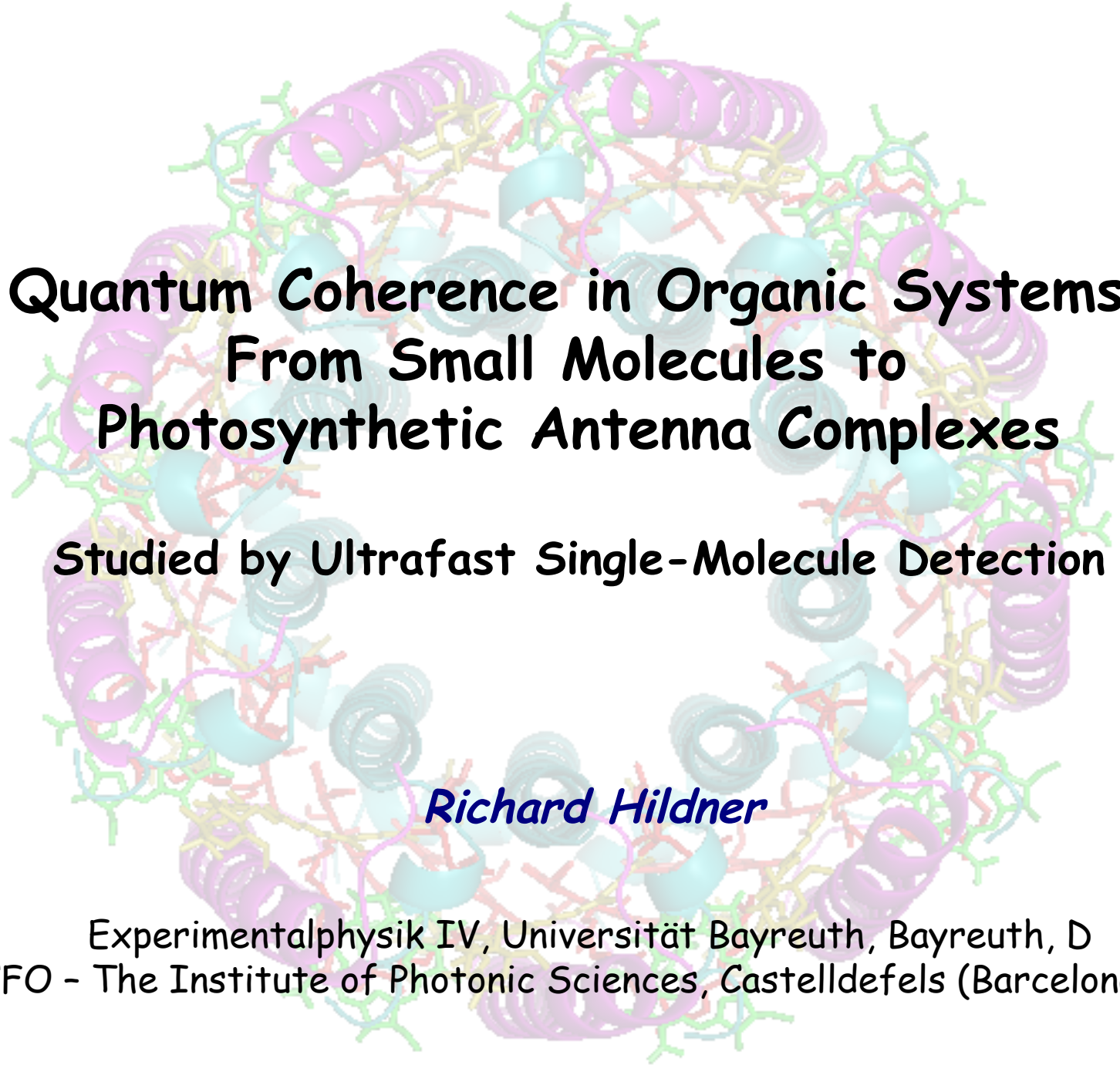


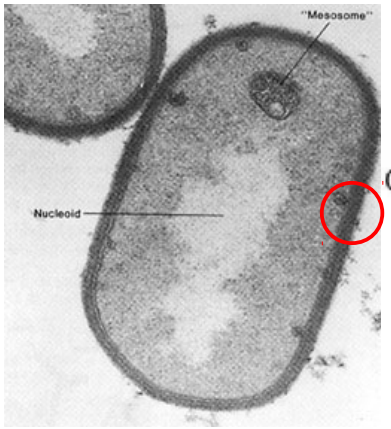
Quantum Coherence in Organic Systems: From Small Molecules to Photosynthetic Antenna Complexes

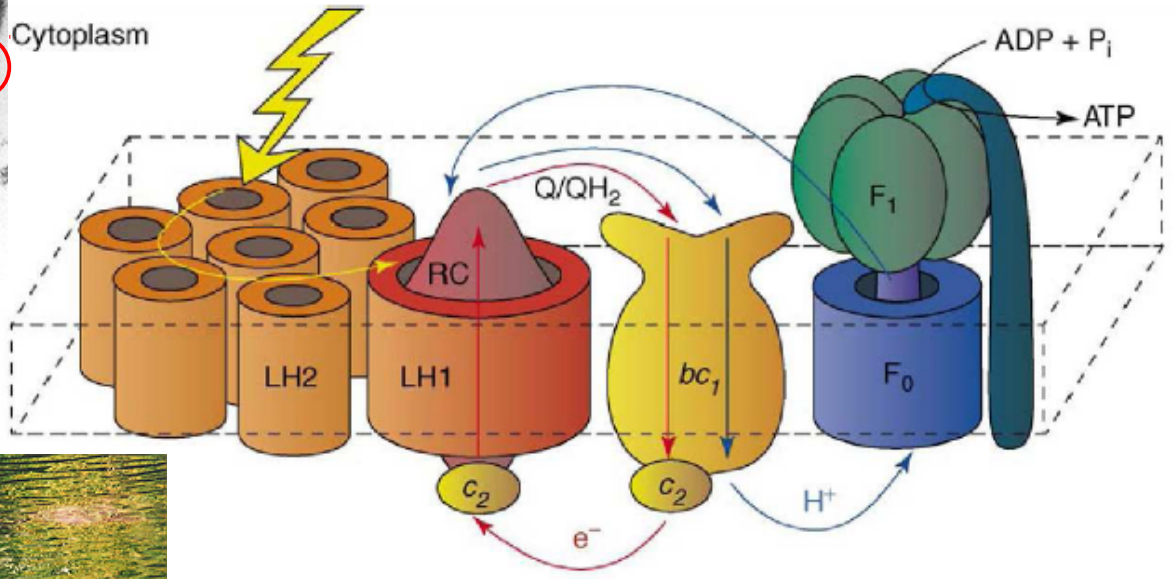
Studied by Ultrafast Single-Molecule Detection

Richard Hildner

Experimentalphysik IV, Universität Bayreuth, Bayreuth, D
ICFO – The Institute of Photonic Sciences, Castelldefels (Barcelona), ES

Bacterial Photosynthesis





Scheuring *et al.*, Curr. Opinion Chem. Bio.. **10** (2006) 387

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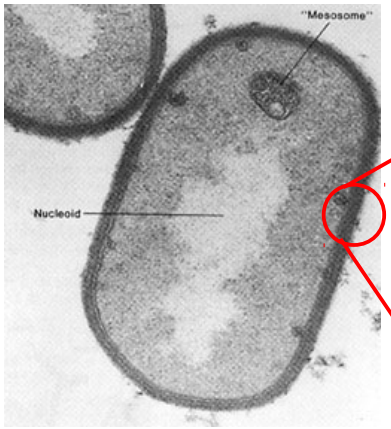

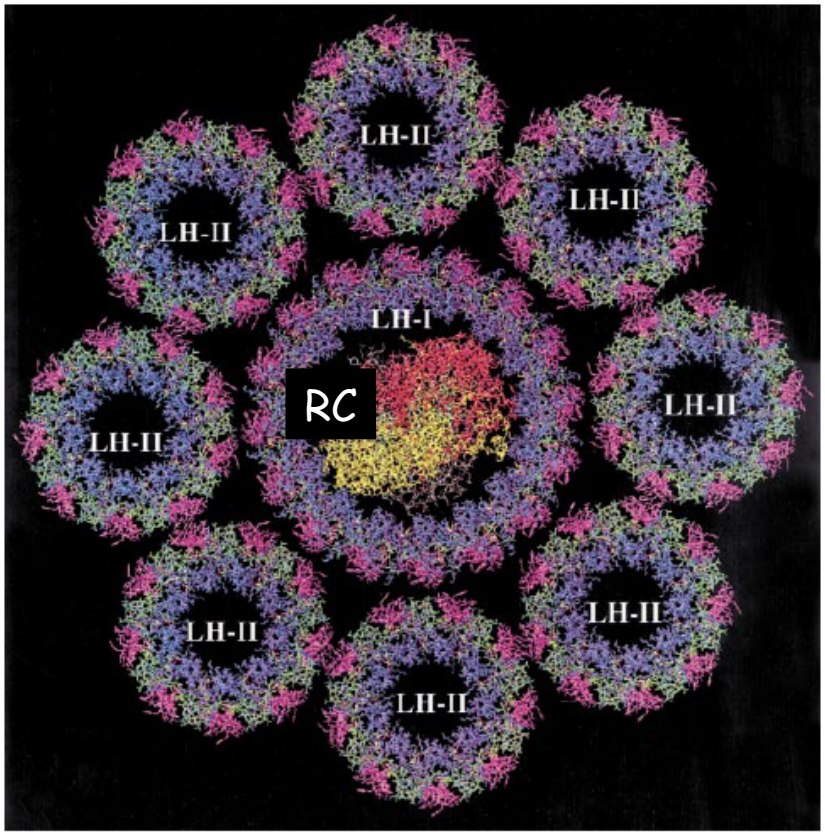

Hu *et al.*, Quart. Rev. Biophys. **35** (2002) 1

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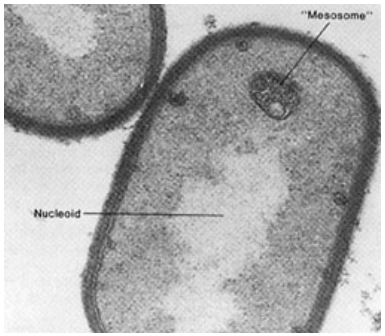

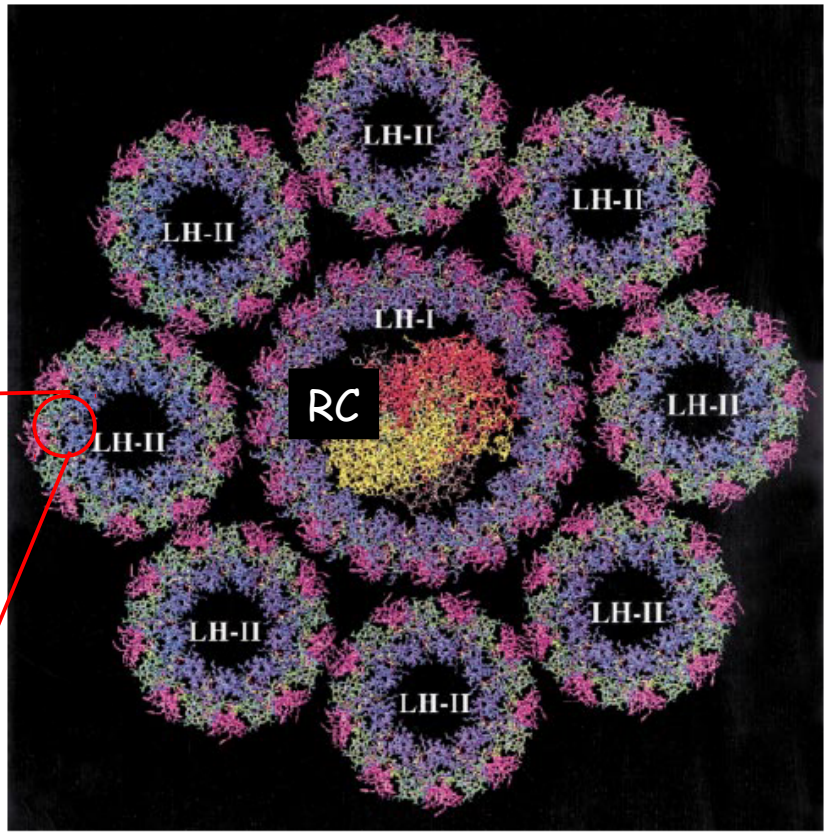

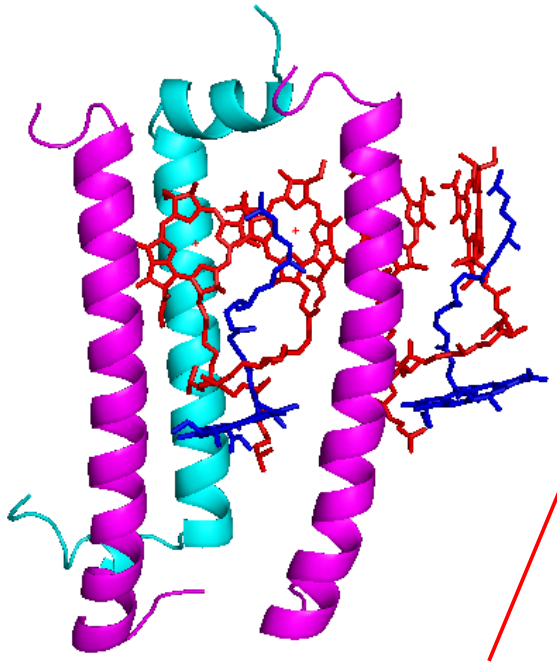

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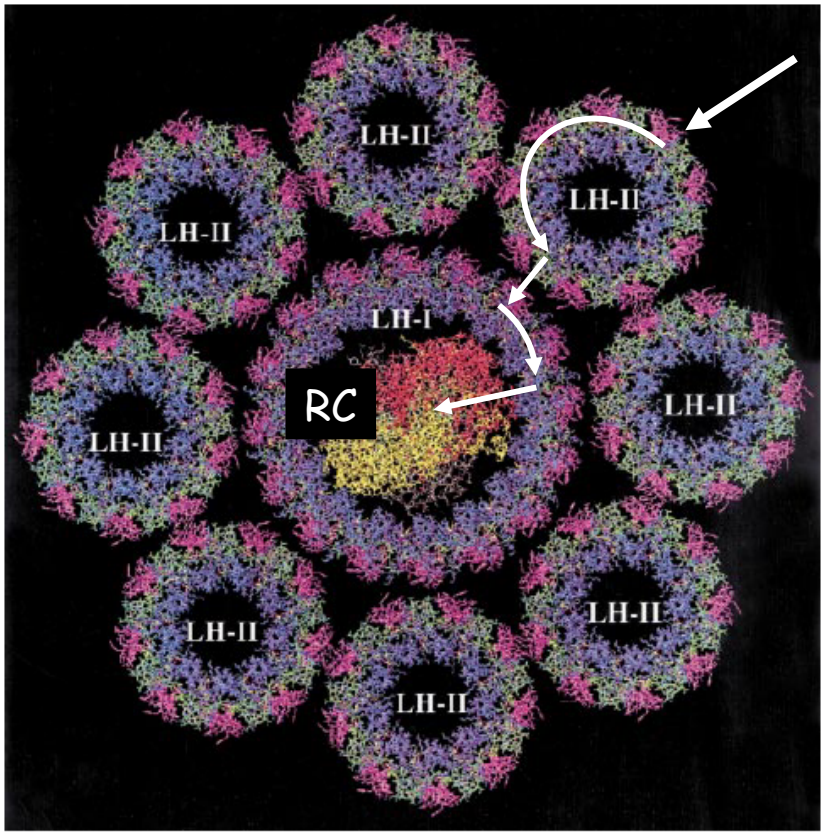
Ultrafast Processes in Photosynthesis

Transport of excitation energy:

- (sub-)ps
- highly directional
- near 100 % quantum efficiency



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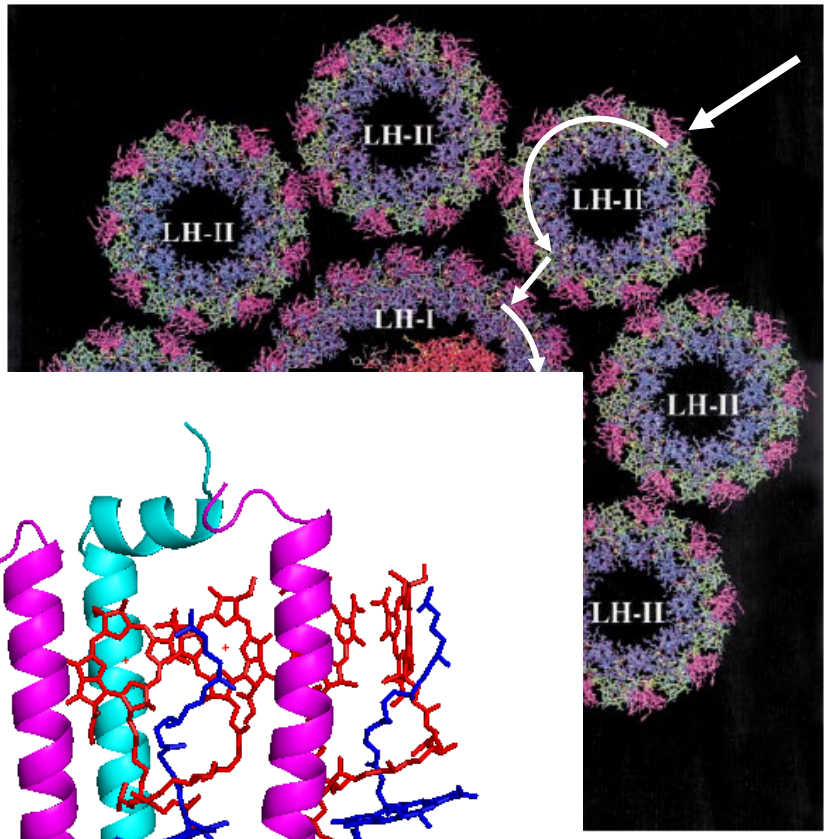

- Spatial organisation of pigments:
  1 molecule/nm^2

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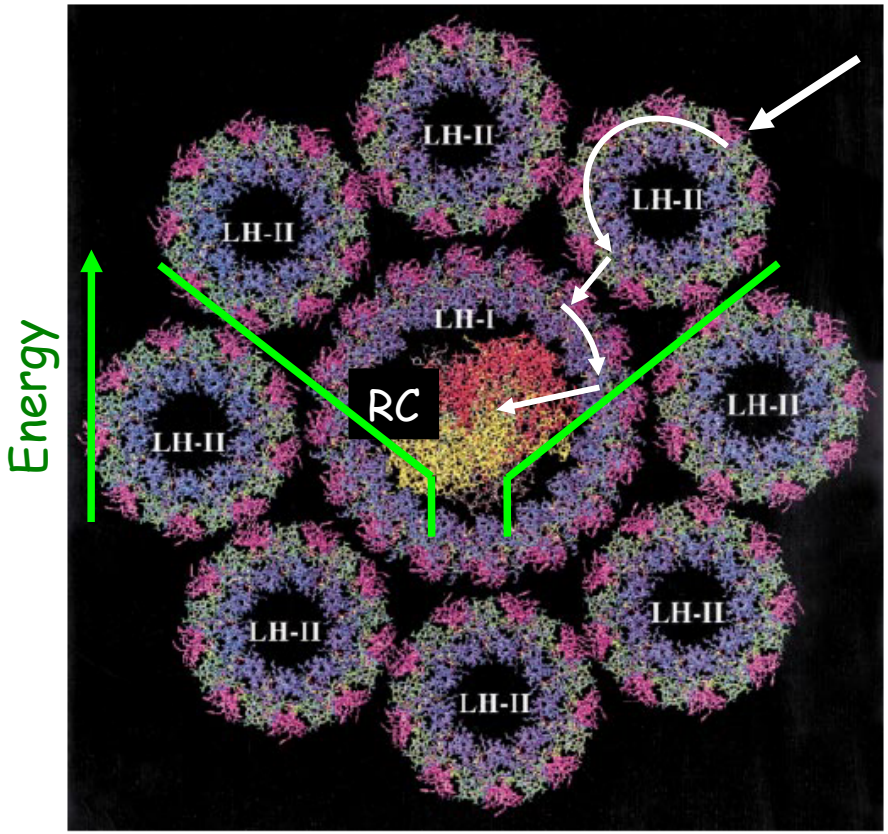


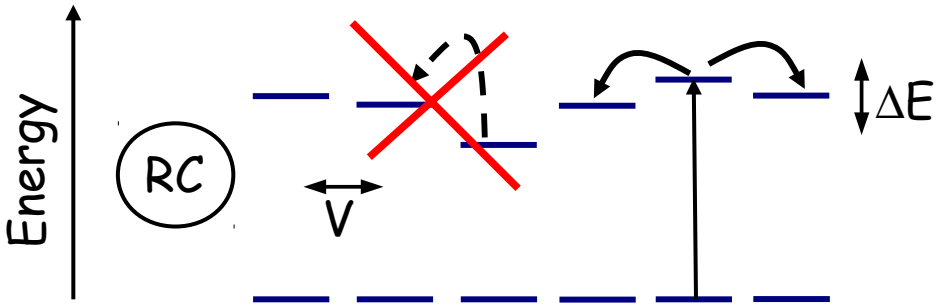
- Spatial organisation of pigments:
  1 molecule/nm^2

- Energy funnel

- ***Quantum coherent transfer?***

Hu *et al.*, Quart. Rev. Biophys. **35** (2002) 1

Weak Coupling Regime: V < ΔE



- energy disorder ΔE due to protein
- electronic coupling V due to proximity

→ incoherent hopping from site to site (Förster)

$$k = \frac{2\pi}{\hbar} V^2 \cdot I = \frac{1}{\tau}\left(\frac{R_0}{R}\right)^6$$

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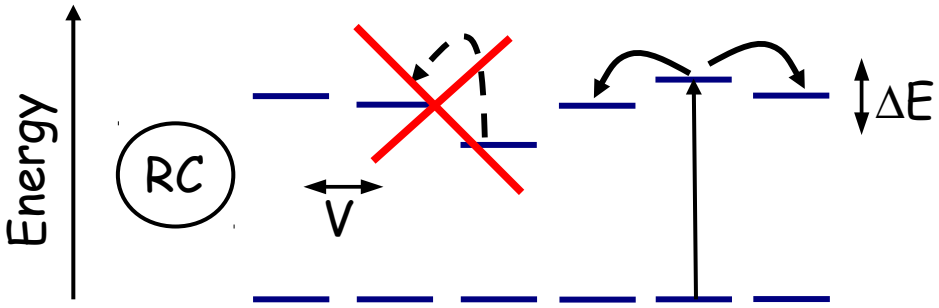

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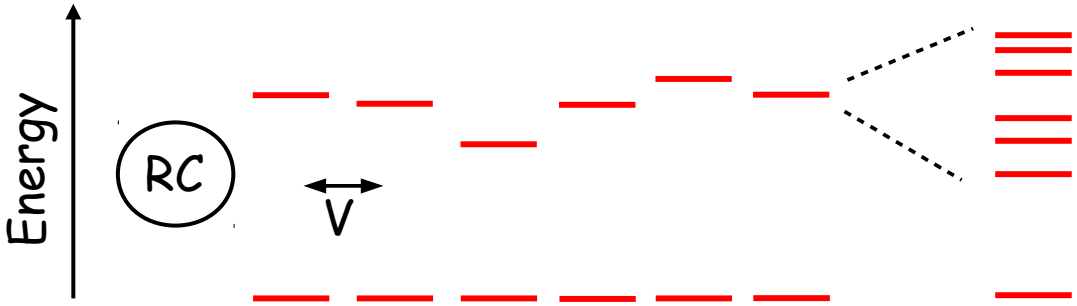
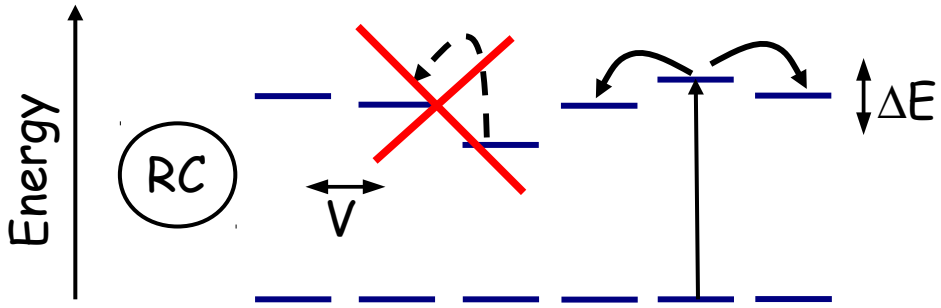


$H = \Sigma E_n |n><n| + \Sigma V_{nm} |n><m|$

→ Exciton states:

$|k> = \Sigma a_n |n>$

Weak Coupling Regime: V < ΔE



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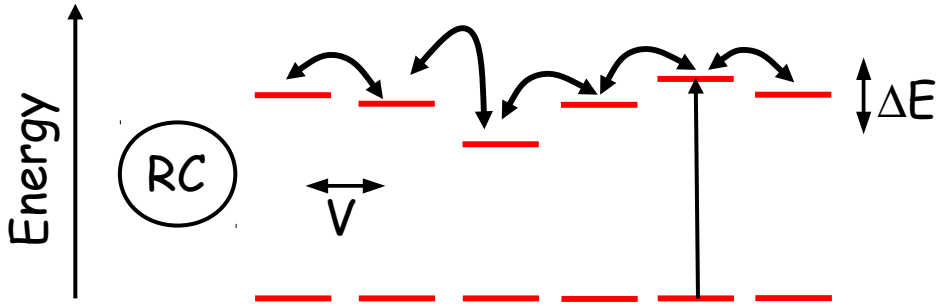


→ coherent delocalisation
→ population oscillations (in site basis)
~ 100 fs for V = 300 cm^{-1}

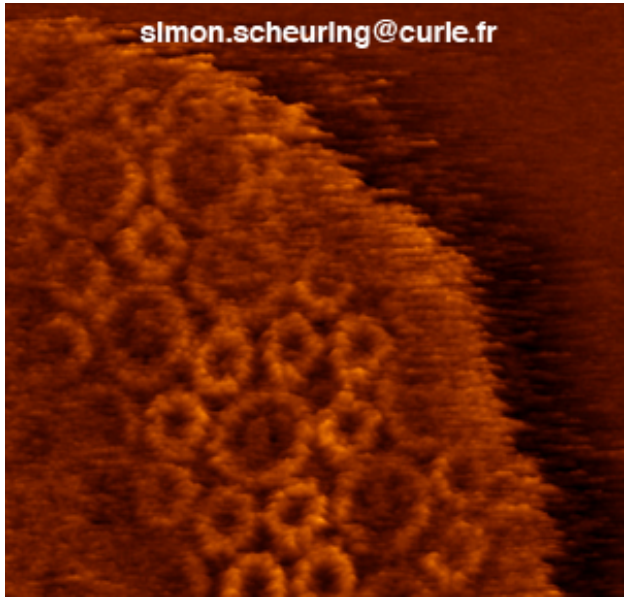
→ energy is available everywhere!

Does Coherence play a biological role?

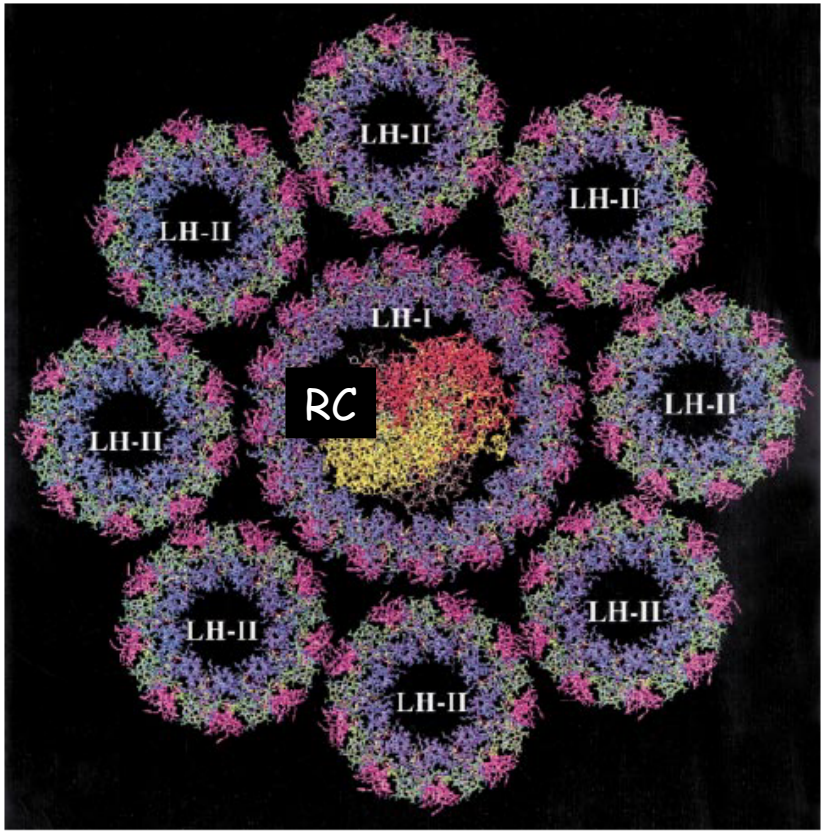
Coherence-assisted transport

Environmentally-assisted transport

Ultrafast Processes in Photosynthesis



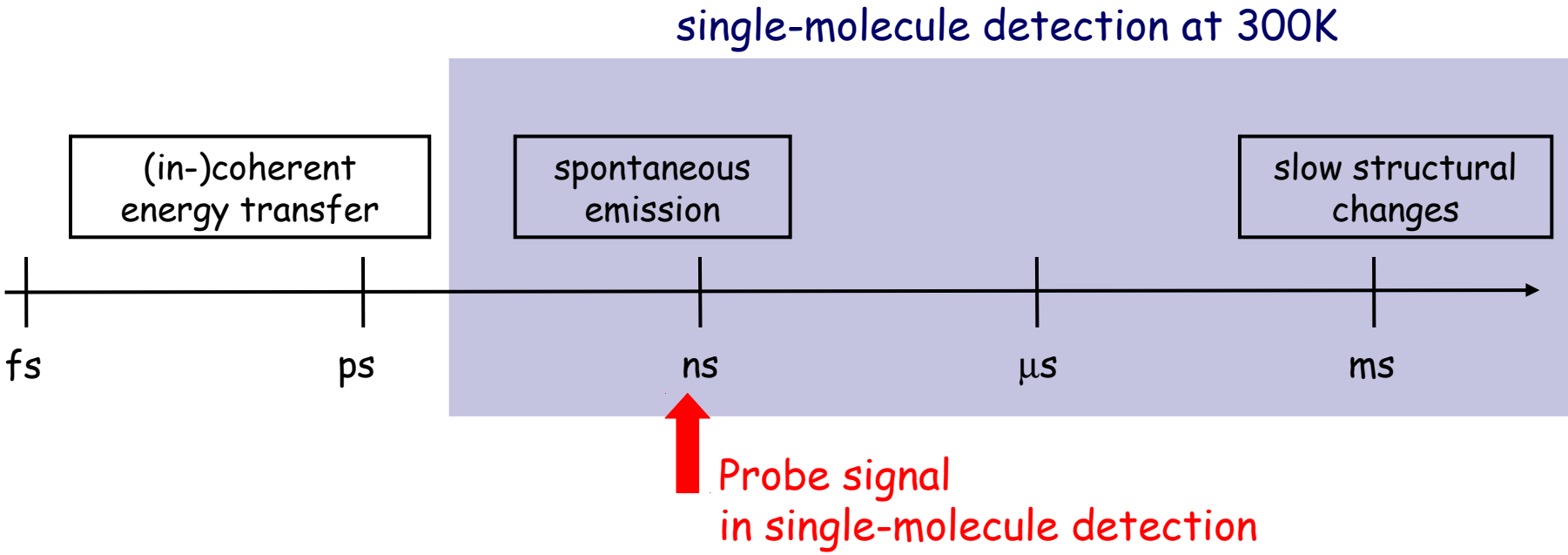
Scheuring *et al.*, EMBO J. **23** (2004) 4127



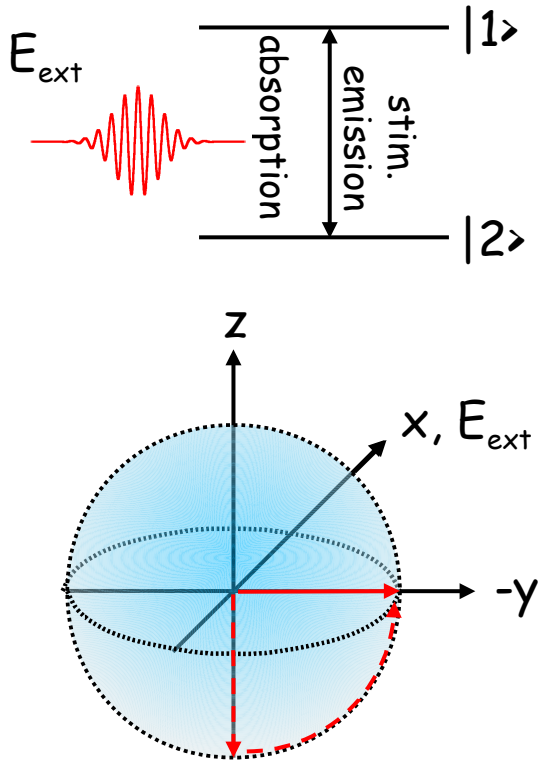
Hu *et al.*, Quart. Rev. Biophys. **35** (2002) 1

→ We have to understand the ultrafast response of single complexes

Ultrafast Single-Molecule Detection?



Principle of Ultrafast SM-Detection



- population oscillations $\omega_R = \frac{\mu_{12}}{\hbar} E_{ext}$
- coherent superposition state

$$\Psi(t) = a_1(t)\,|1\rangle + a_2(t)\,|2\rangle$$

$$\left.\begin{aligned} x &= a_2 a_1^{*} + a_1 a_2^{*} \\ y &= i\cdot\left(a_2 a_1^{*} - a_1 a_2^{*}\right) \end{aligned}\right\} \text{ coherences}$$

$$z = |a_1|^2 - |a_2|^2 \quad \text{population}$$

Feynman, Vernon, Hellwarth, J. Appl. Phys. 1957

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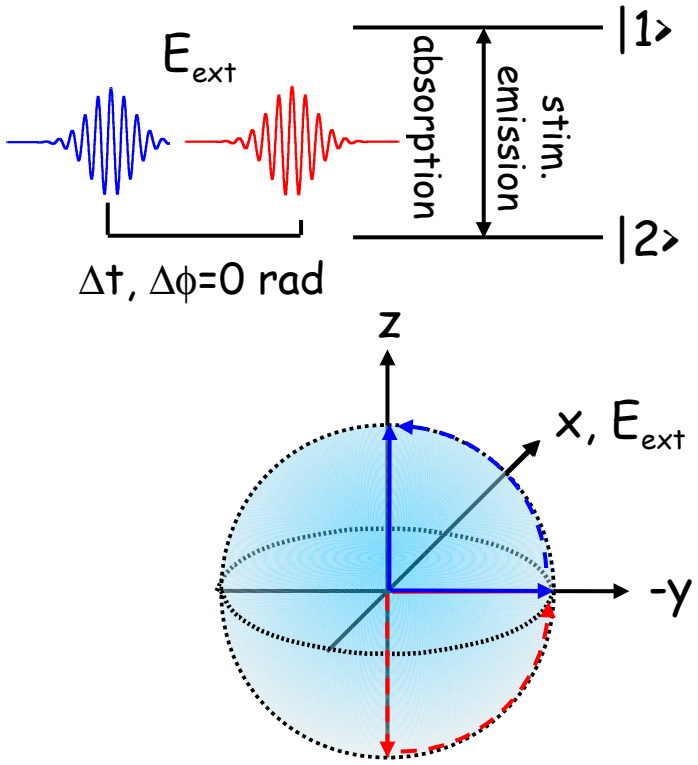

- population oscillations $\omega_R = \frac{\mu_{12}}{\hbar} E_{ext}$
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$$\Psi(t) >= a_1(t)\,1> + a_2(t)\,2>$$

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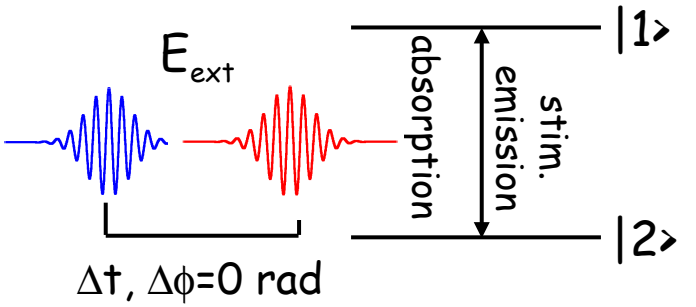
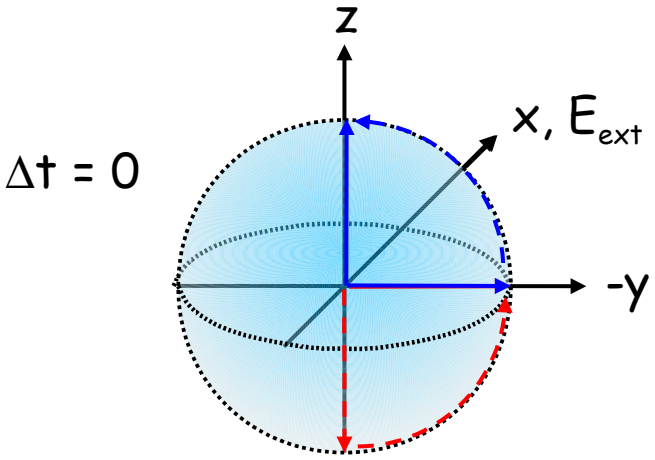
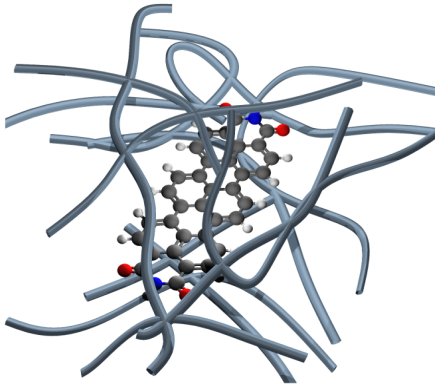




- environment 'destroys' coherence

→ pure dephasing time T_2^*



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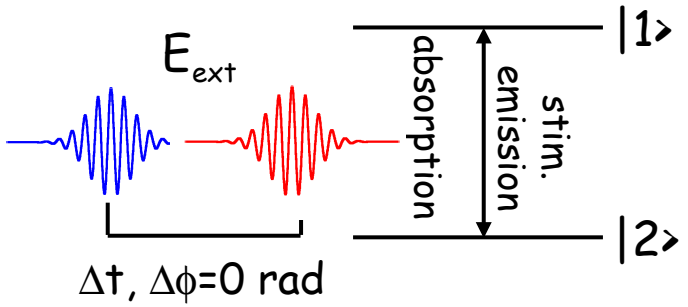

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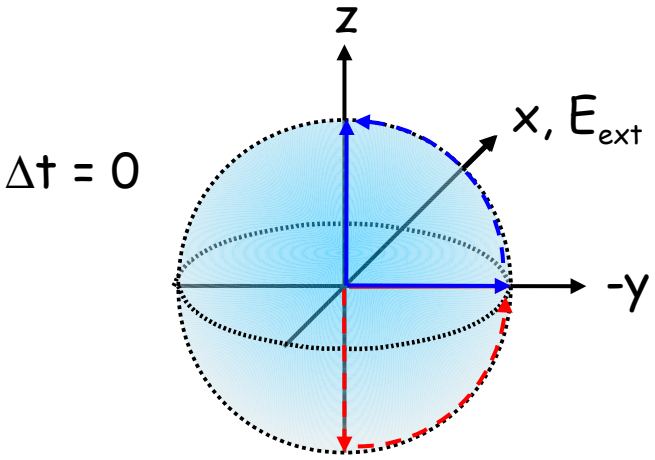

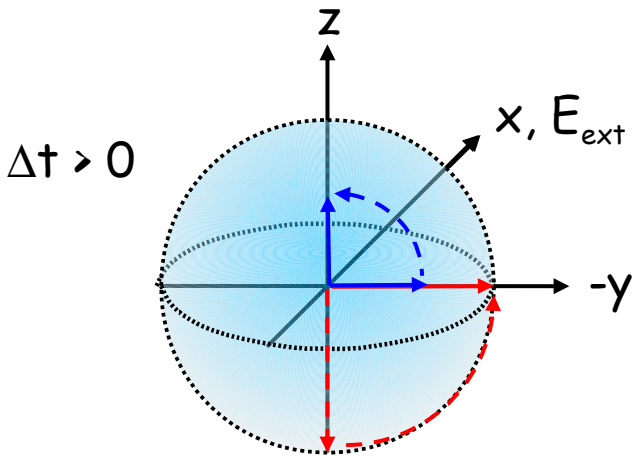

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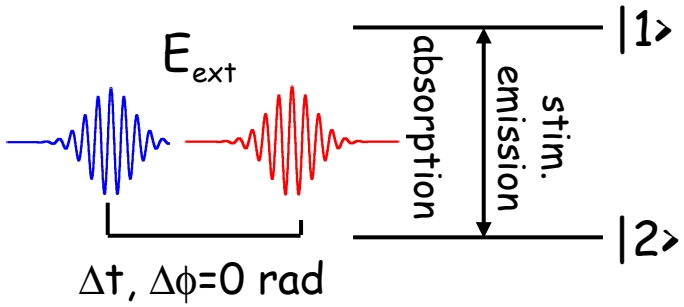

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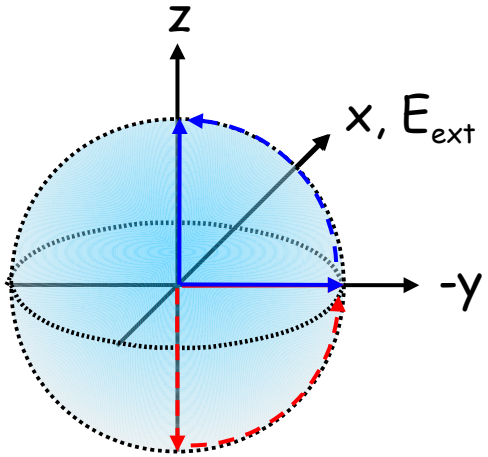
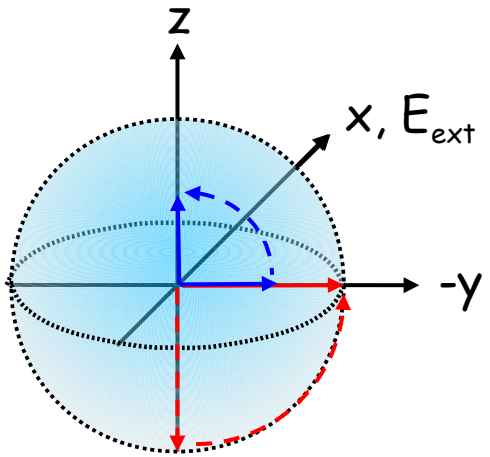
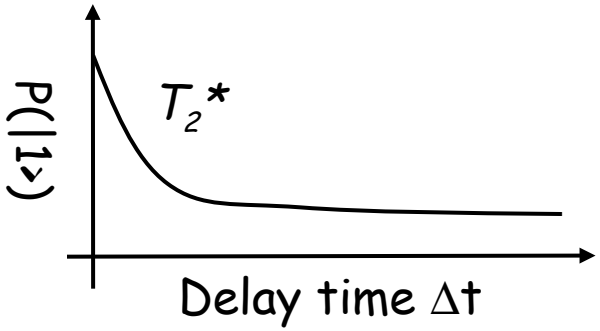


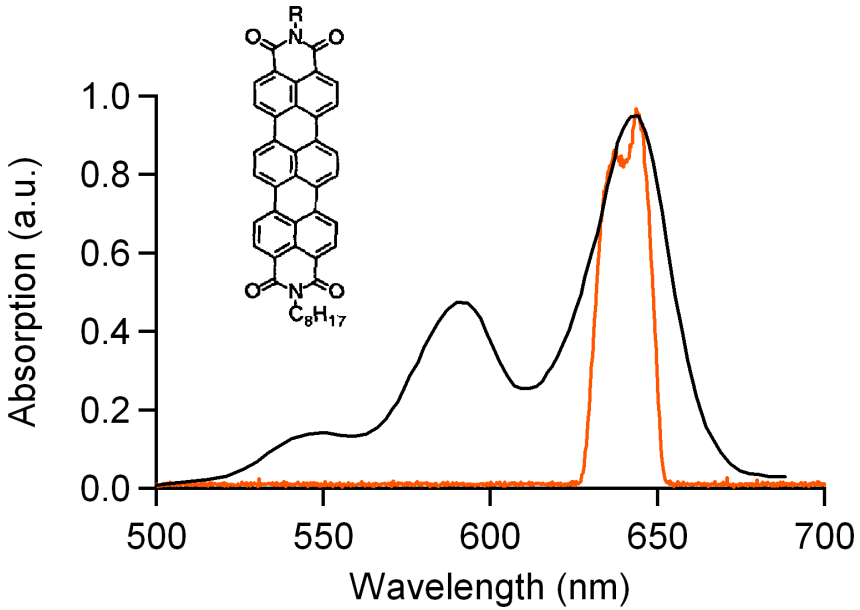




⟺ delay-dependent fluorescence

Ultrafast Single-Molecule Detection

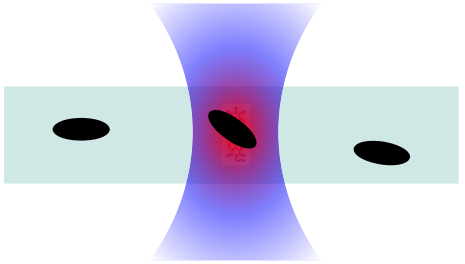
Terrylenediimide, TDI

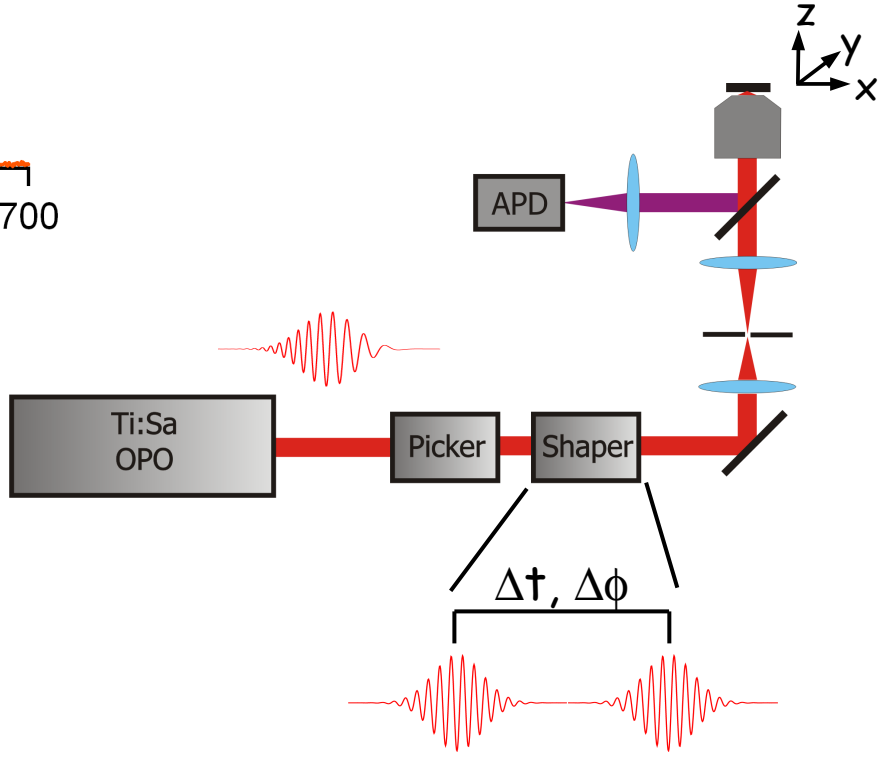


$\lambda_C \approx 630$ nm

$\Delta\lambda \approx 20$ nm

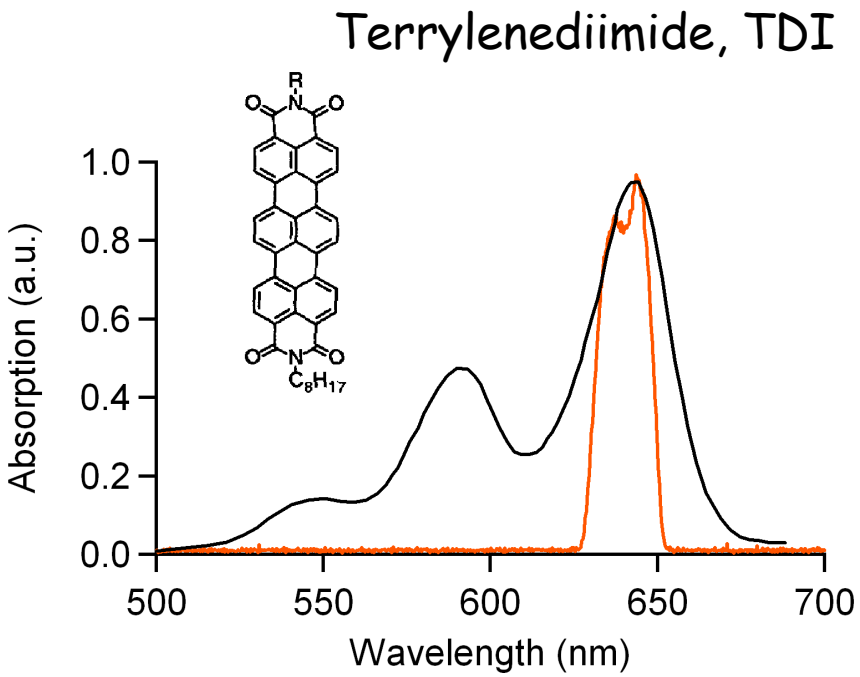
$\tau_{TL} \approx 75$ fs





Brinks, Hildner *et al.* Opt. Express 2011

Ultrafast Single-Molecule Detection



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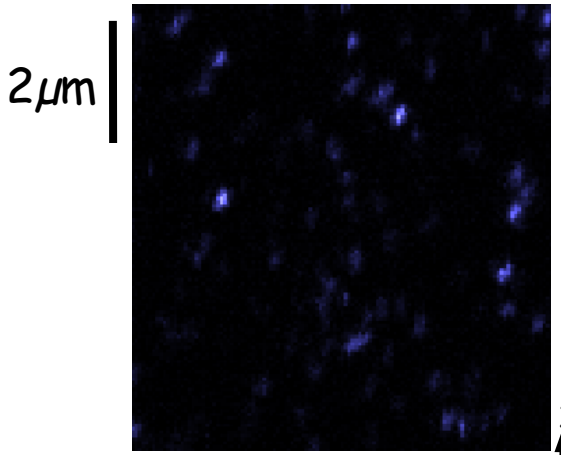
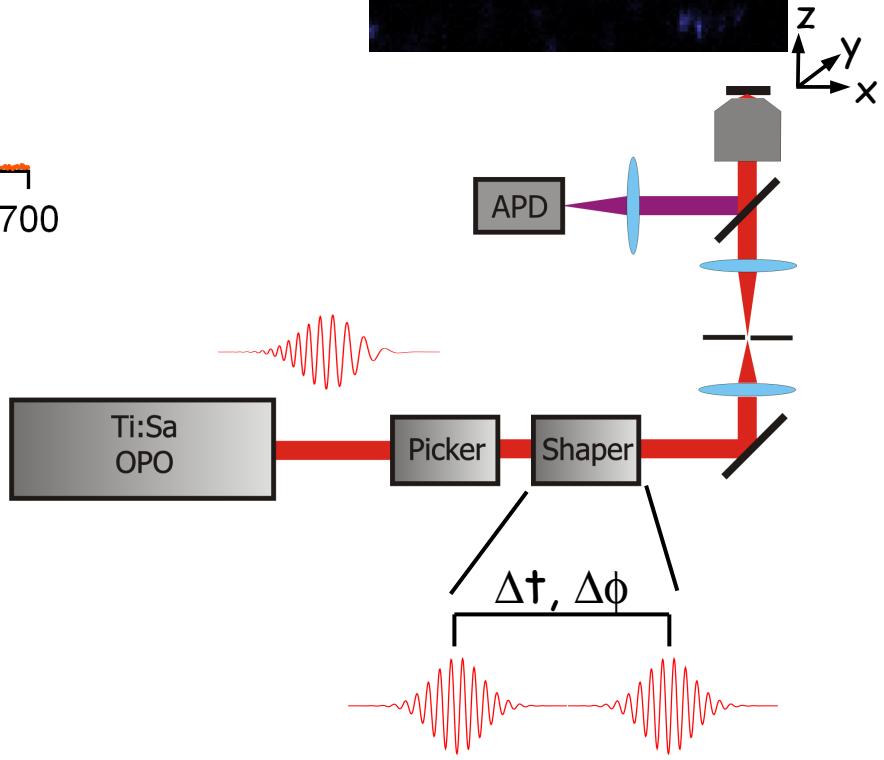
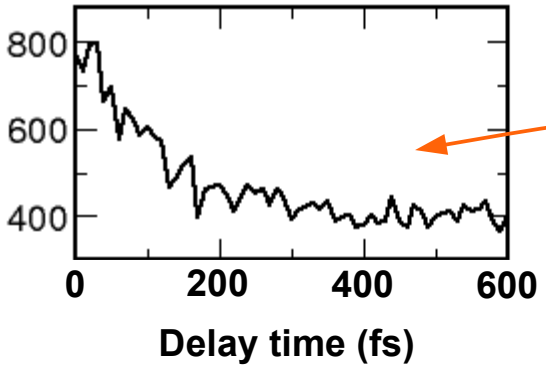
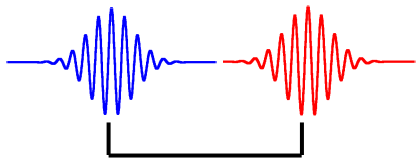




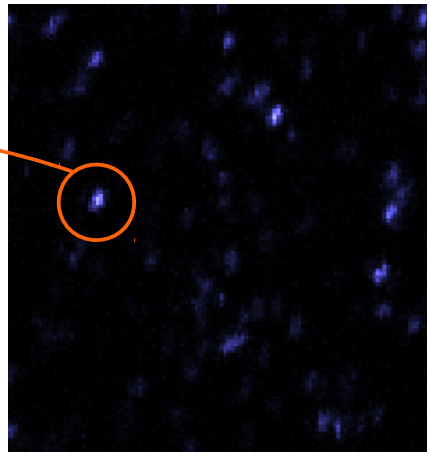
Brinks, Hildner *et al.* Opt. Express 2011

Coherence Decay of Single TDI





Δt, $\Delta\phi$=0 rad



Hildner, Brinks, van Hulst, Nature Phys. 2011

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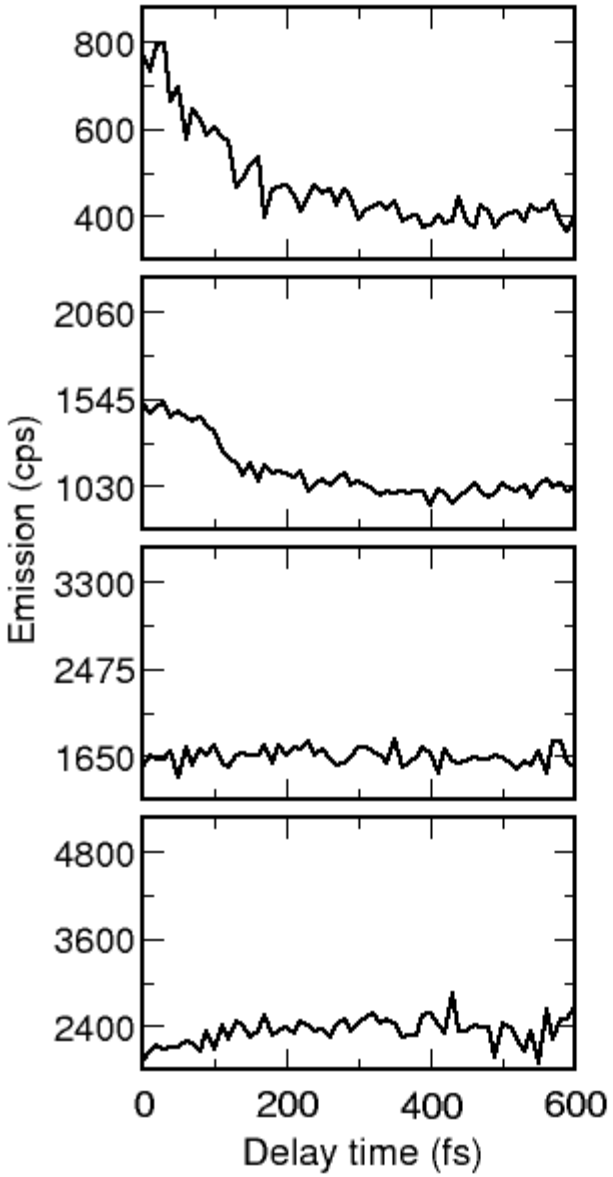

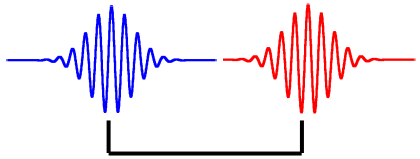

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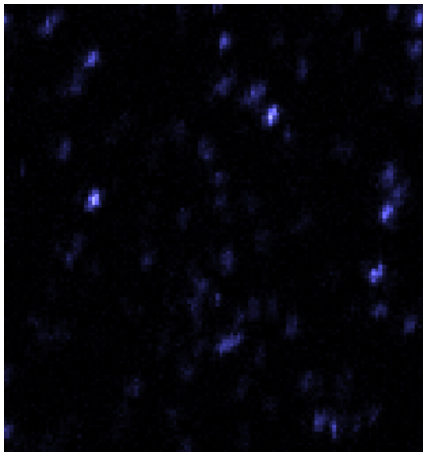
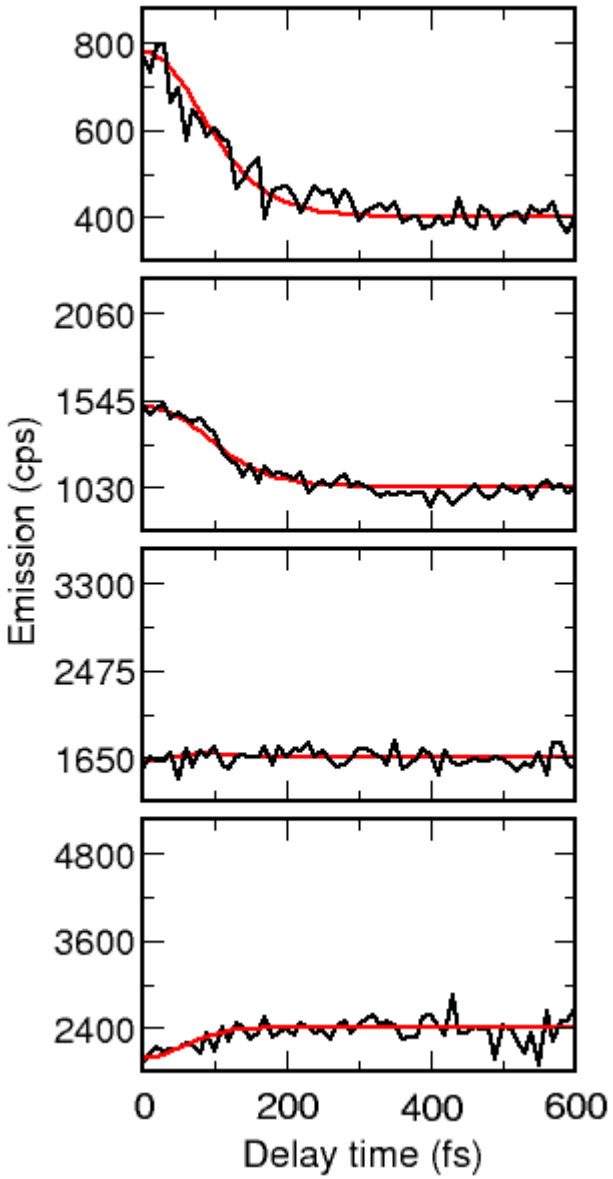


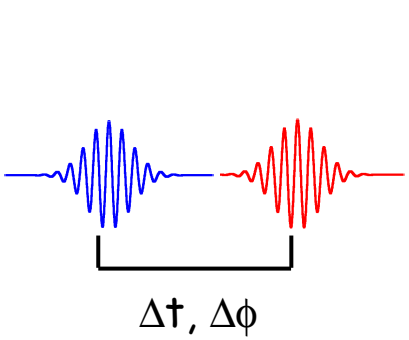
Hildner, Brinks, van Hulst, Nature Phys. 2011

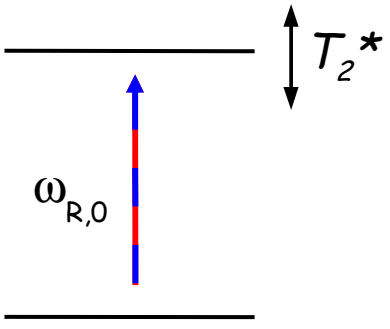
Rabi-Oscillations at 300 K



Density-matrix formalism:

- Rabi-frequency $\omega_{R,0}$
- pure dephasing time T_2^*





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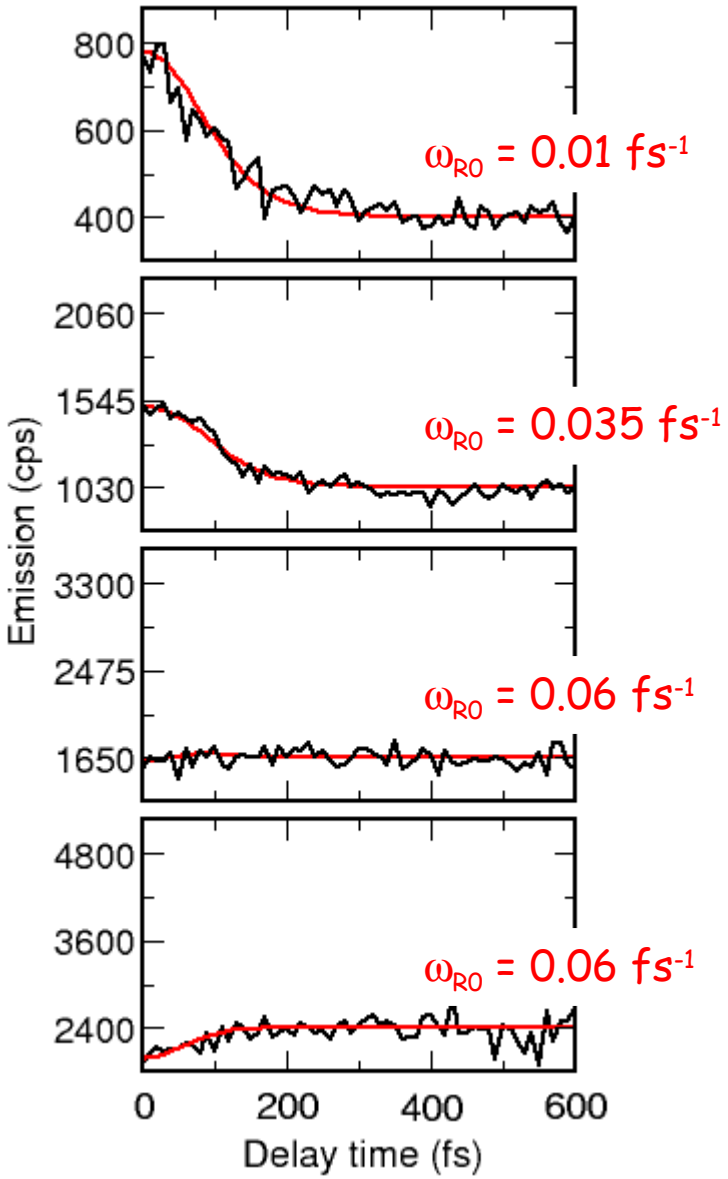
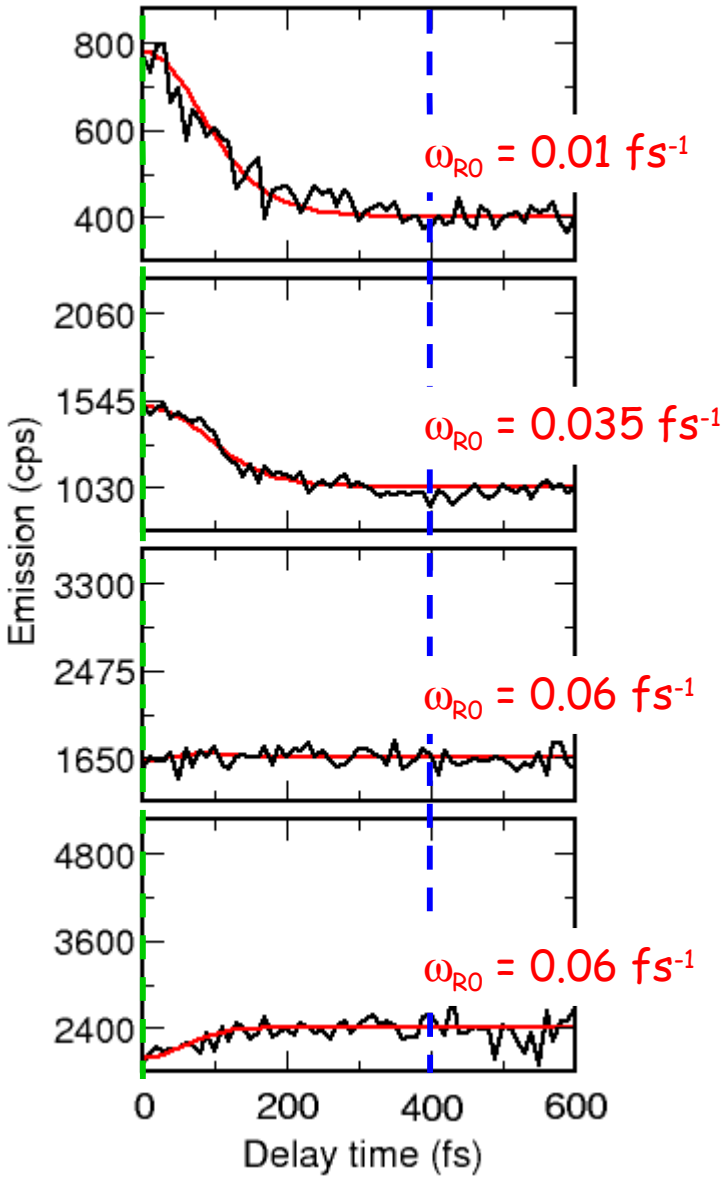
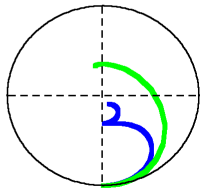
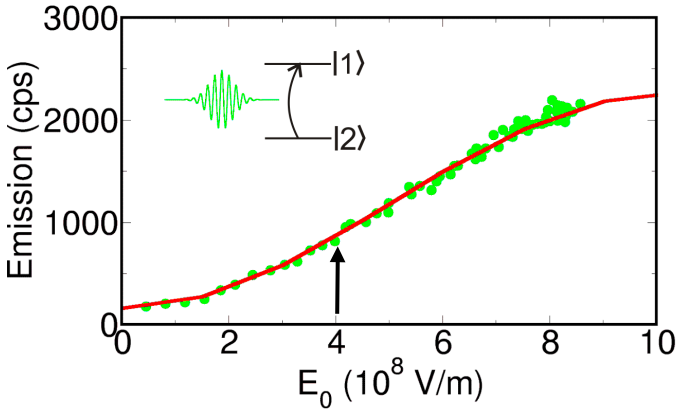


increasing Rabi-frequency/
light – molecule interaction

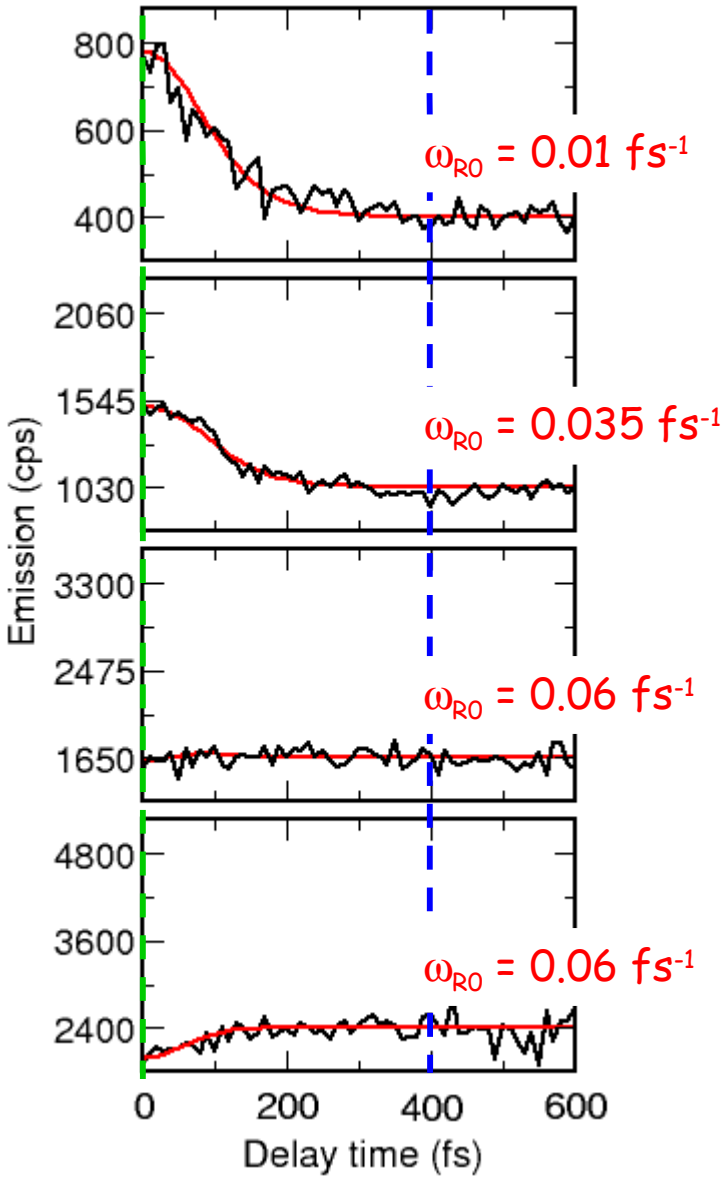
Rabi-Oscillations at 300 K

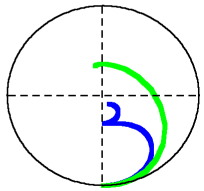


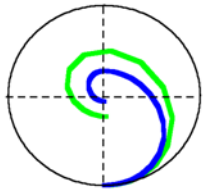


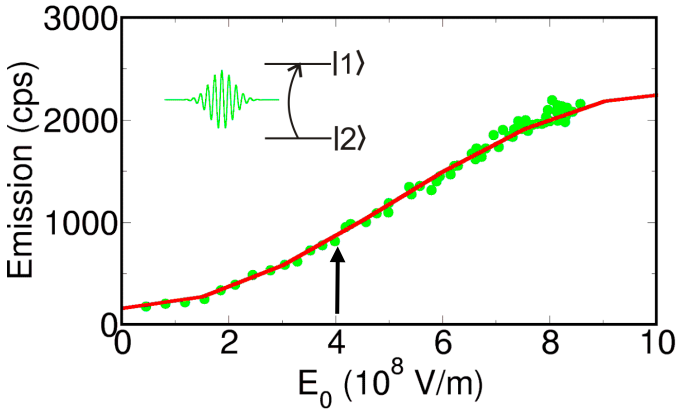


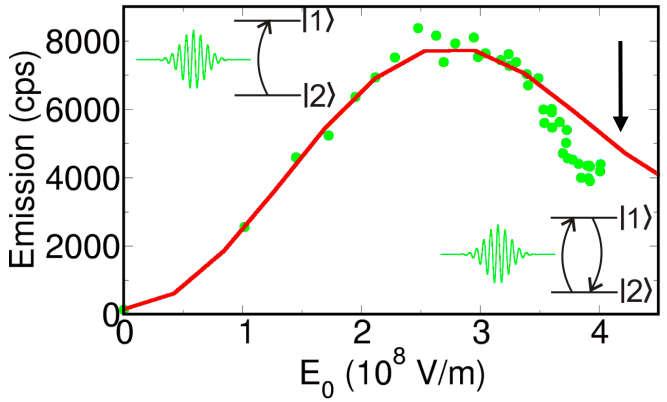
Rabi-Oscillations at 300 K



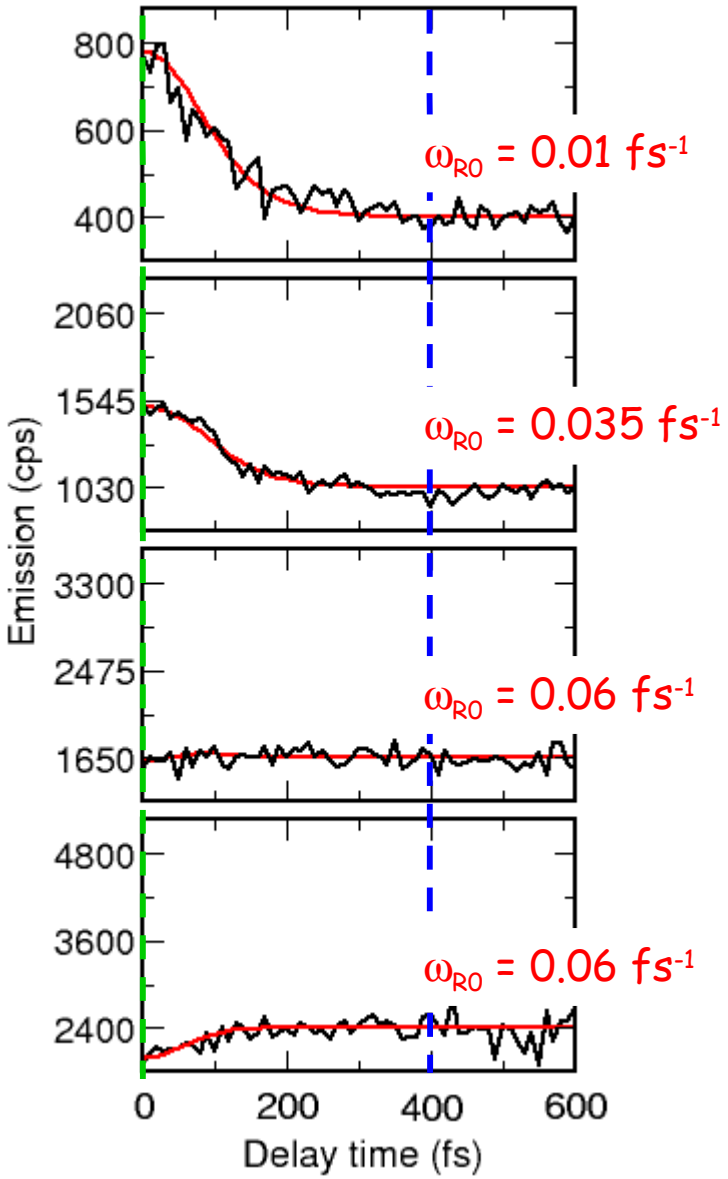


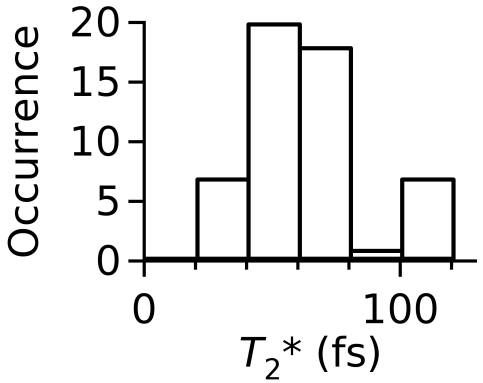


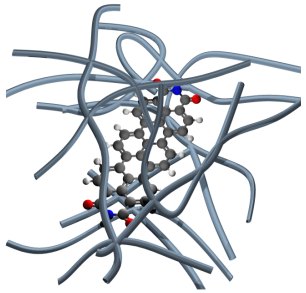




Dephasing at Room Temperature

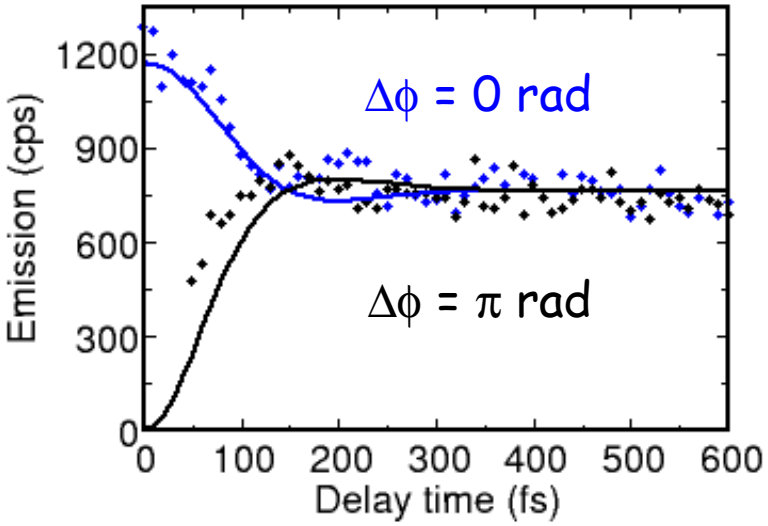


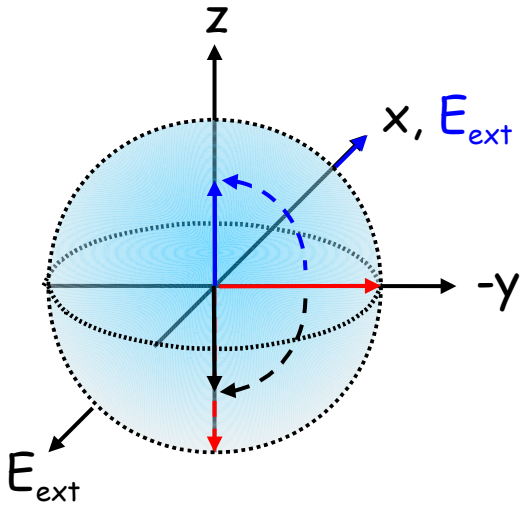


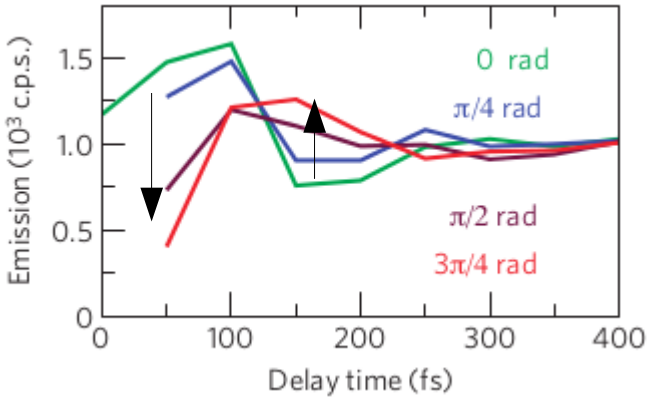


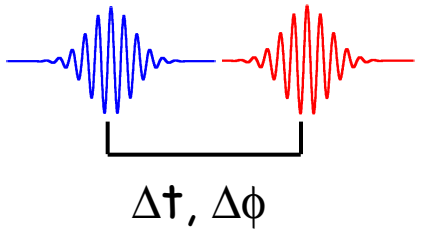
Hildner, Brinks, Stefani, van Hulst, PCCP 2011

Quantum Optics with Organic Molecules



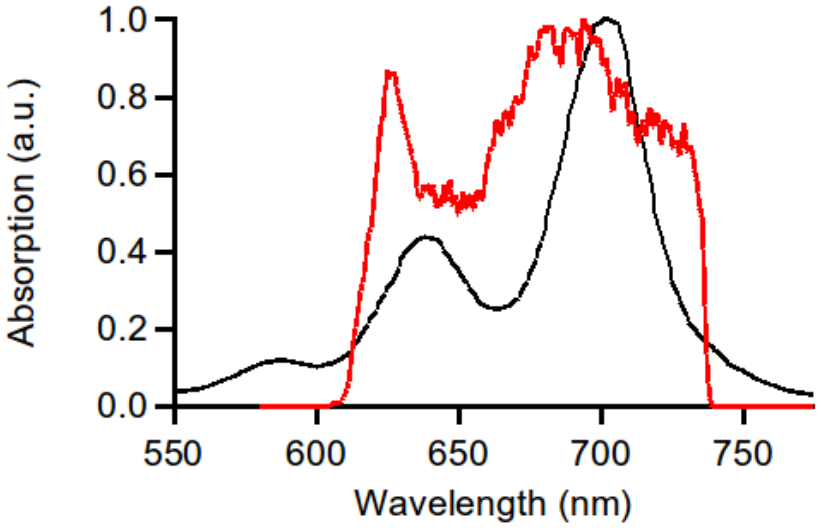




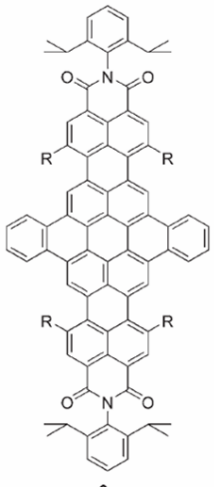


Hildner, Brinks, van Hulst, Nature Phys. 2011

Beyond 2-level systems

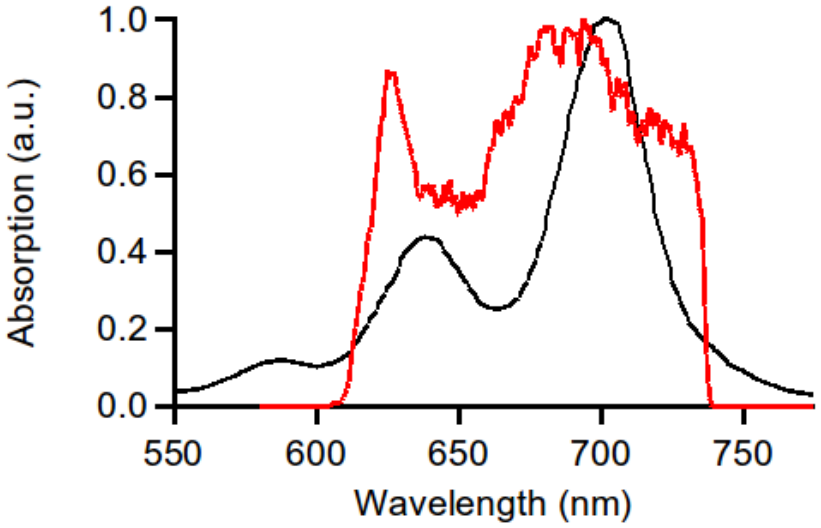


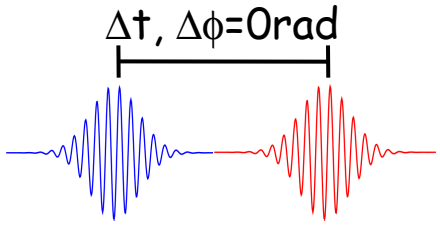
Dinaphtoquarterrylene, DNQDI

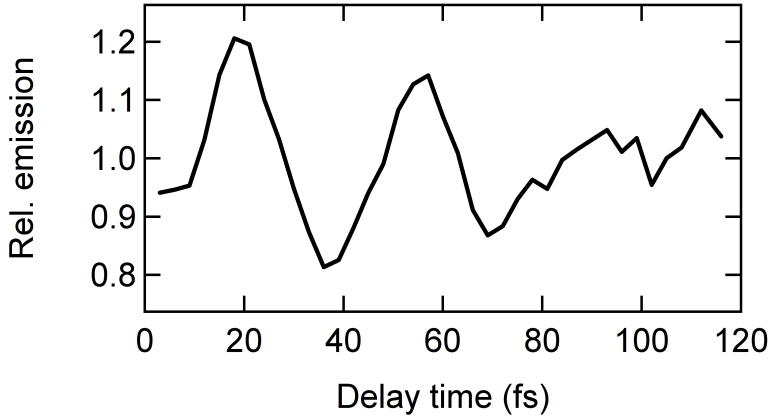


120 nm bandwidth
→ 15 fs pulse width

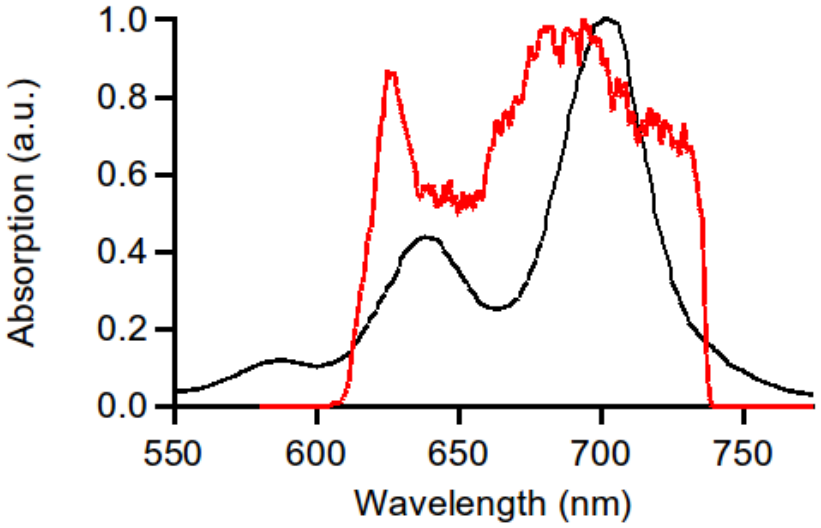
SM Wave-Packet Interference

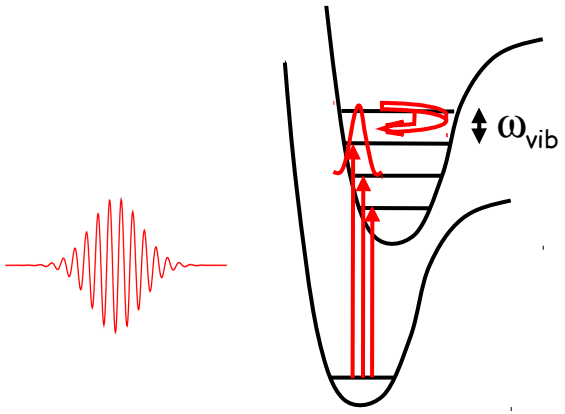


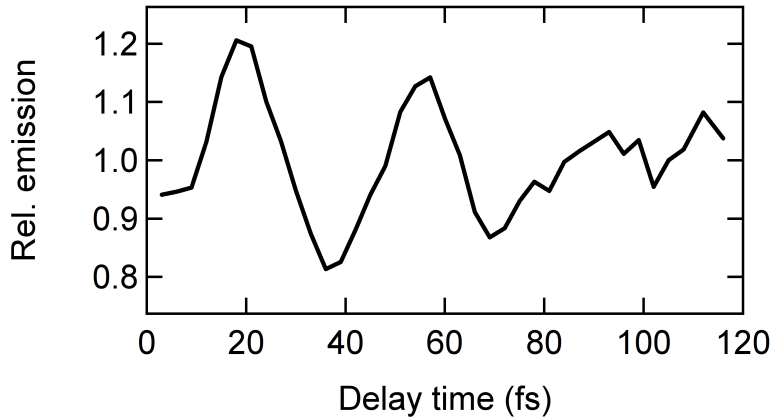




SM Wave-Packet Interference







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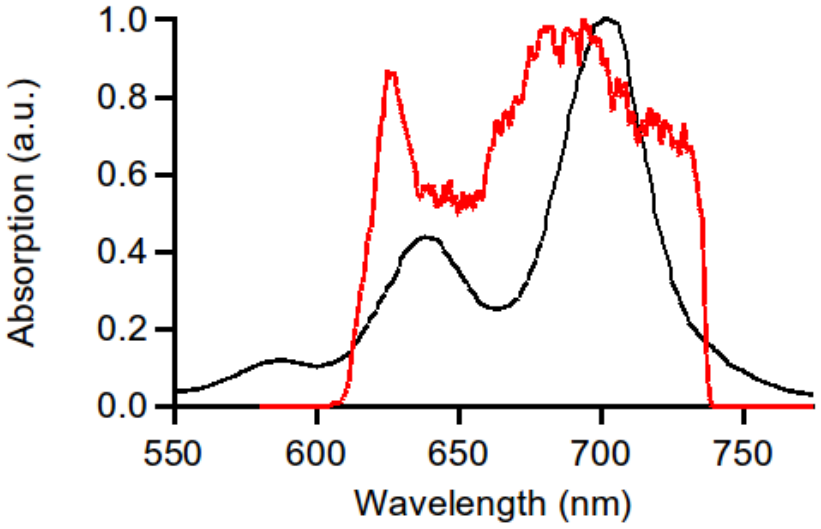
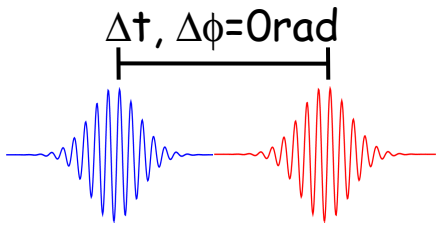
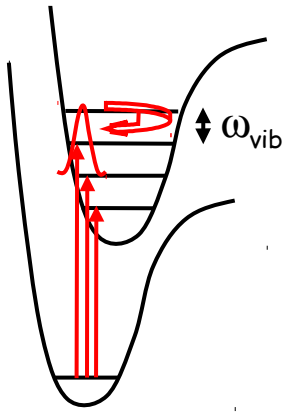
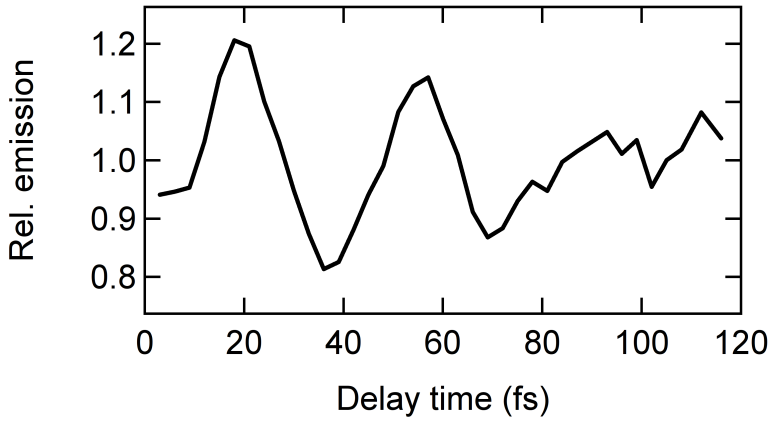
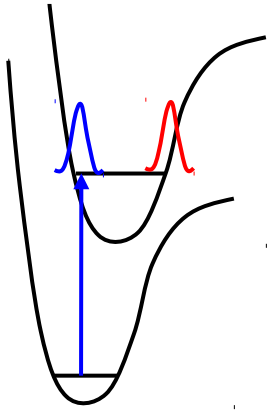






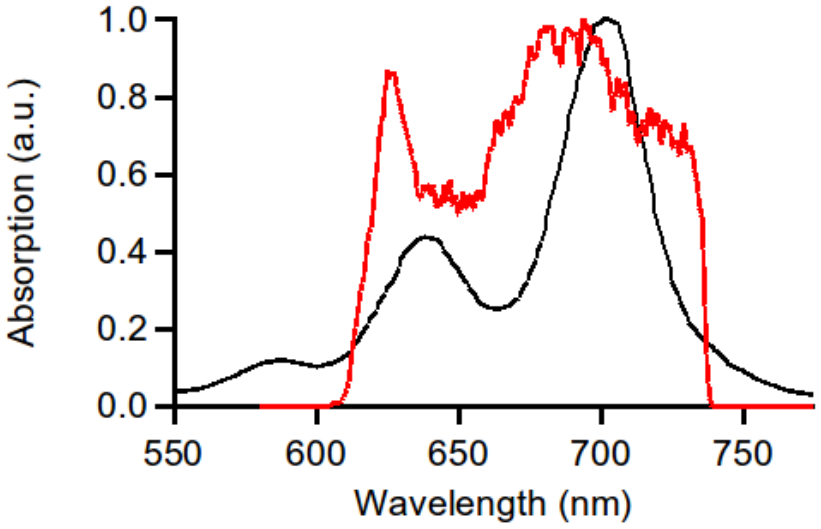


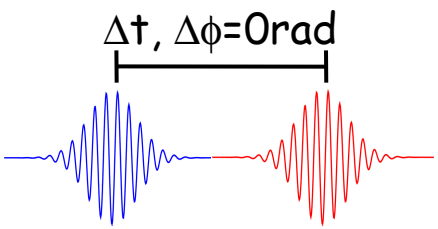


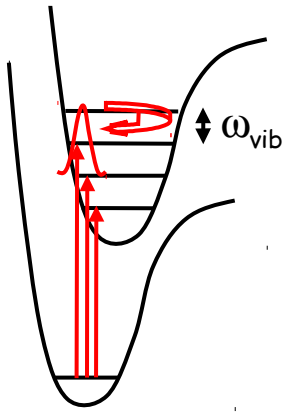
no interference

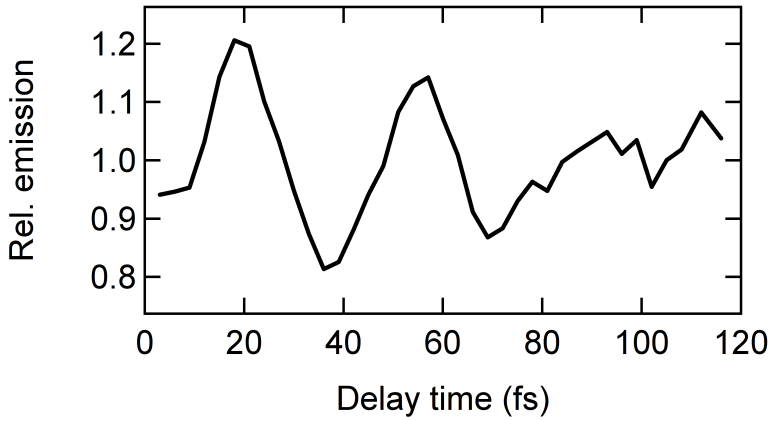
$P(S_1) \sim E_1^2 + E_2^2$

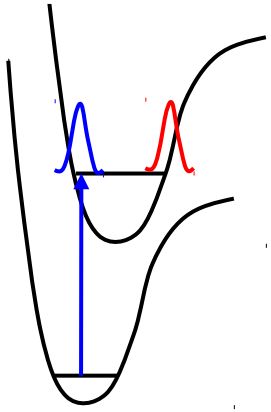
SM Wave-Packet Interference

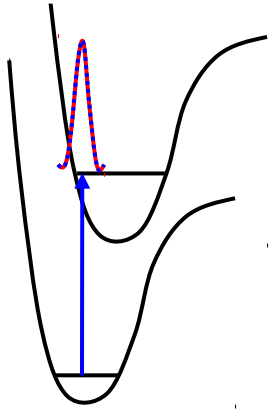












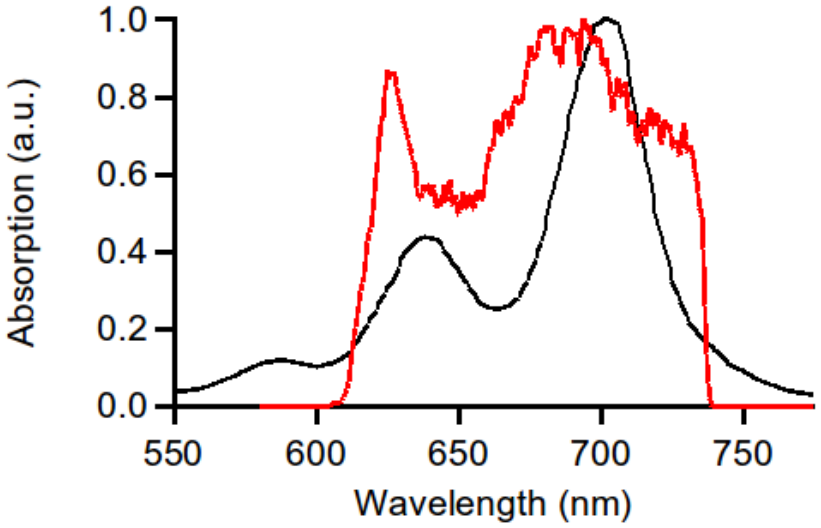
no interference

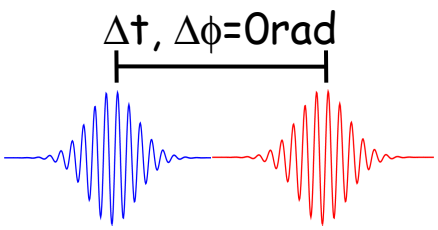
$P(S_1) \sim E_1^2 + E_2^2$

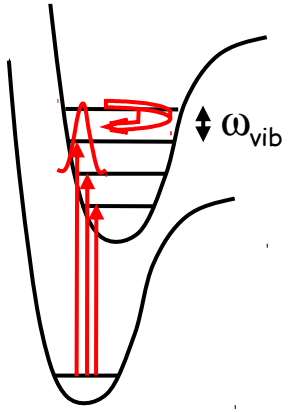
constr. interference

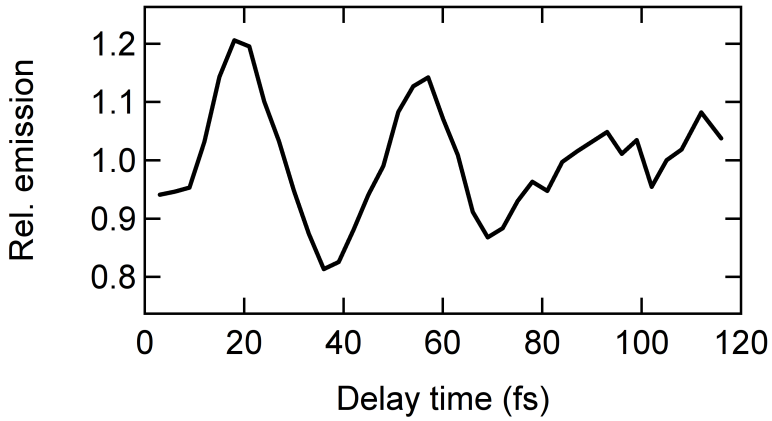
$P(S_1) \sim E_1^2 + E_2^2 + 2E_1E_2$

SM Wave-Packet Interference







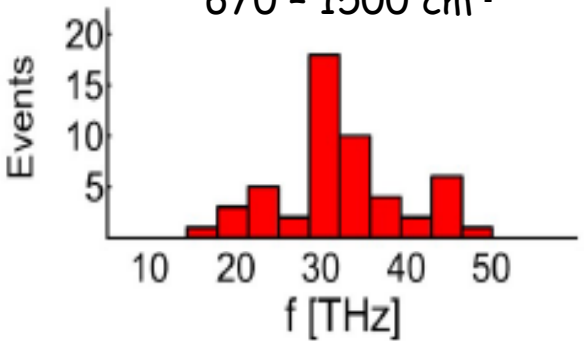


Fourier

Analysis

vibr. frequency:

670 – 1500 cm^{-1}



Brinks, Stefani, Kulzer, Hildner et al., Nature 2010

Summary

Femtosecond quantum optics with single molecules at 300 K

Wave-packet interference

Coherent fs-dynamics in single LH antenna complexes

Acknowledgements

People: Daan Brinks
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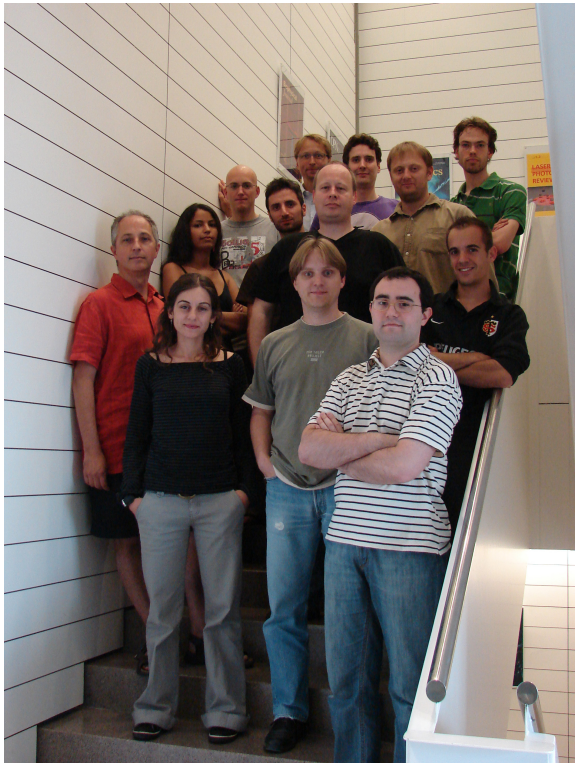
Florian Kulzer
Tim Taminiau
Niek van Hulst

ICFO Institut de Ciències Fotòniques

Klaus Müllen — MPI Mainz

Richard Cogdell — Uni Glasgow



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Consolider-Ingenio "Nanolight.es"
ERC Advanced Grant

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