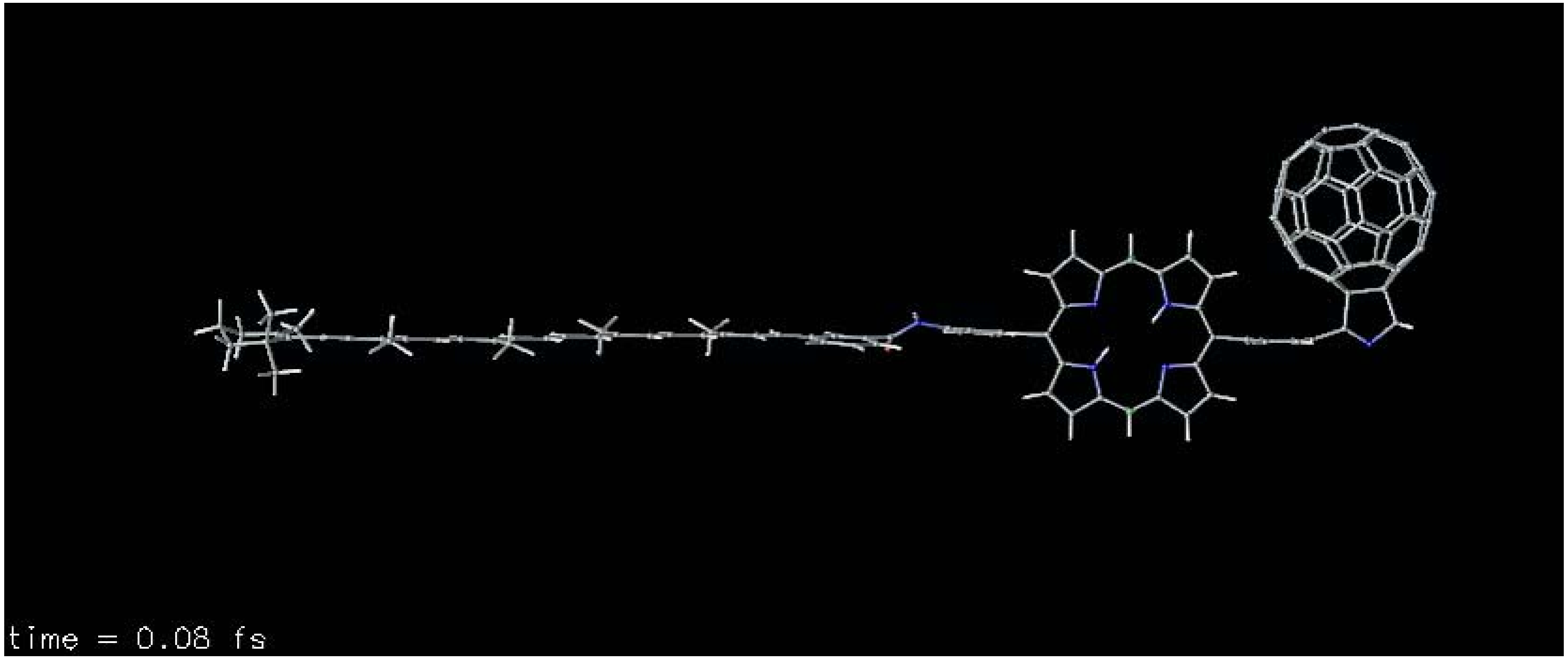
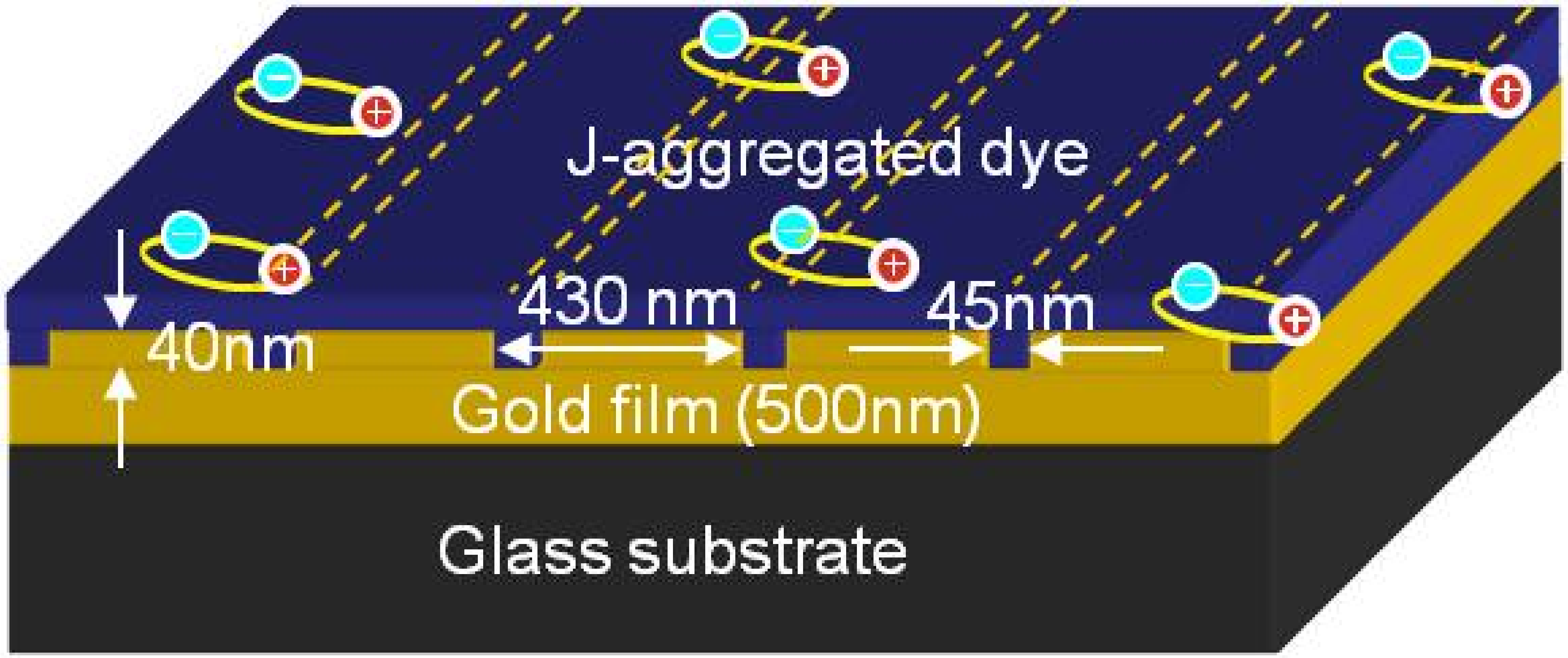
Light to Current Conversion in an Artificial Light Harvesting System



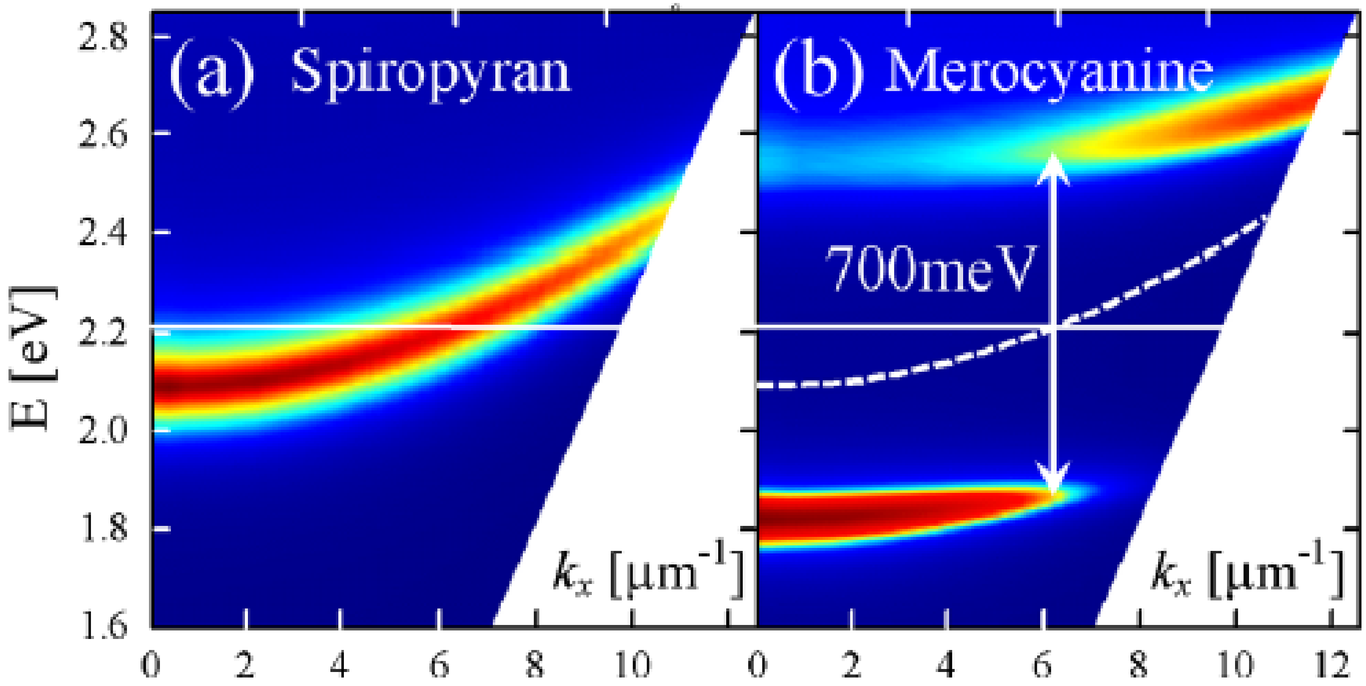
C. A. Rozzi et al., Nature Comm., 4, 1602 (2013).

Case I: strongly coupled Exciton + SPP



Photochromic molecules on silver films

Angle-resolved transmission spectra

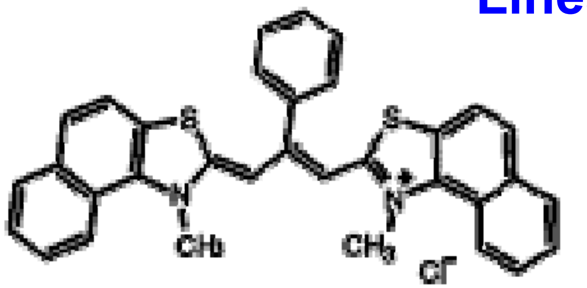


- Strong exciton-SPP coupling
- Ultrastrong coupling regime
- Switching capability
- Dynamics ???
- Nanostructures ???

J. Bellessa et al., PRL 93, 036404 (2006)
J. Dintinger et al., PRB 71, 035424 (2005)
P. Vasa et al., PRL 101, 116801 (2008)
T. Schwartz et al., PRL 106, 196405 (2011)

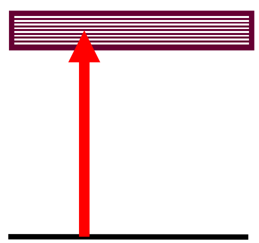
J-aggregated (cyanine) dye

Linear optical properties



2,2'-dimethyl-8-phenyl-5,6,5',6'-dibenzothiacarbocyanine chloride

Two level system

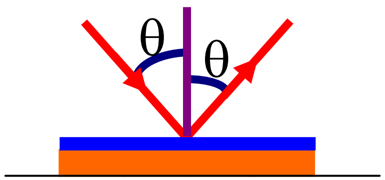


$|1\rangle$ One exciton aggregate state

Dipole moment: 100D per exciton

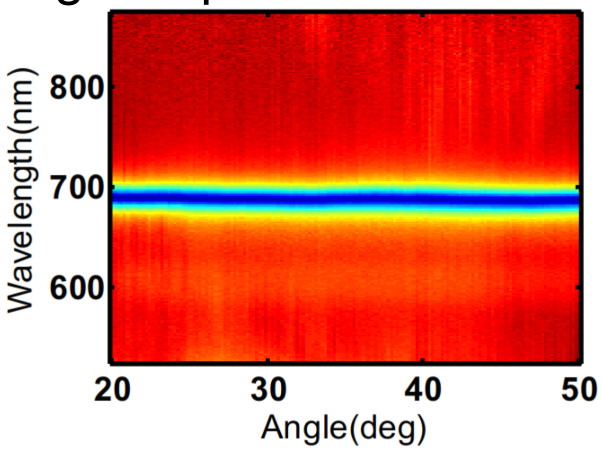
$|0\rangle$ Ground state

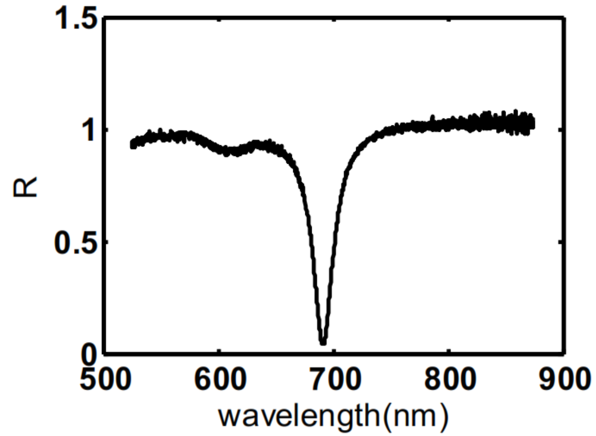
Broad band laser pulse



Without grating

Angle depedent Reflectivity(R)





Narrow absorption spectrum

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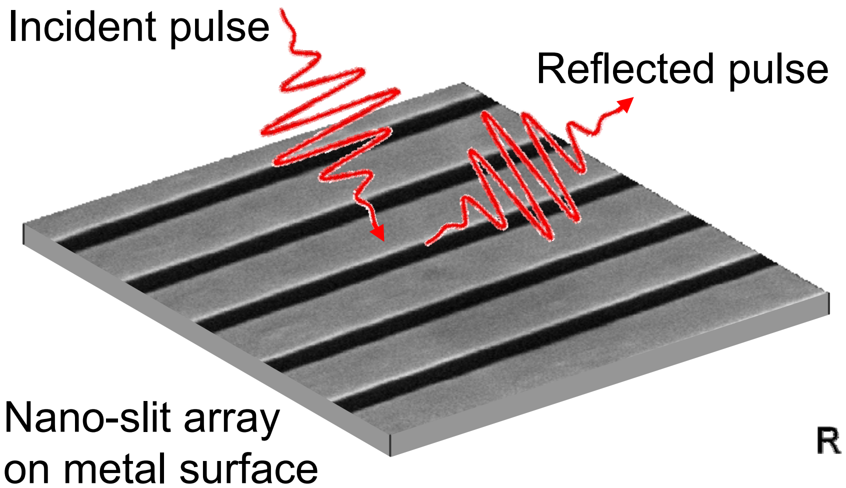
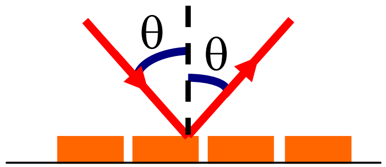
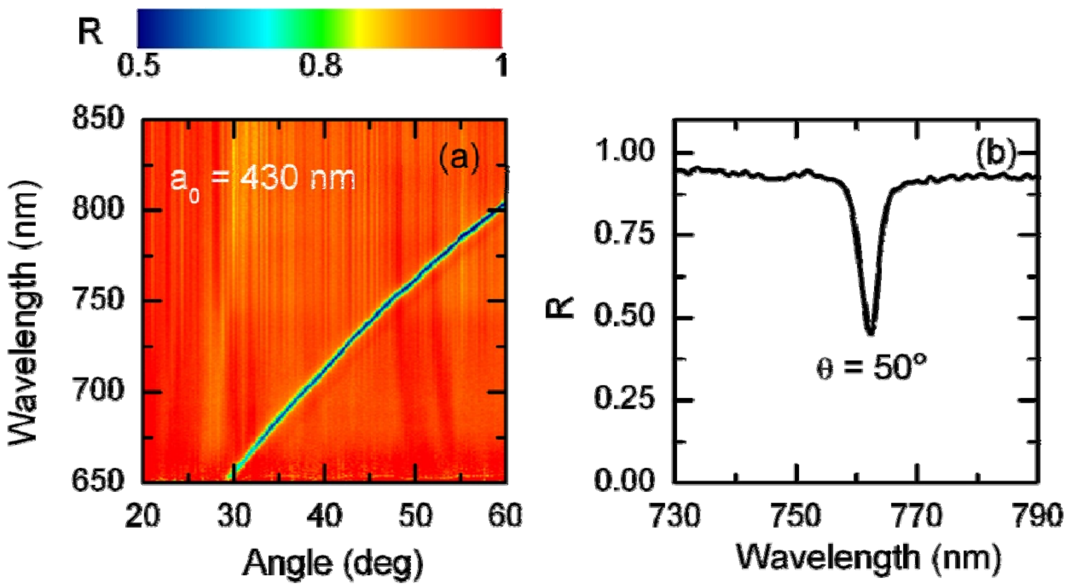
Nanostructured gold gratings: SPP resonators





Angle resolved linear reflectivity

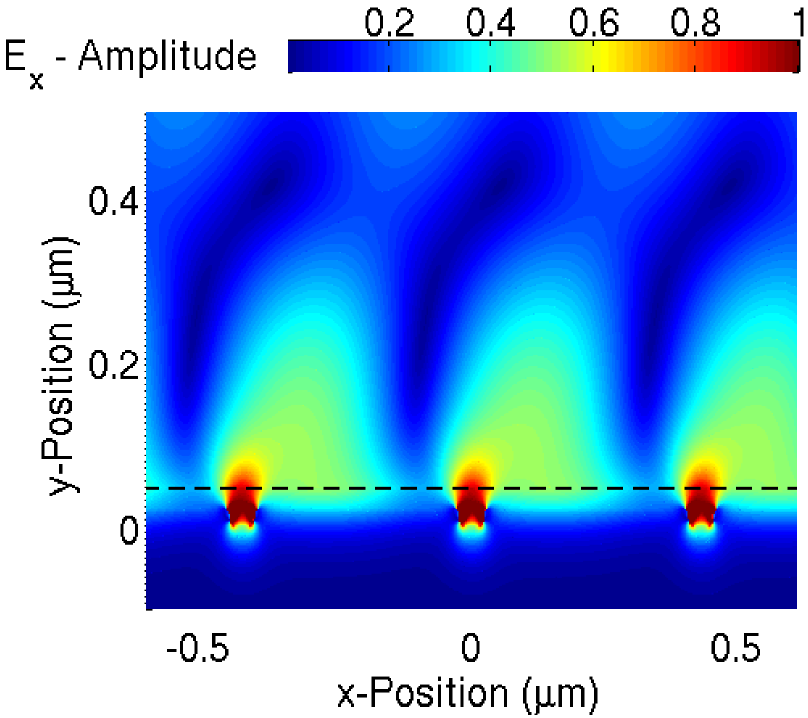
Reflectivity of a nano-slit array on gold film

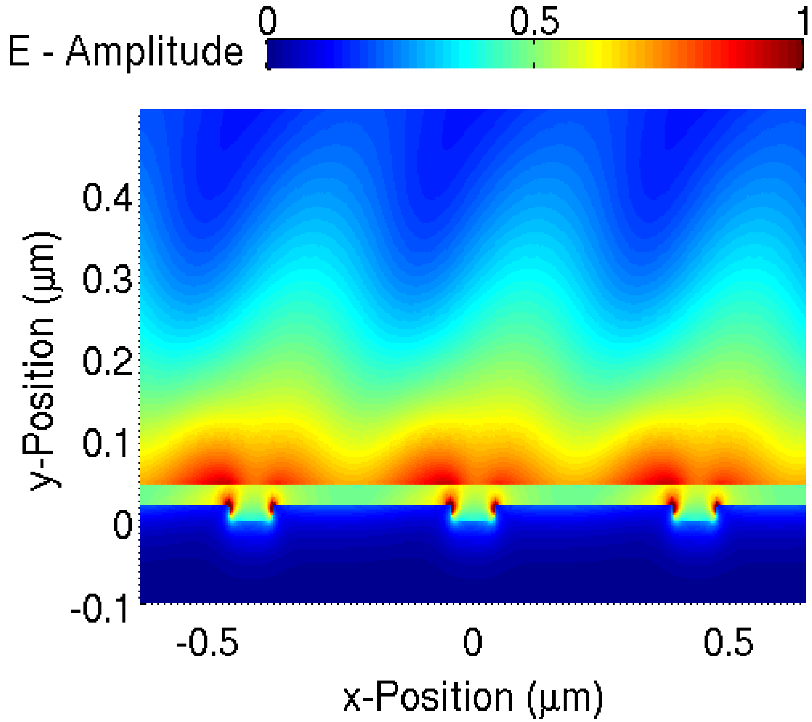


Grating parameters optimized for long SPP lifetimes

Electric field localization in nanoslit arrays

Electric field distributions inside the nanostructures





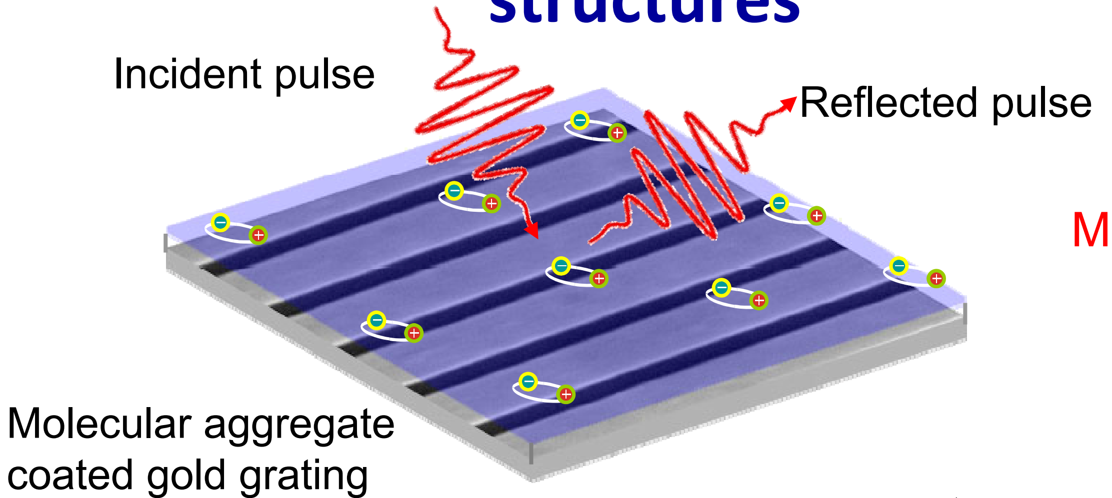
Rabi splitting energy

$$\Omega_R = \hbar \int \vec{\mu}_X(\vec{r}) \cdot \vec{E}_{SPP}(\vec{r})\, d\vec{r}$$

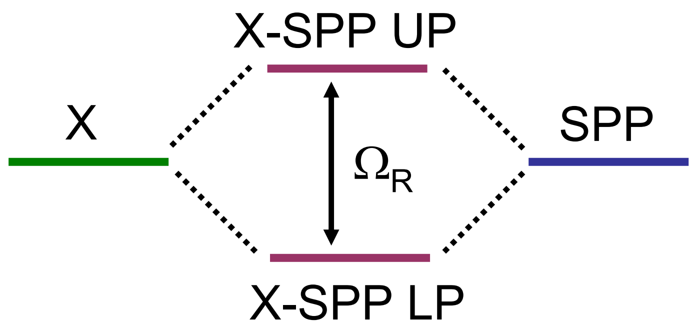
Vacuum field strength per mode

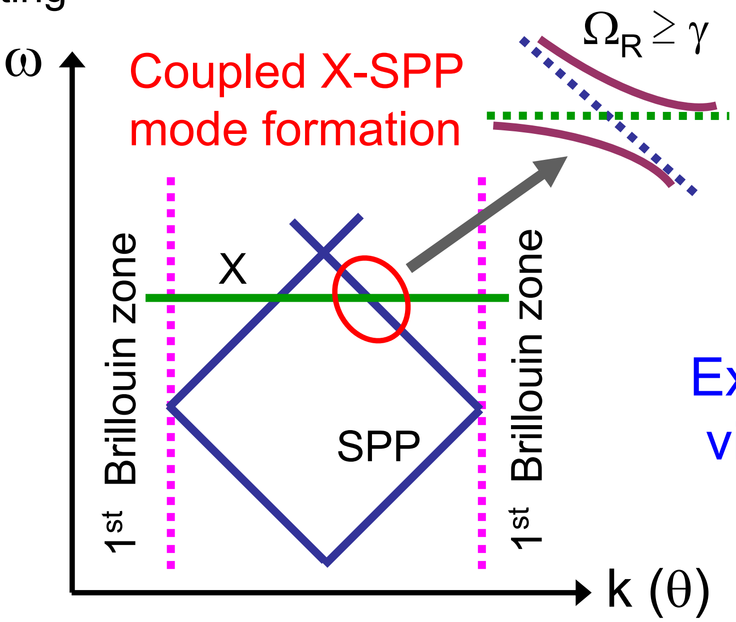
$$E_{SPP} = \sqrt{\frac{\hbar\omega}{\varepsilon\varepsilon_0 V}}$$

Linear optics of metal-J aggregate hybrid structures



Mode overlap and dipole coupling:
Polariton formation



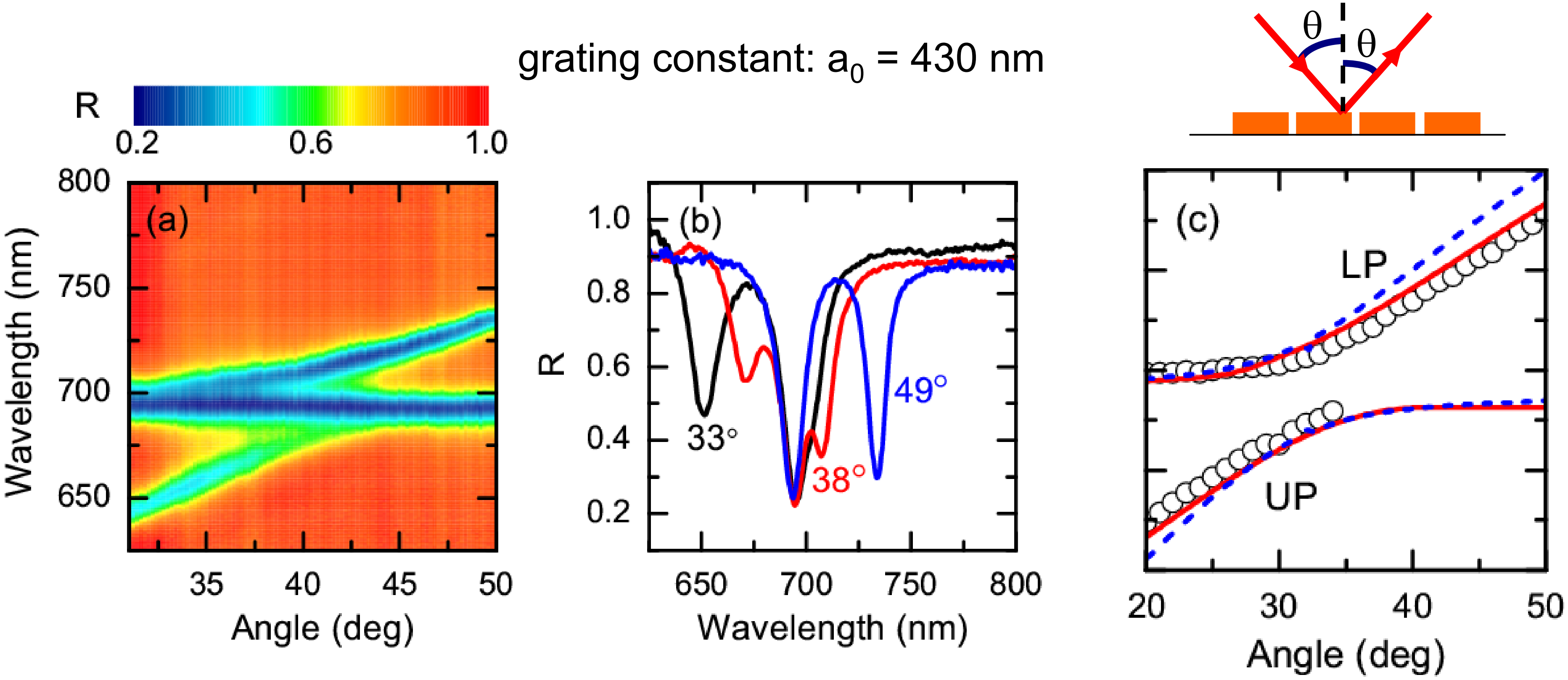


Exciton (X) and SPP coupled
via *optical dipole interaction*

P. Vasa et al., ACS Nano 4, 7759 (2010)

Linear reflectivity: Strong coupling between excitons and surface plasmon polaritons

grating constant: a_0 = 430 nm



Rabi splitting energy of ~60 meV
A substantial fraction of excitons that do not couple to SPP

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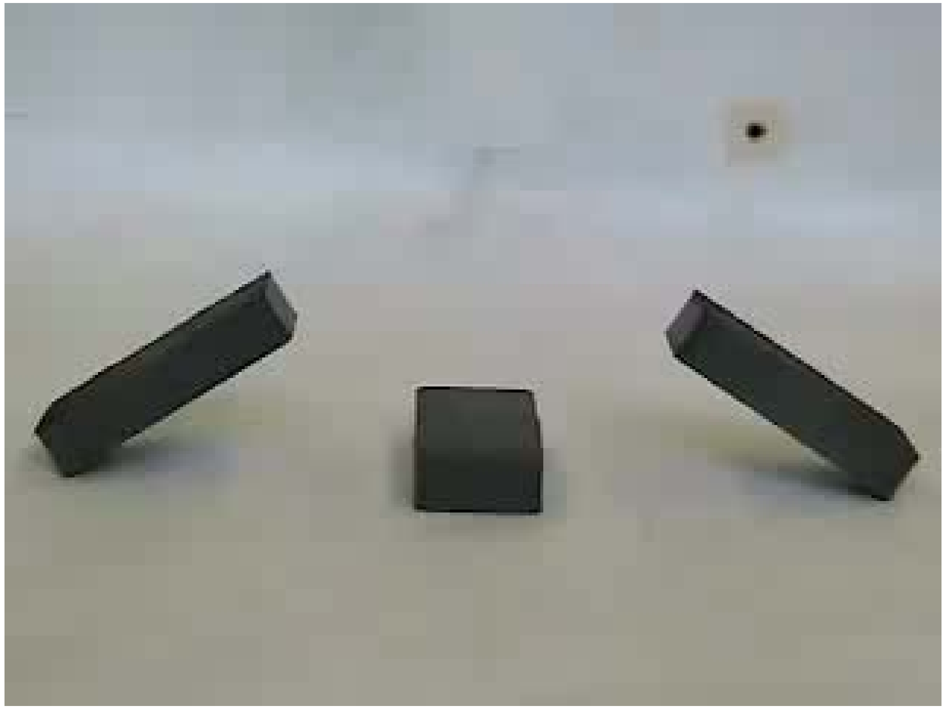
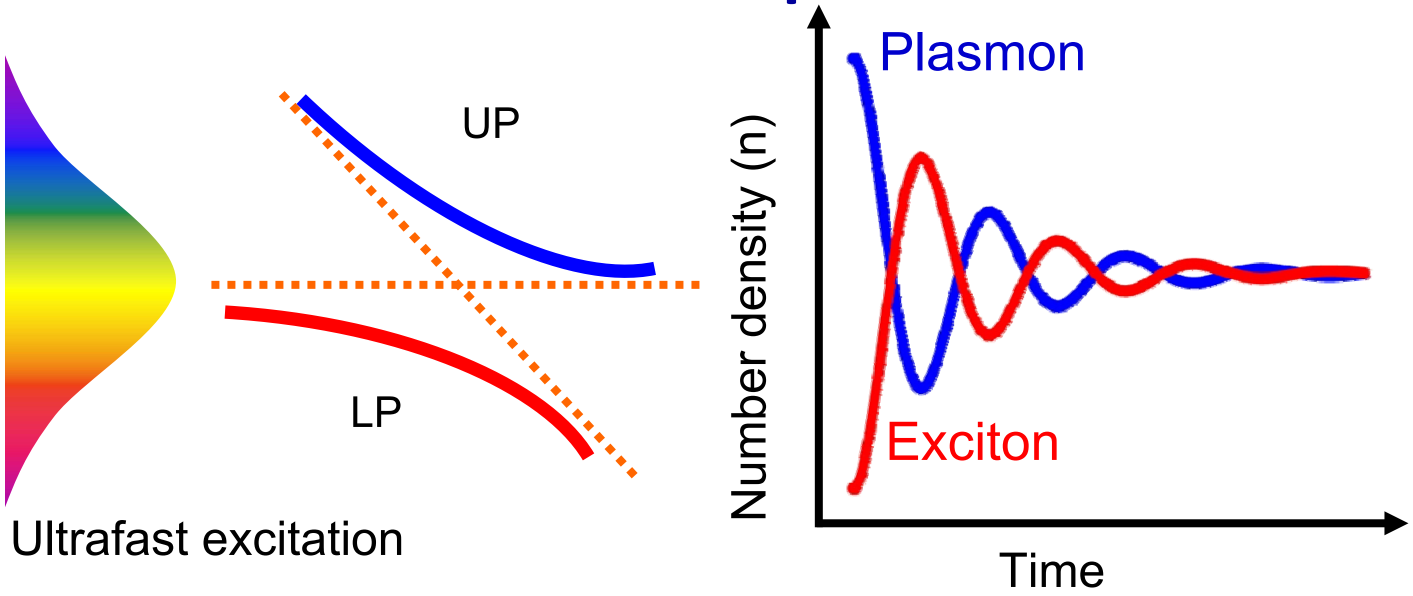
Exciton-SPP dynamics
in the strong coupling regime



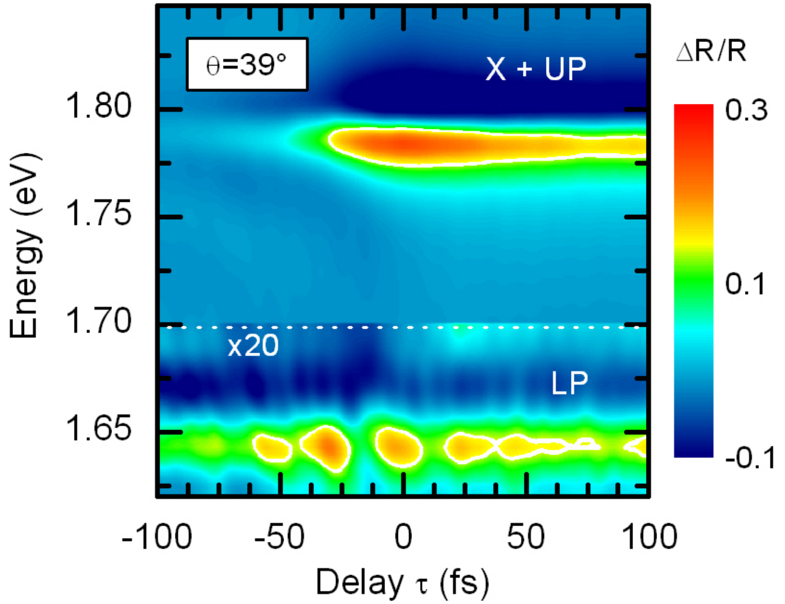
www.youtube.com

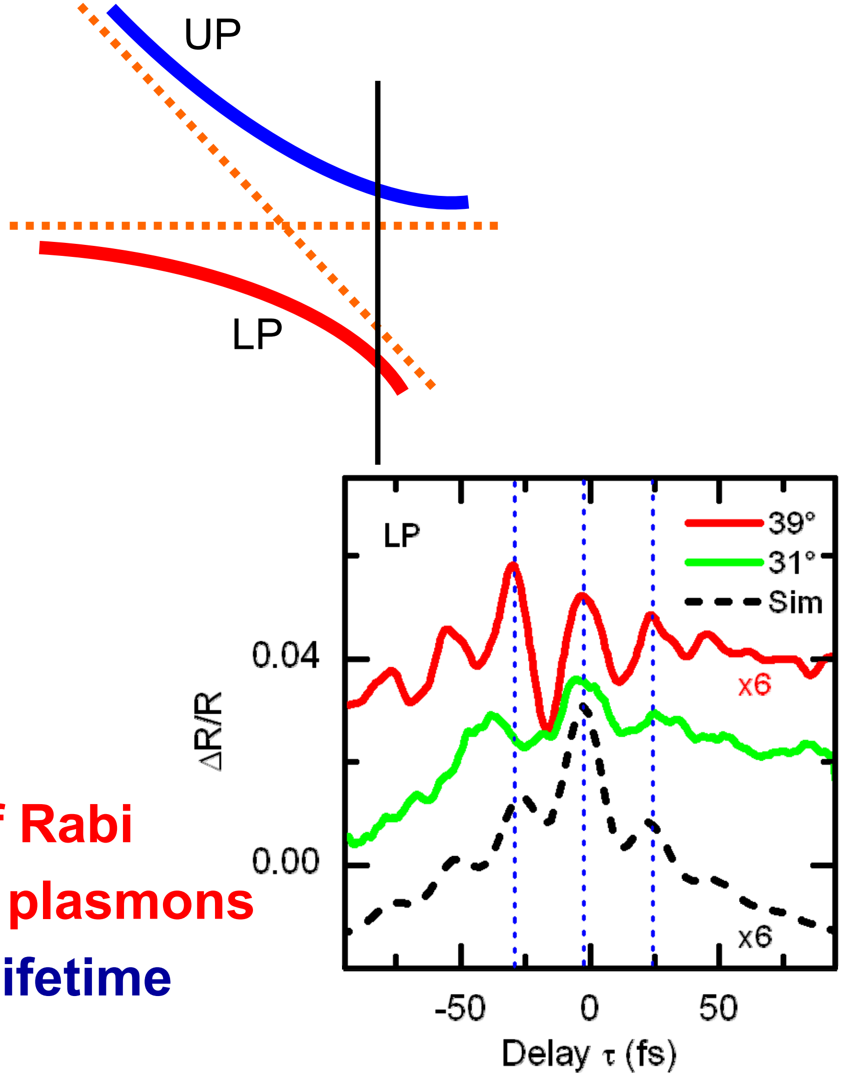
Exciton-SPP coupling: Time-domain representation



Periodic exchange of electromagnetic energy between excitons and surface plasmon polaritons

Real-time observation of Rabi oscillations





- **First real-time observation of Rabi oscillations between excitons and plasmons**
- **Strong reduction in radiative lifetime**

P. Vasa et. al, Nature Photonics 7, 128 (2013)

Density matrix simulations

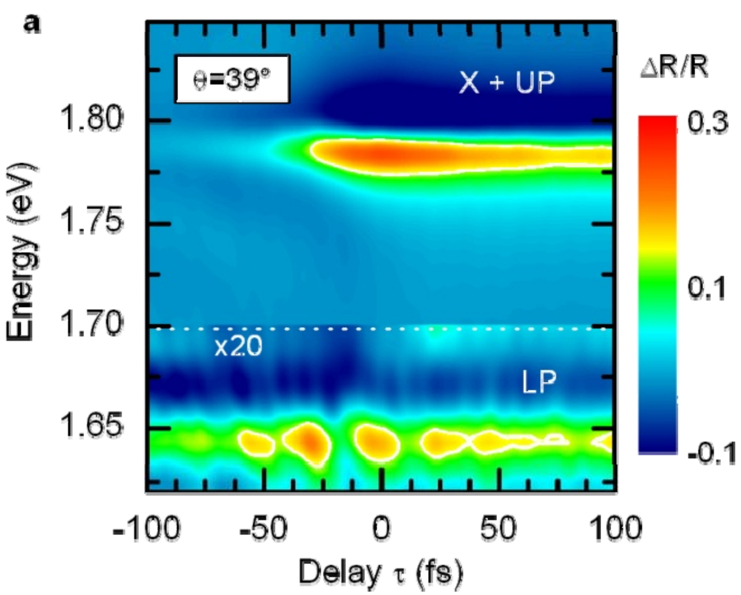
Exciton creation (**population n_x**) reduces the Rabi splitting!

$$\Omega_R(t) = \Omega_R^0 \cdot \sqrt{1 - n_X(t)}$$

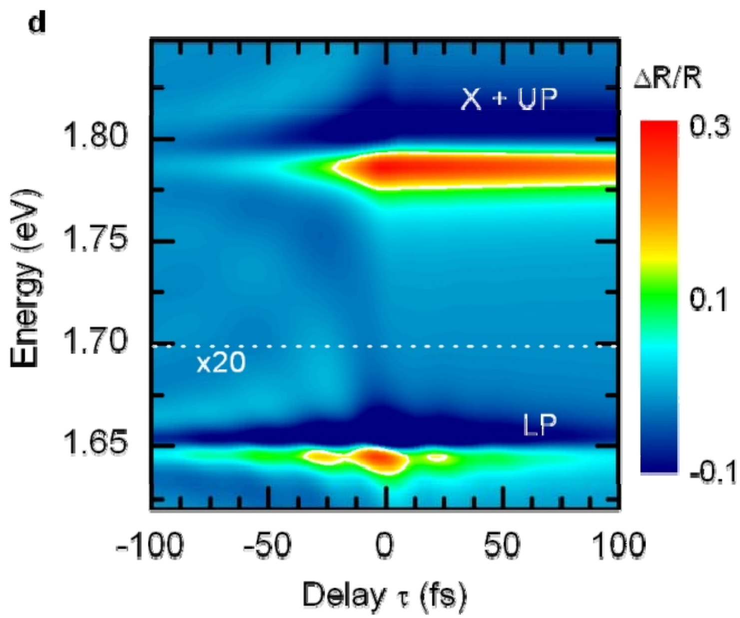
Parametric variation of the Rabi frequency

P. Vasa et al., ACS Nano 4, 7559 (2010)

Experiment



Simulation



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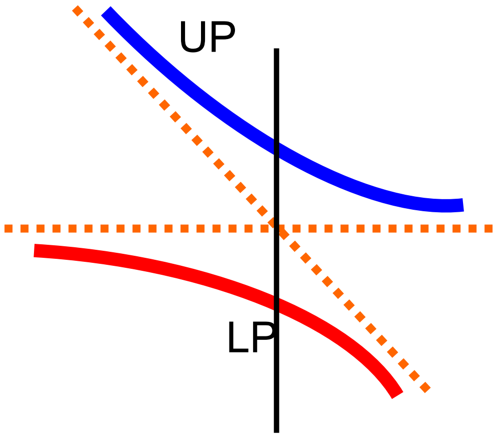
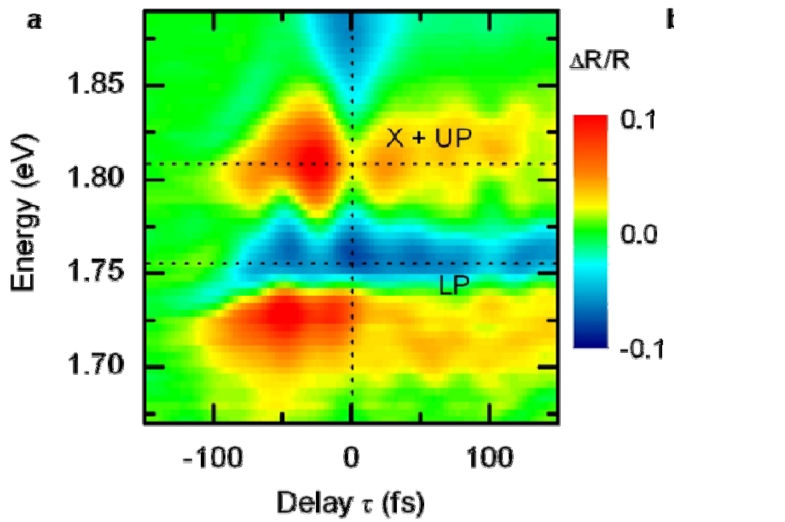
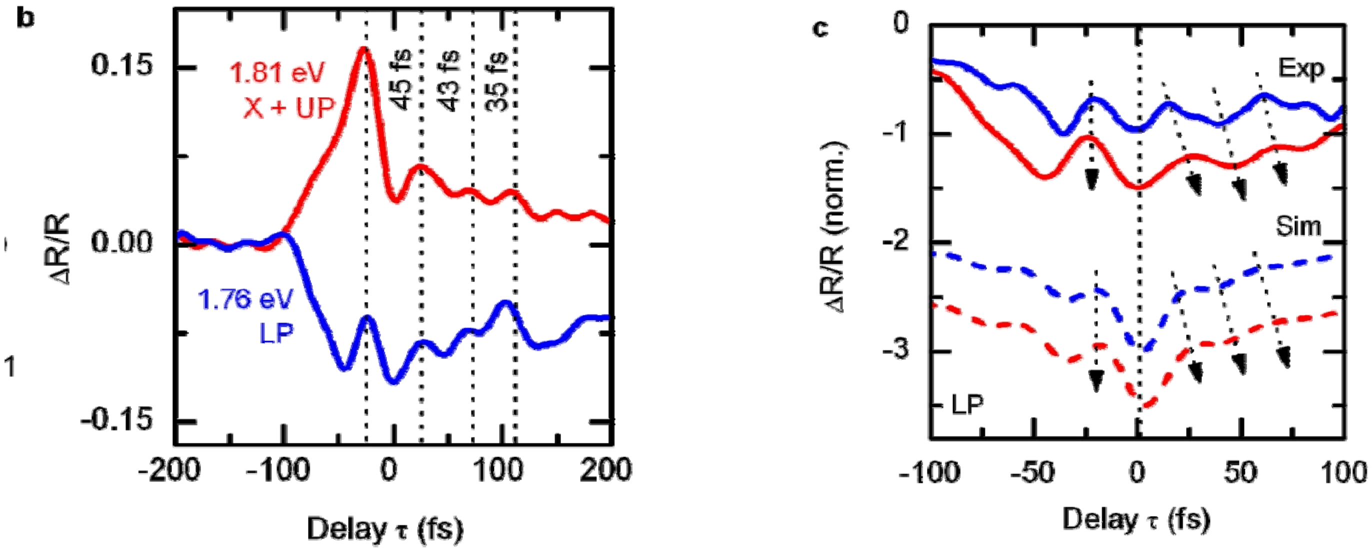
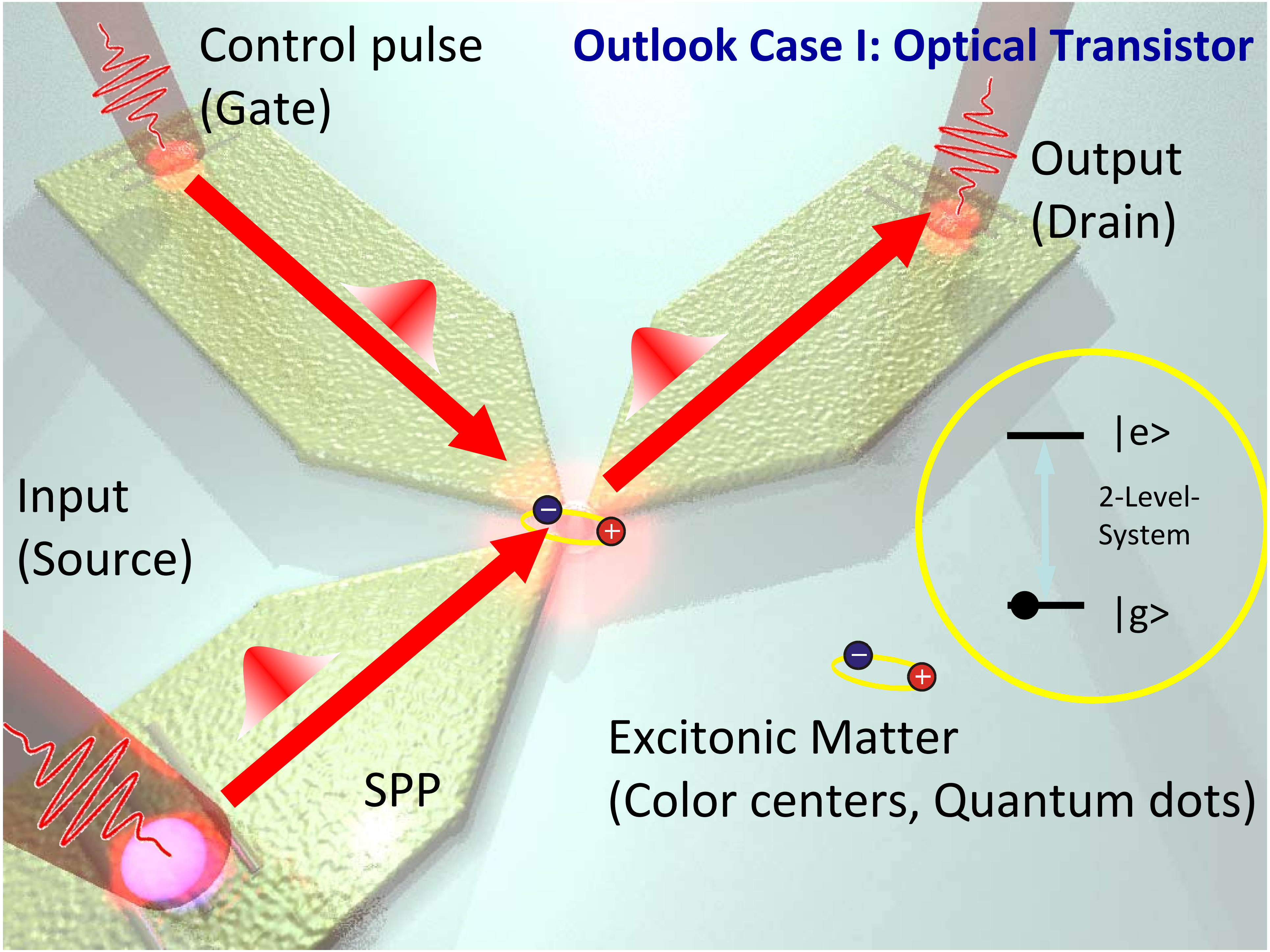
UP/LP Rabi oscillations



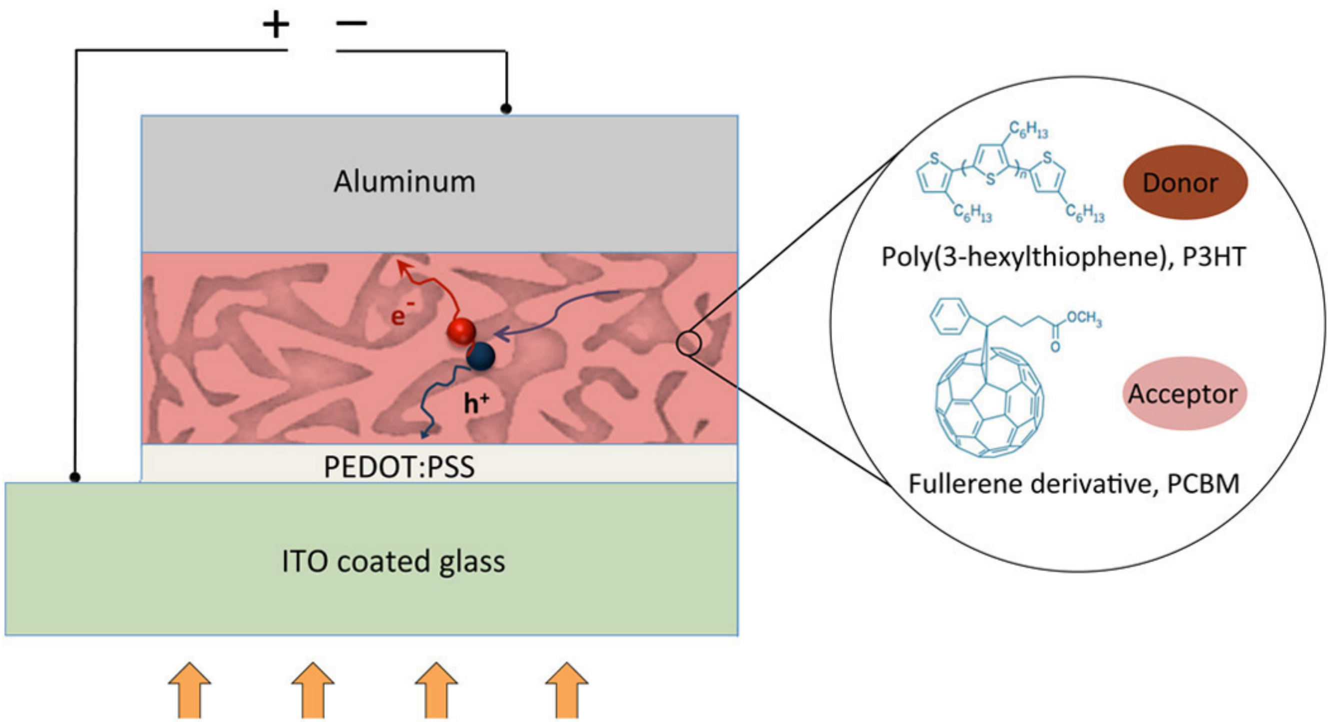





Outlook Case I: Optical Transistor
Control pulse
(Gate)
Output
(Drain)
Input
(Source)
|e>
2-Level-
System
|g>
SPP
Excitonic Matter
(Color centers, Quantum dots)

Case II: Organic Solars Cells as Light Harvesting Systems

1. **Absorption** of a photon leads to the formation of an exciton in the polymer
2. **Exciton Diffusion** to a polymer:acceptor interface (if necessary)
3. **Exciton Dissociation** leading to spatially separated charges
4. **Charge Transport** to the electrodes



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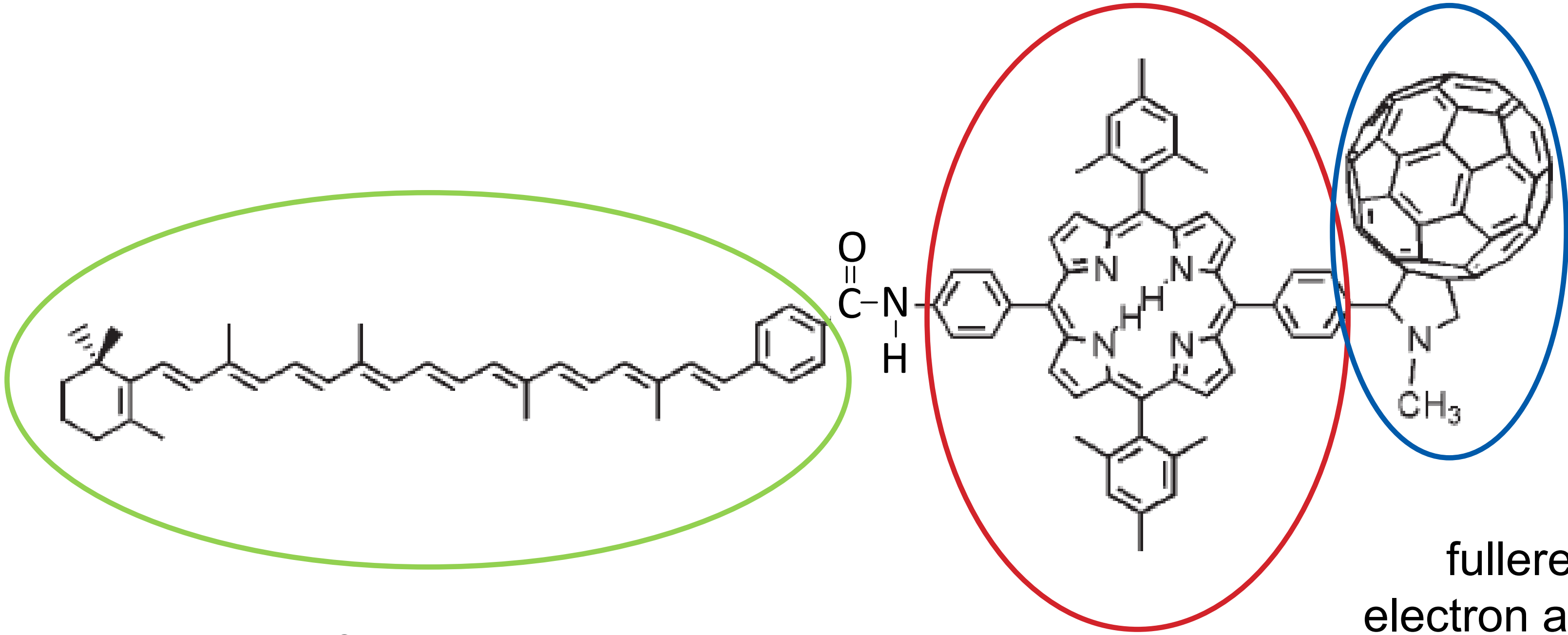
A supramolecular triad: an artificial model system mimicking solar energy conversion



β-carotene:
hole stabilization
(hole acceptor)

porphyrin:
light absorption

fullerene:
electron acceptor

C. A. Rozzi, S. M. Falke et al., Nature Comm 4, 1602 (2013).

Triad: photoinduced charge transfer dynamics

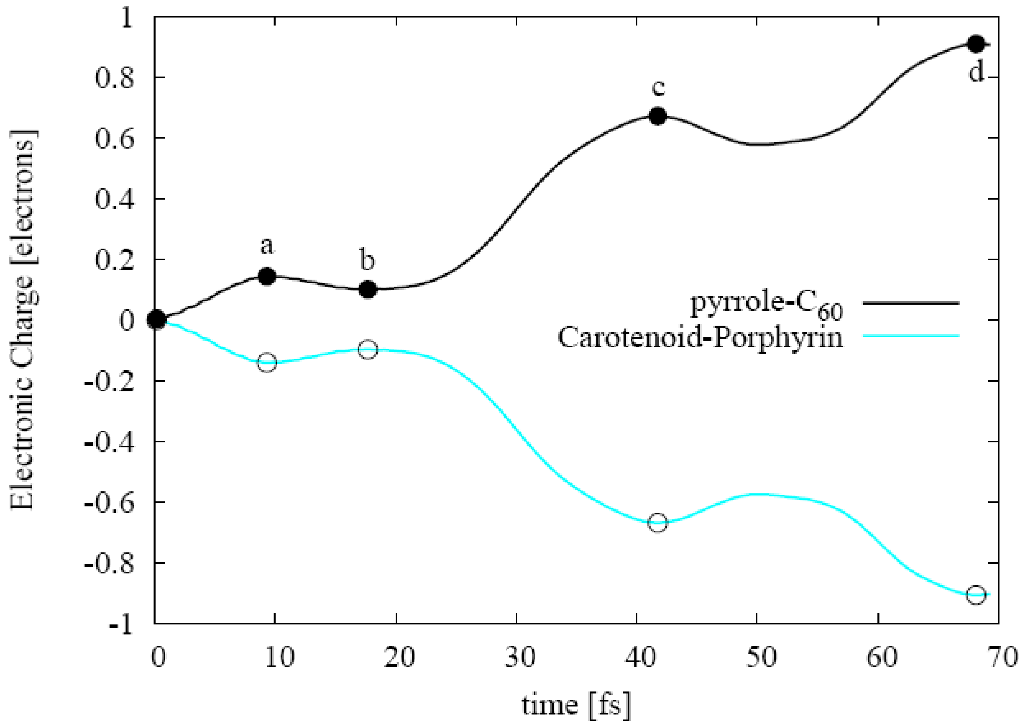
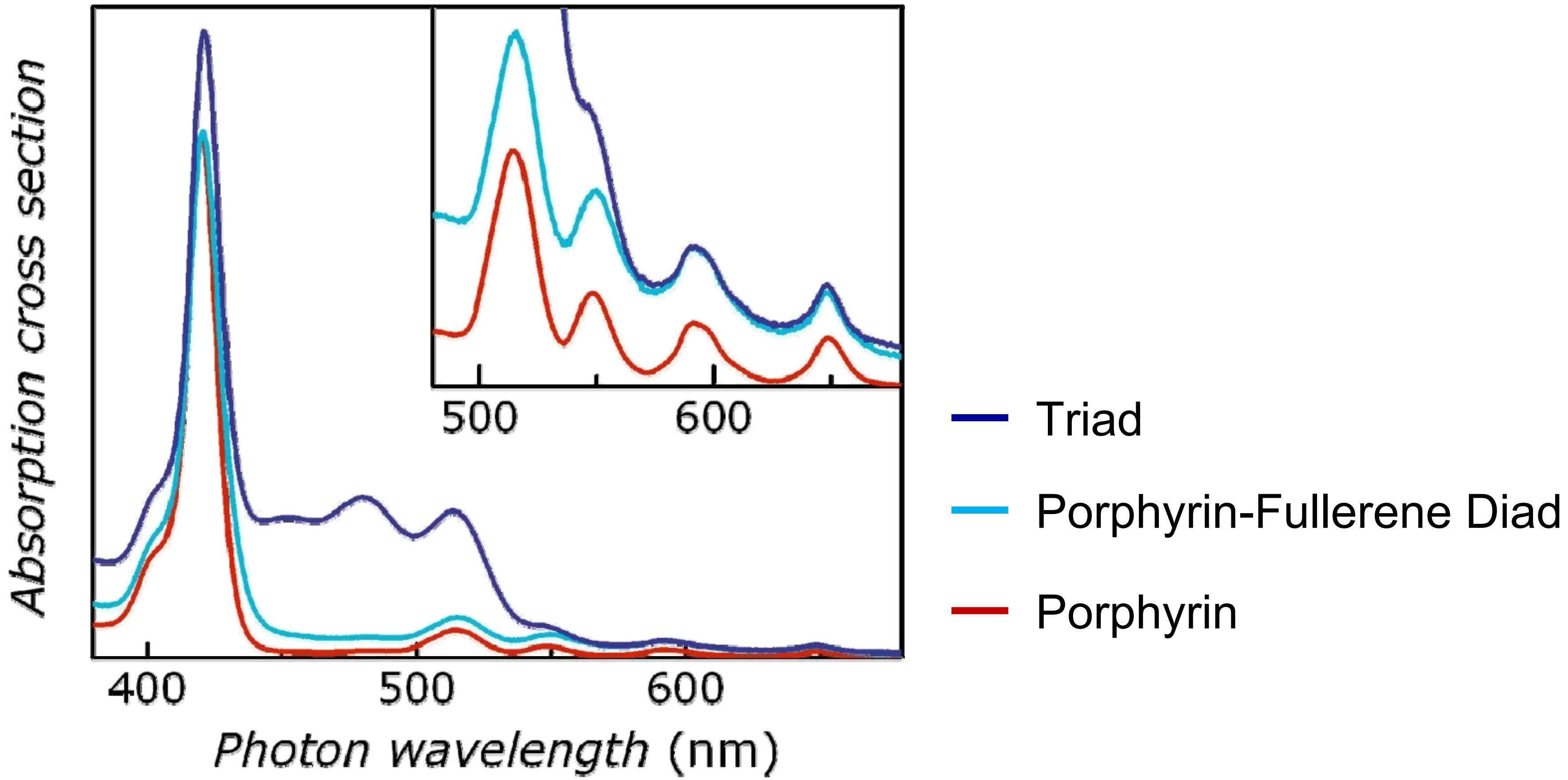


Figure 6.2: Fraction of electrons transfered to the pyrrole-C_{60} part (black line) from the Carotenoid-Porphyrin part (cyan line) of the triad as a function of time after excitation.

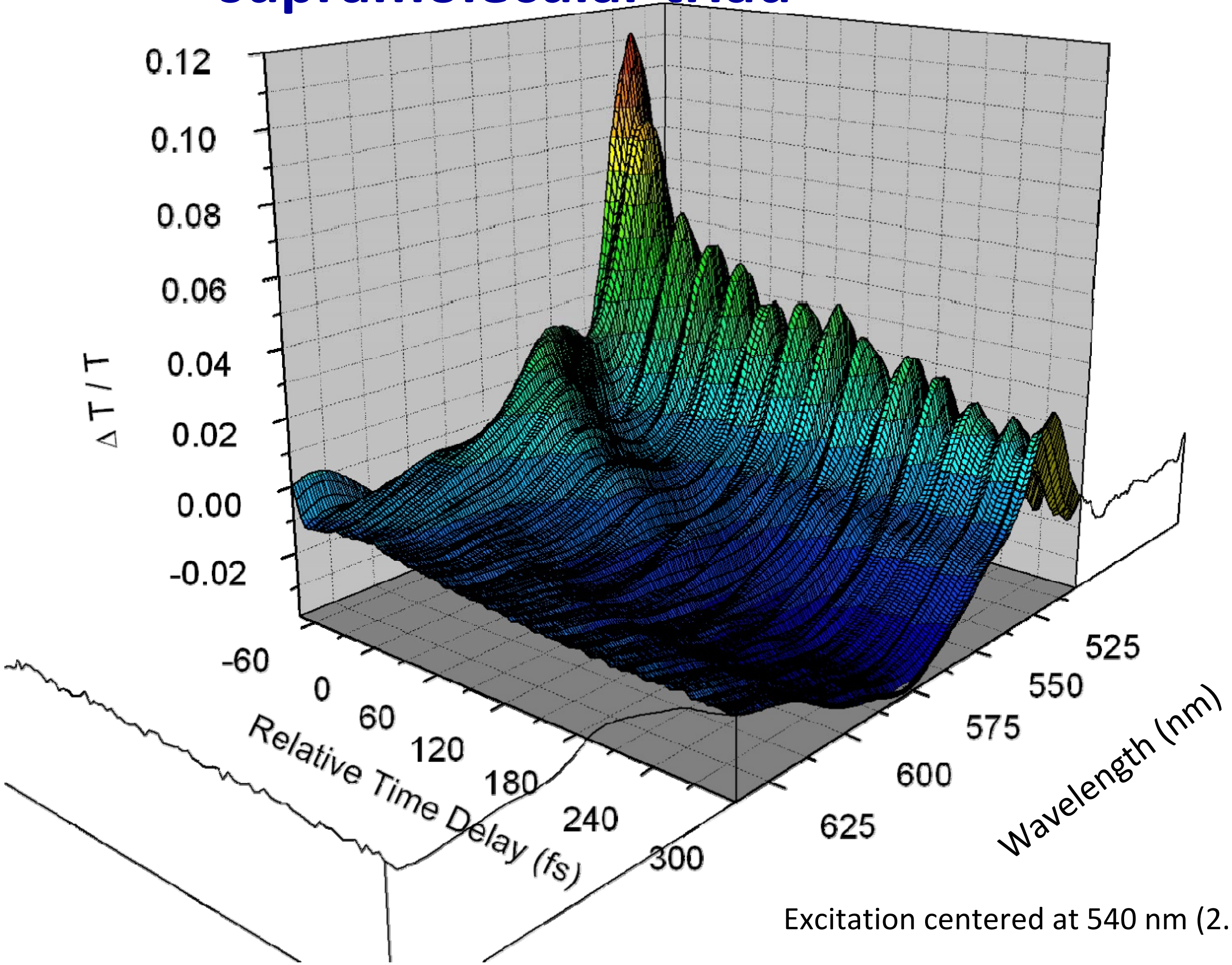
Courtesy: Nicola Spallanzani, Franca Manghi and Elisa Molinari (U Modena)

Triad: absorption spectra



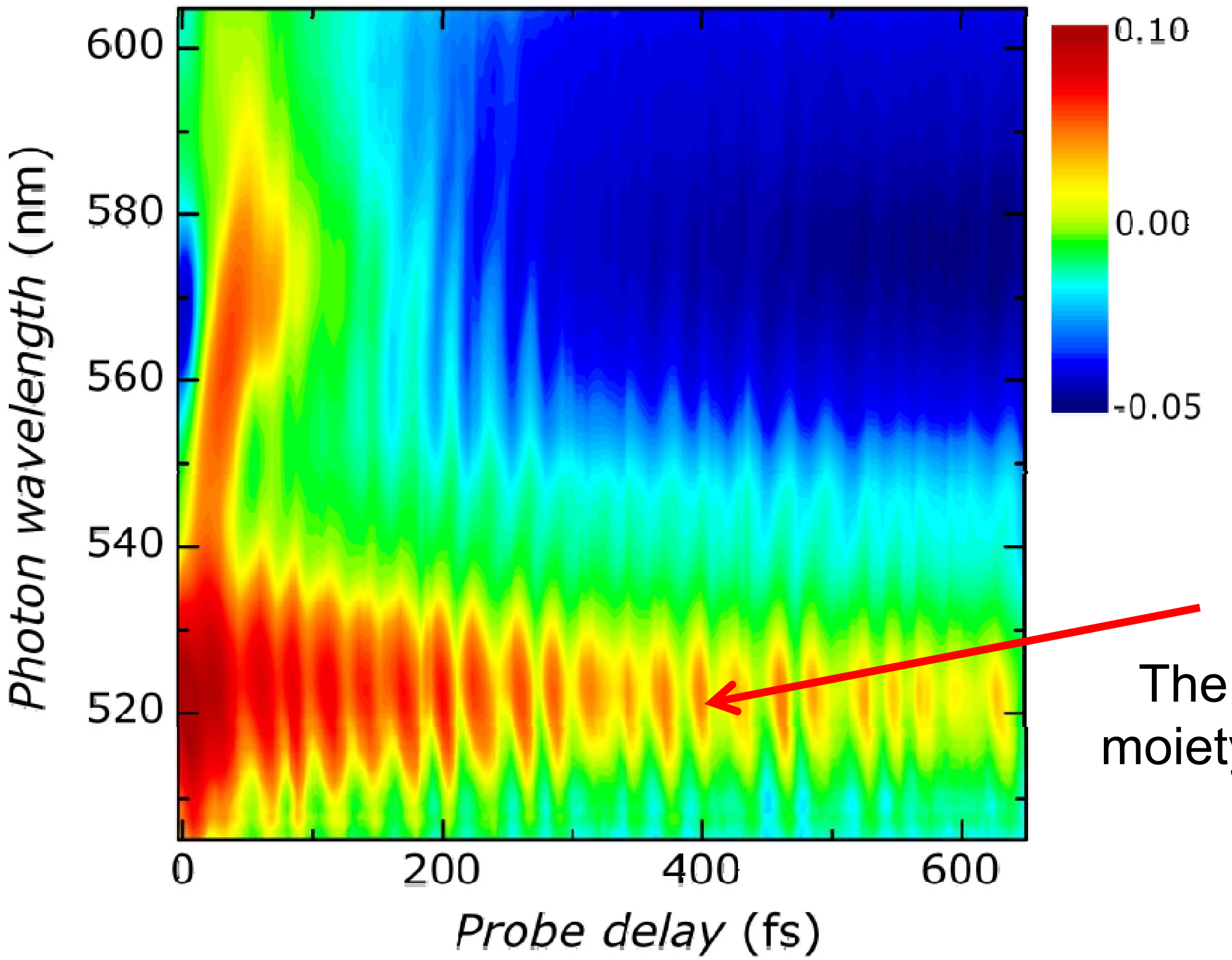
s. also G. Kodis et al, J. Phys. Org. Chem. 17, 724 (2004).

Ultrafast pump-probe spectroscopy of supramolecular triad



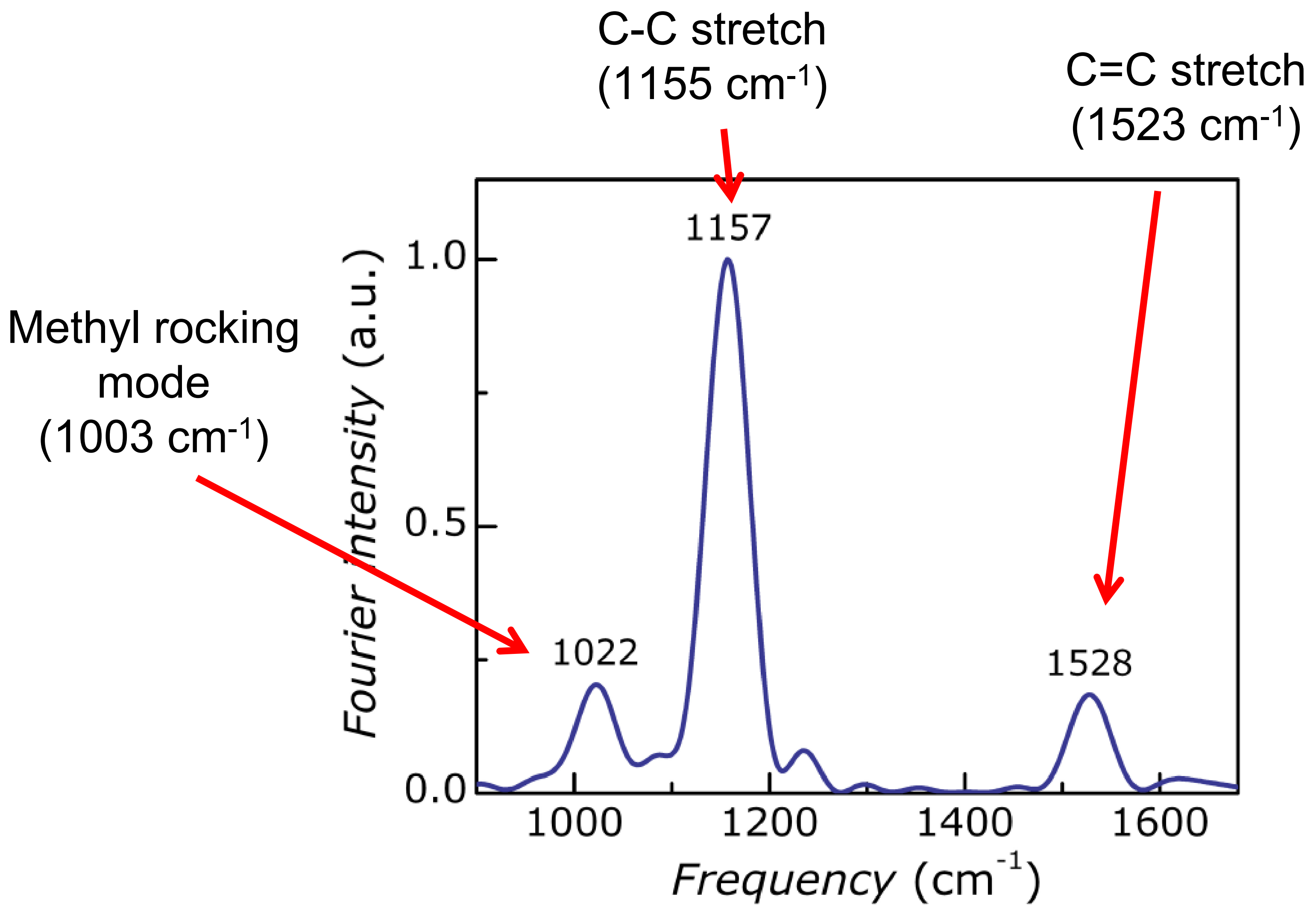
Excitation centered at 540 nm (2.296 eV)

Pump-Probe Trace (Δ T / T) of Triad (Excitation on the porphyrin)

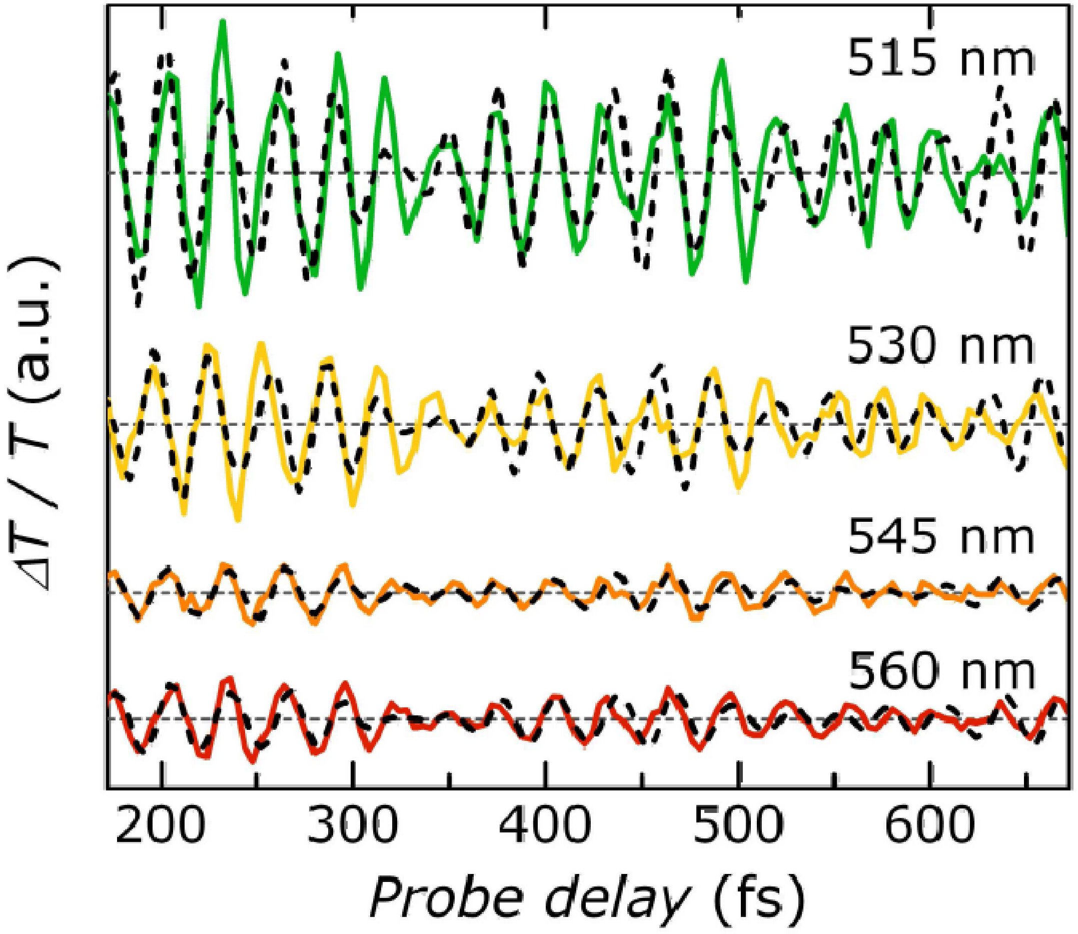


The carotene moiety oscillates

Analysis of the carotene oscillations



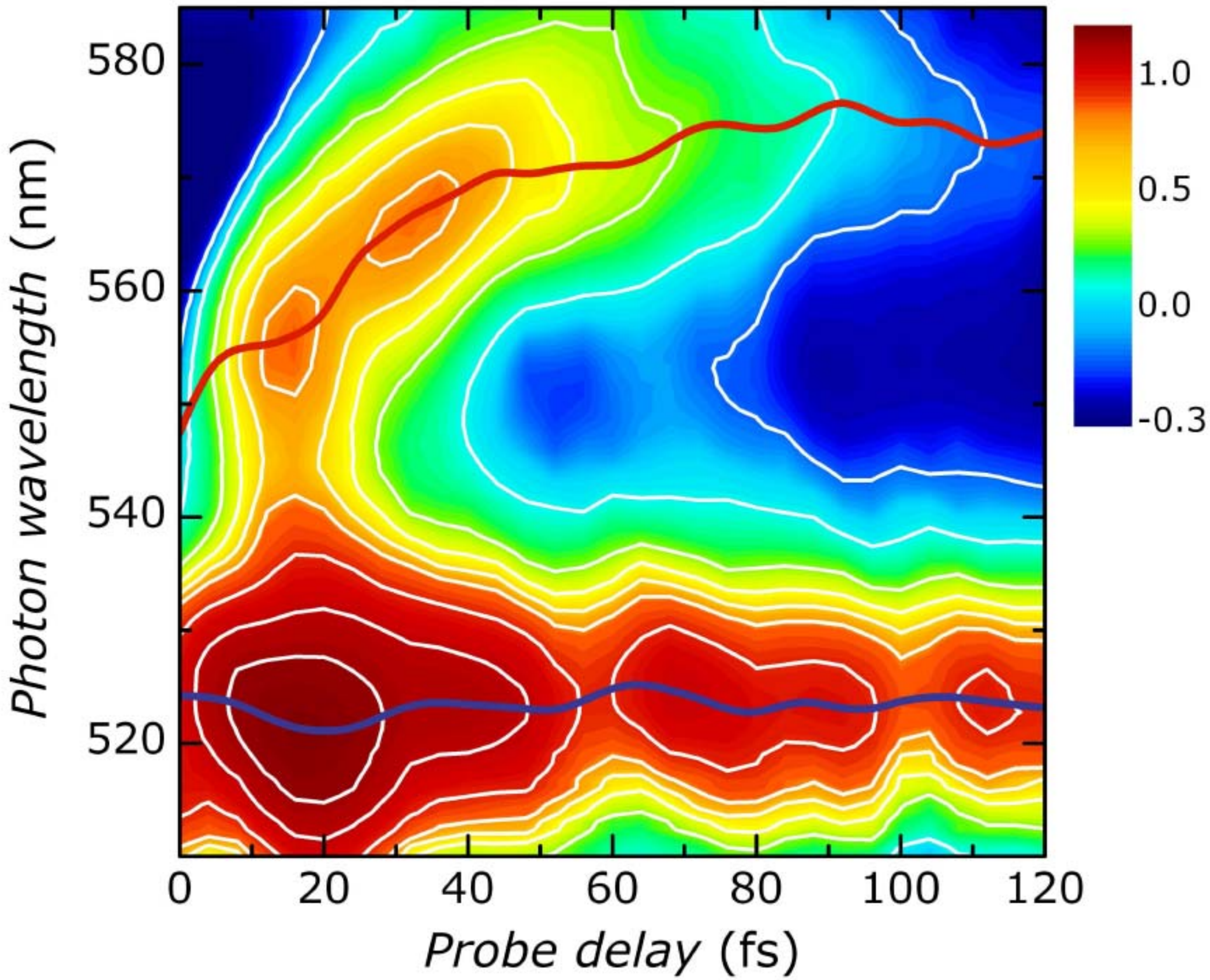
Analysis of the carotene oscillations



Now that we understand the carotene oscillations …

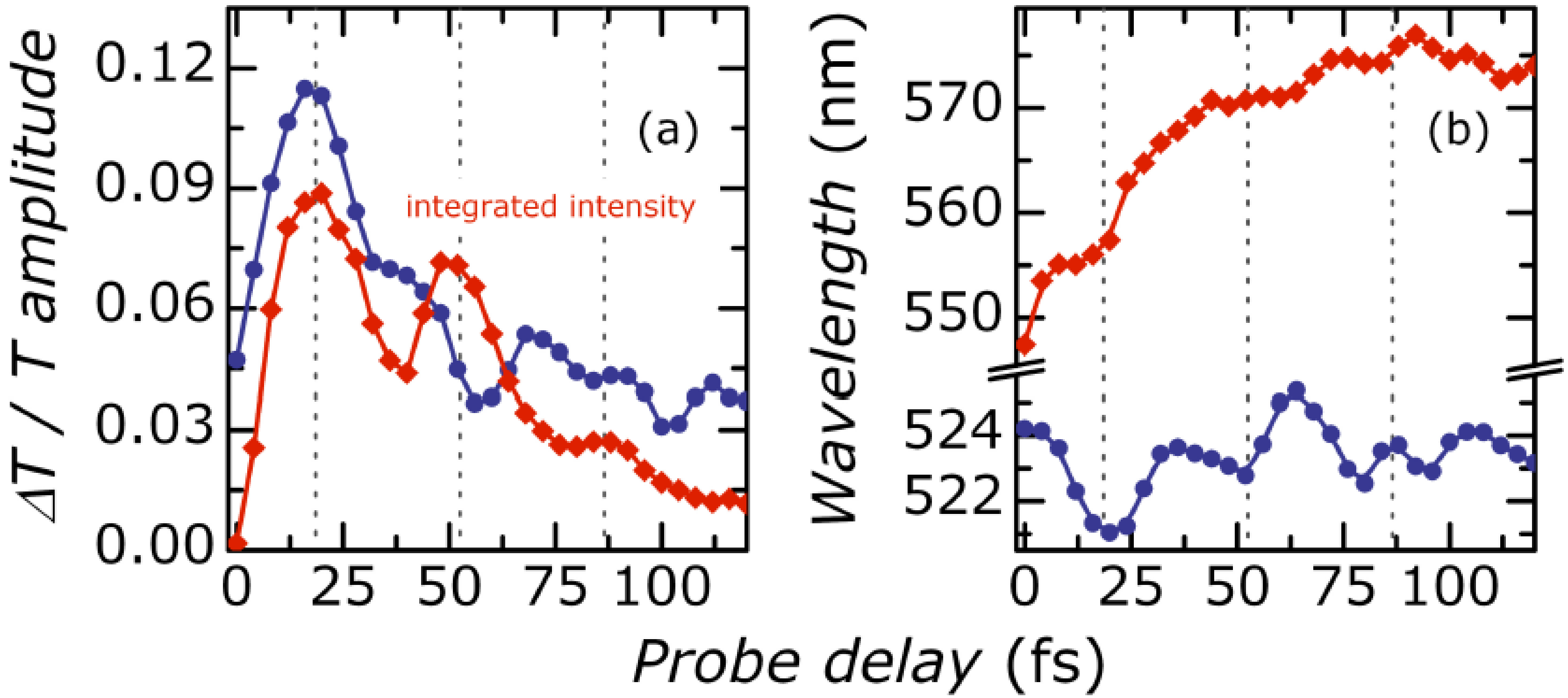
… we can safely remove them from the data

Pump-Probe Trace (Δ T / T) of Triad (Excitation on the porphyrin)



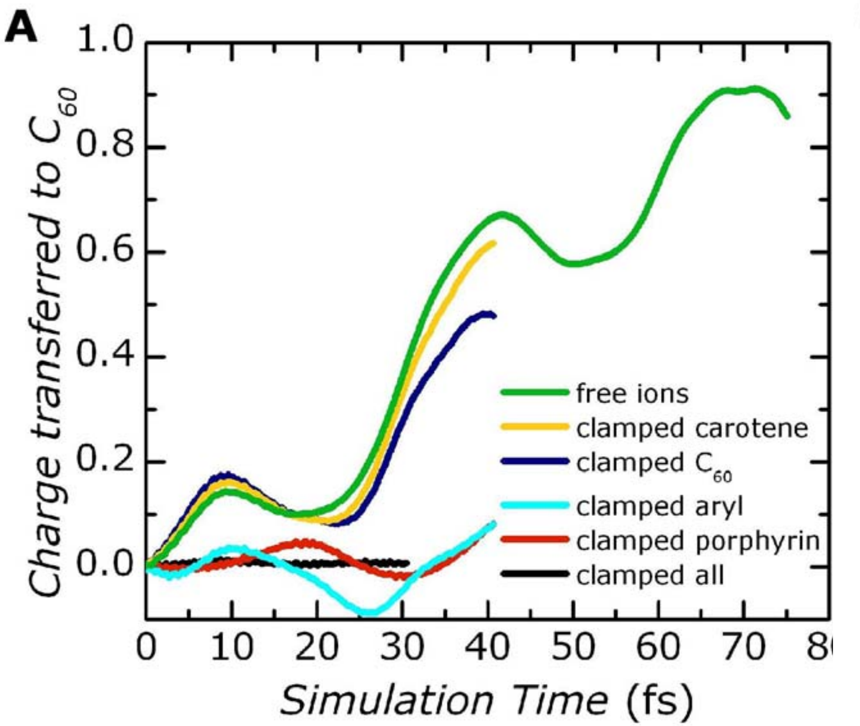
Pump-Probe Trace (Δ T / T) of Triad (Excitation on the porphyrin)

Coherent oscillations of the **resonance wavelength** of the charge transfer band

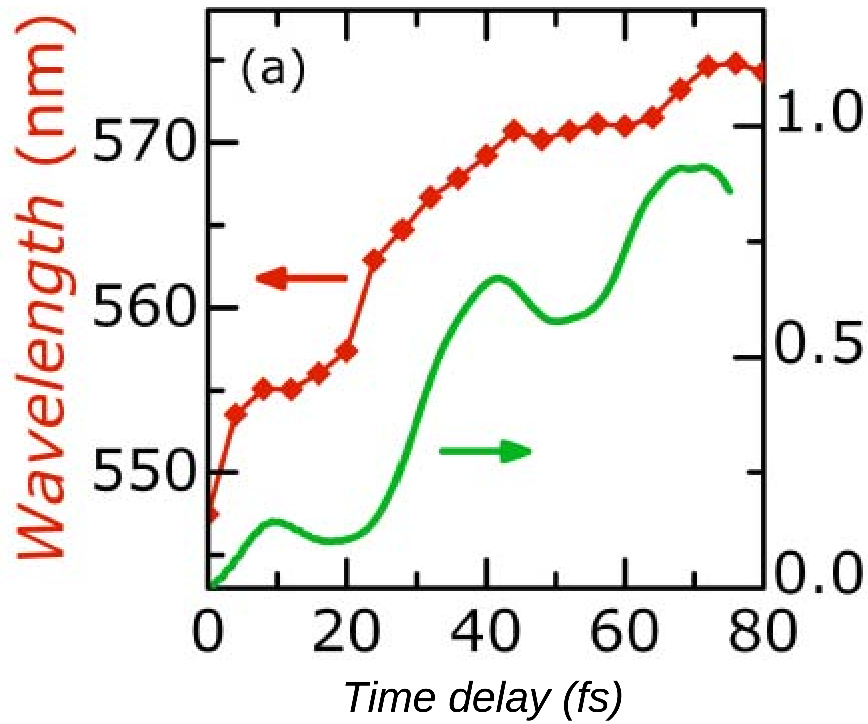


Coherent charge oscillations

DFT Calculations



Comparison Experiment-DFT



C. A. Rozzi, S. M. Falke et al., Nature Comm 4, 1602 (2013).

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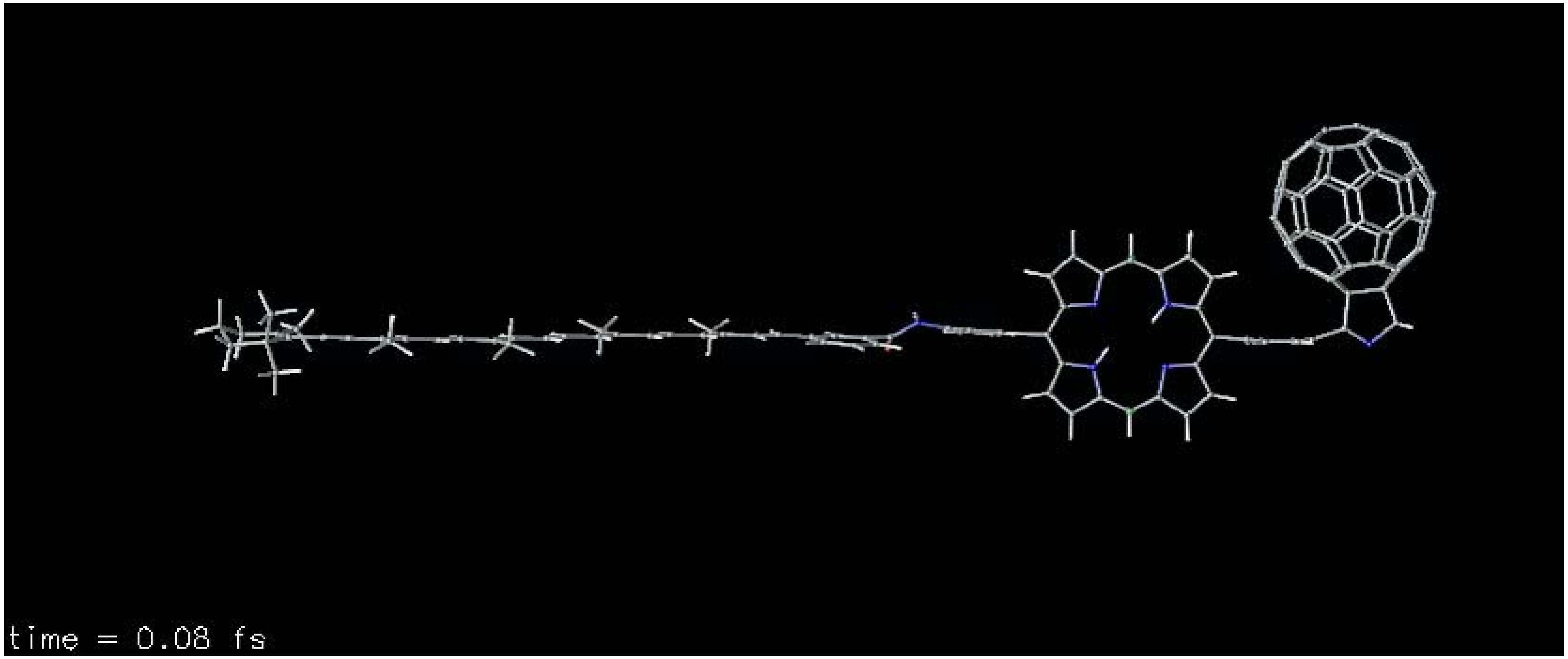
Coherent dynamics – DFT Simulations



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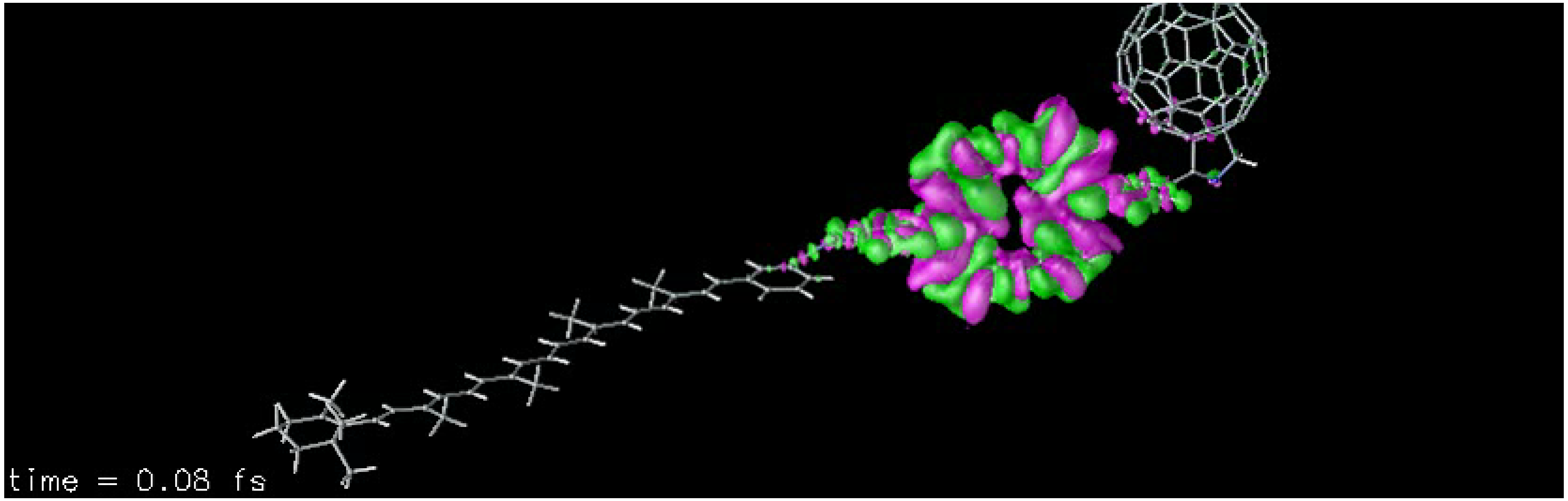
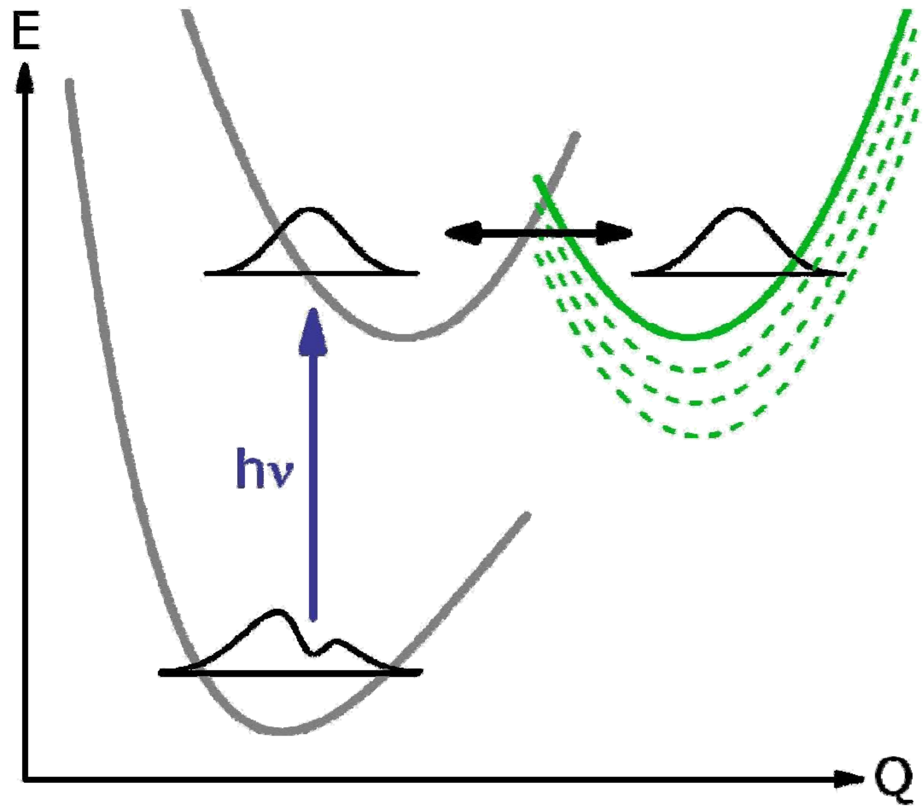
Coherent dynamics – DFT Simulations



Linker groups locked

Qualitative picture for the electron transfer



The coupling between electronic and nuclear degrees of freedom is important

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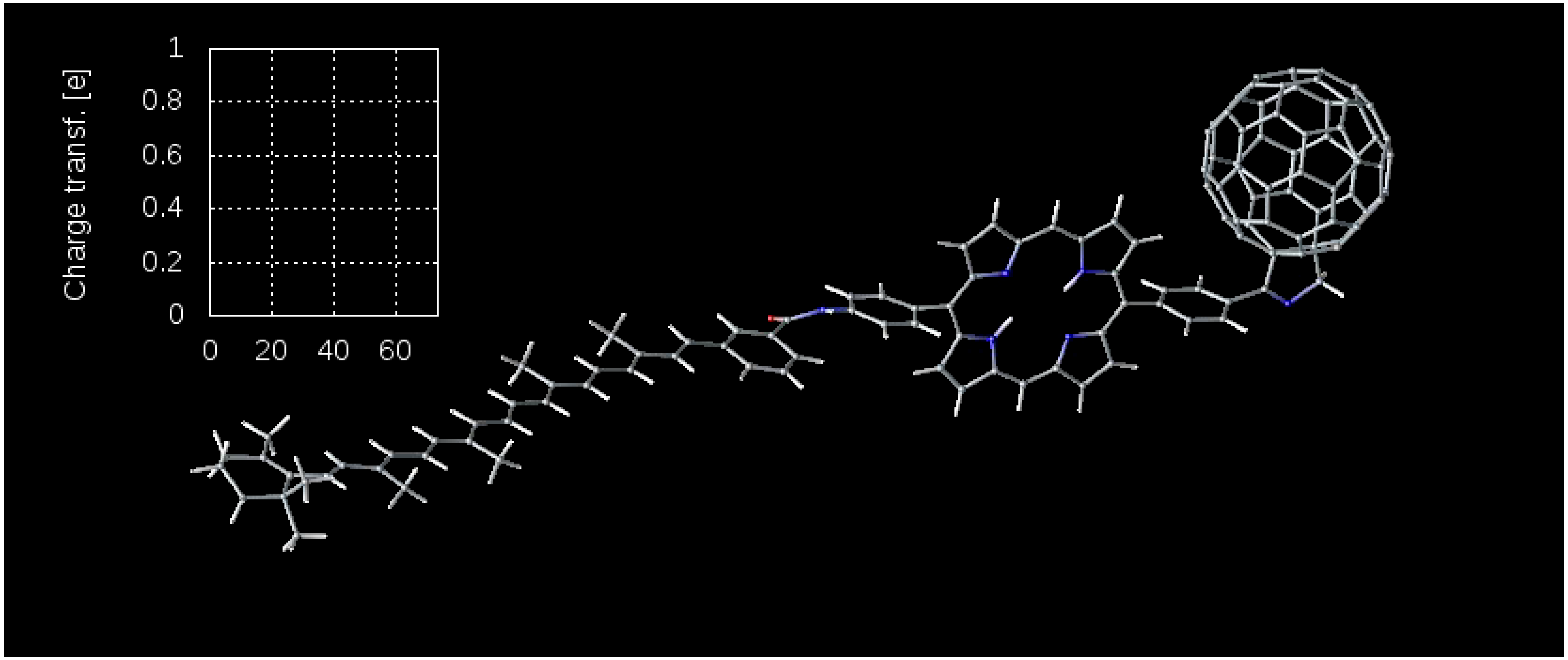
Coherent dynamics – DFT Simulations



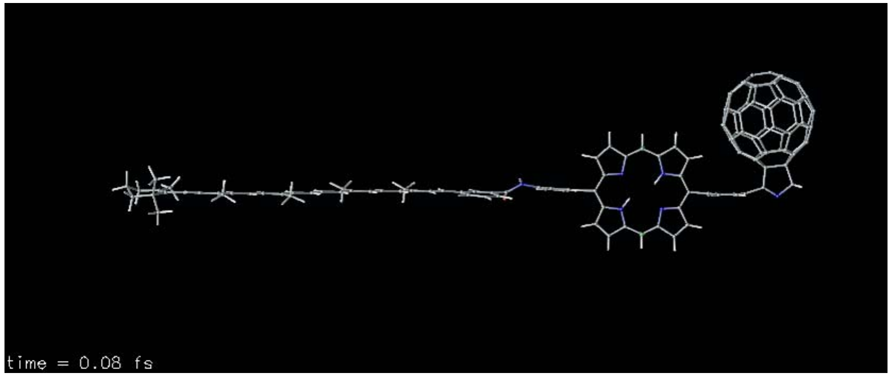
Motion of the ionic lattice

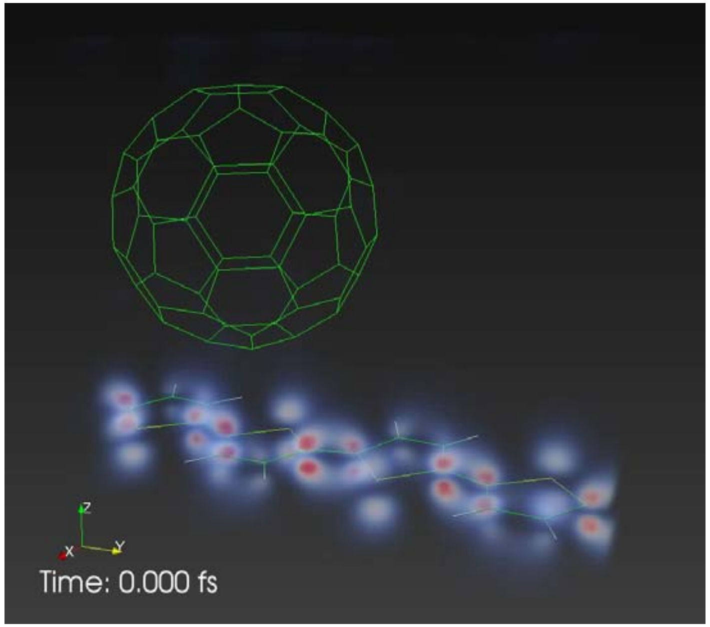
Summary Case II: Light Harvesting

- Two different case studies for quantum-coherent charge transfer dynamics

  Supramolecular C-P-C60 triad (covalently bound)

  Organic solar cell P3HT/PCBM (non-covalently bound)





- The quantum coherent coupling between electrons and nuclei is of central importance for the charge transfer in artificial light harvesting and organic solar cell systems

C. A. Rozzi et al., Nat. Comm. 4, 1602 (2013)
S. M. Falke et al., submitted (2014)

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Thank you!

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