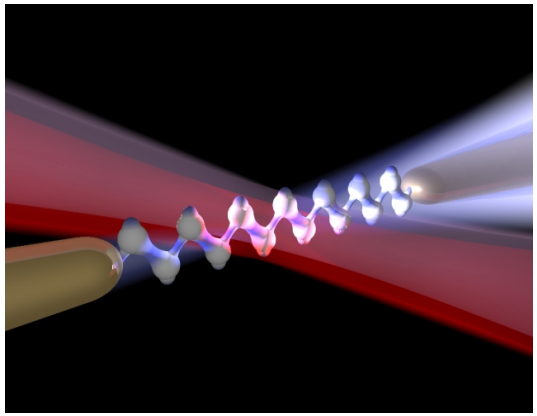


Excitations in strong fields and time-resolved excitations

Vibronic coupling: most important, often ignored, and a challenge for ab-initio theory

Ignacio Franco

November 6-9, 2012

CECAM-HQ, Lausanne

Previously in this meeting

- **Non-adiabaticity**
- Thermoelectrics and heat transport
- Thermoelectrics and catalysis
- Electronic excitations
- Semiconductors and nanostructures

The time for dynamics

The basic question:

What are the dynamical effects introduced by vibronic couplings during and after excitation of matter with a time-dependent external field and how do we capture them theoretically?

Non-equilibrium
What happens?
How long does it take?

Material's response to external stimuli

as an observational tool

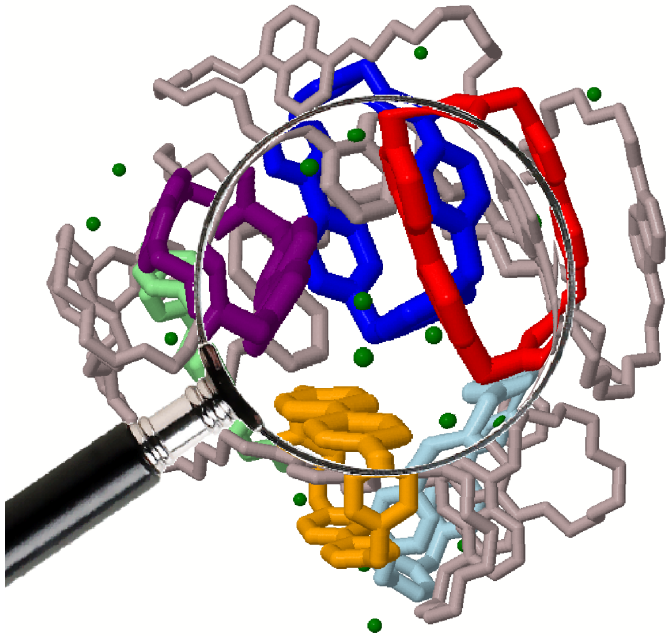
$h\nu$

$\mathbf{E}$

$\mathbf{H}$

$\mathbf{F}$

...



Info about the workings of the molecular world

Material's response to external stimuli

as a **control** tool

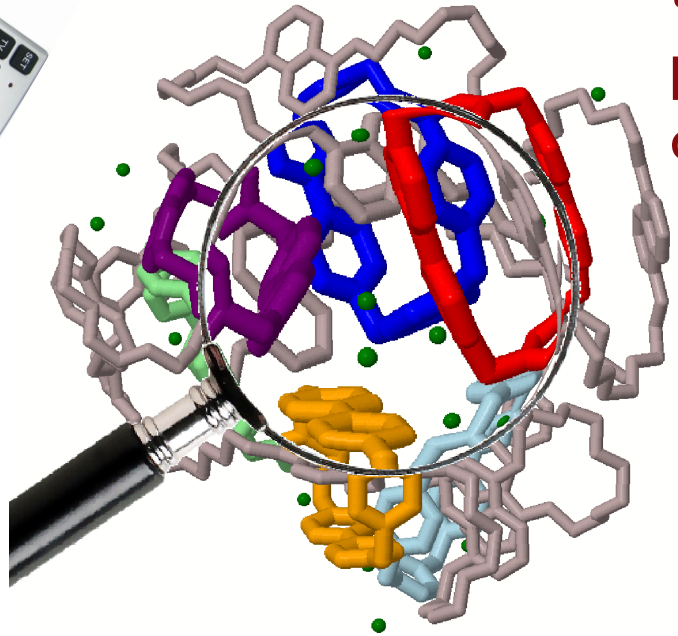
$h\nu$

E

H

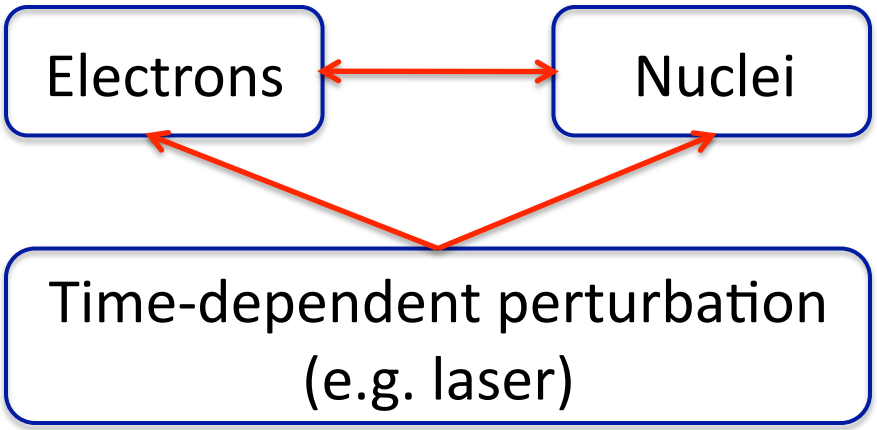
F

...



Active control tools to manipulate properties + dynamics of matter

Spectroscopy and control in vibronic systems



Effects
beyond linear
response

In principle, the problem requires following the coupled dynamics of electronic and vibrational degrees of freedom in the presence of an external time-dependent potential

Now, some representative experiments/simulations

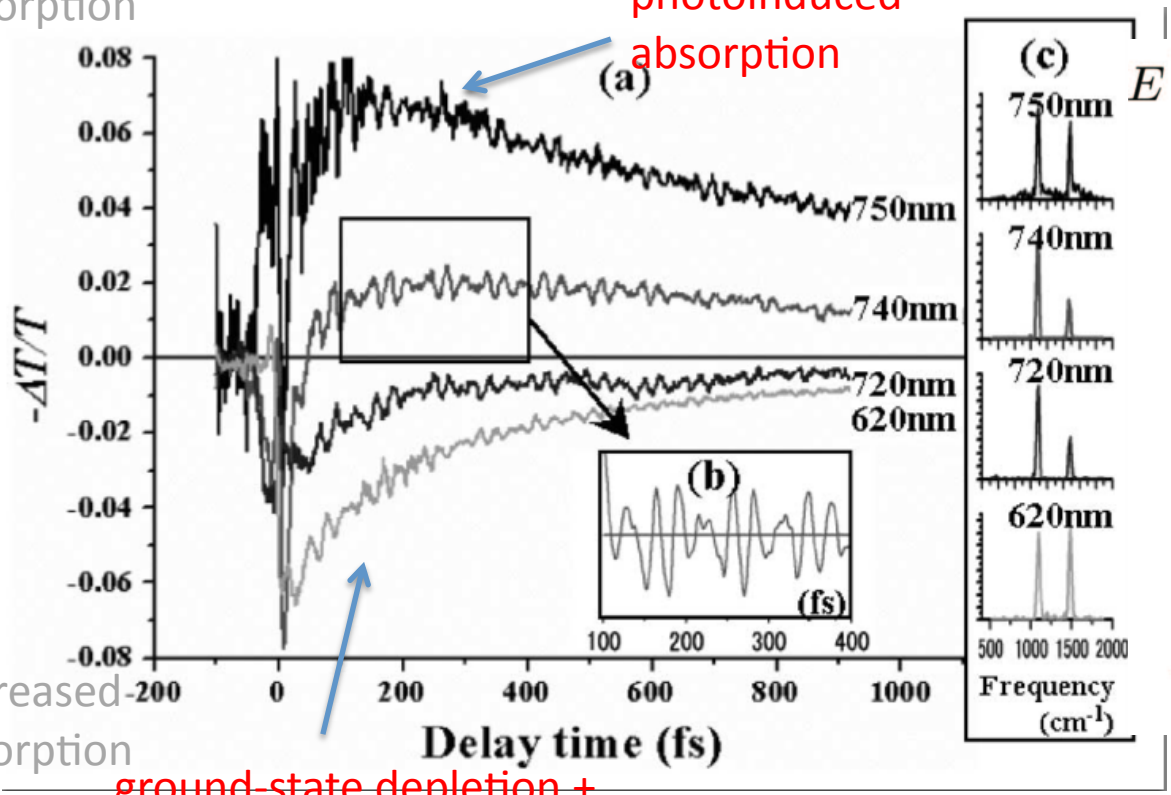
Vibronic effects: Vibrations upon photoexcitation

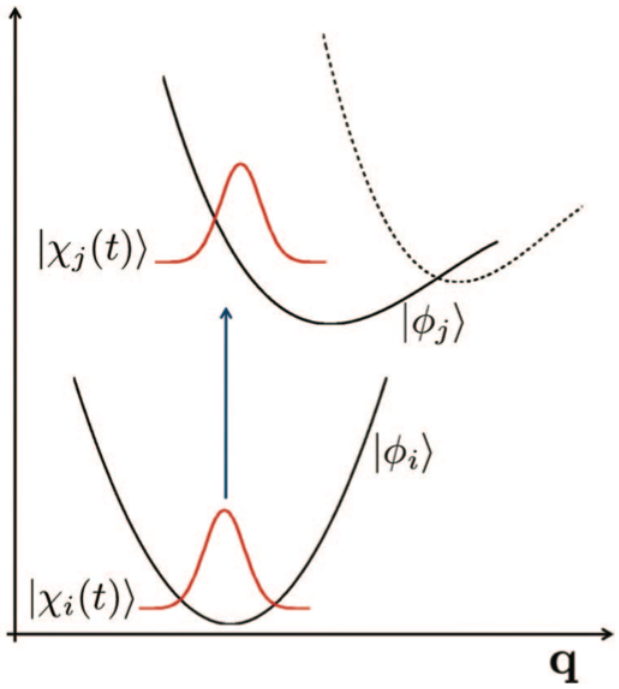
Vibrational motion in trans-polyacetylene after impulsive photoexcitation

Pump-probe experiment with sub-5 fs laser pulse reveals carbon-carbon stretching

increased absorption

photoinduced absorption





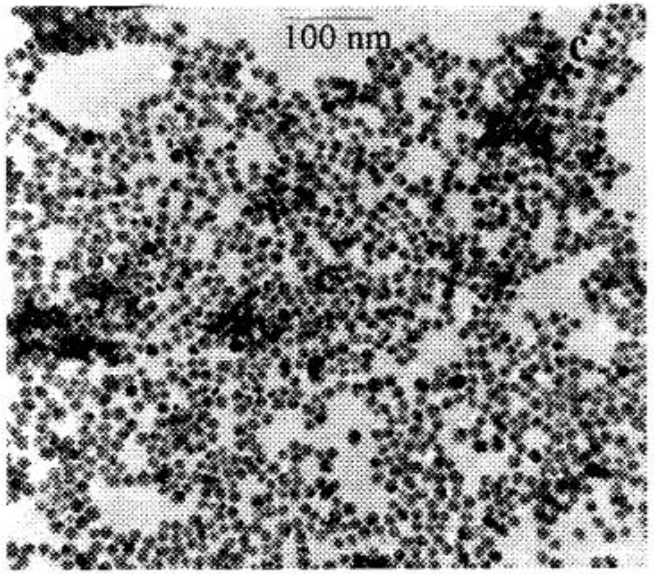
decreased absorption

ground-state depletion + stimulated emission

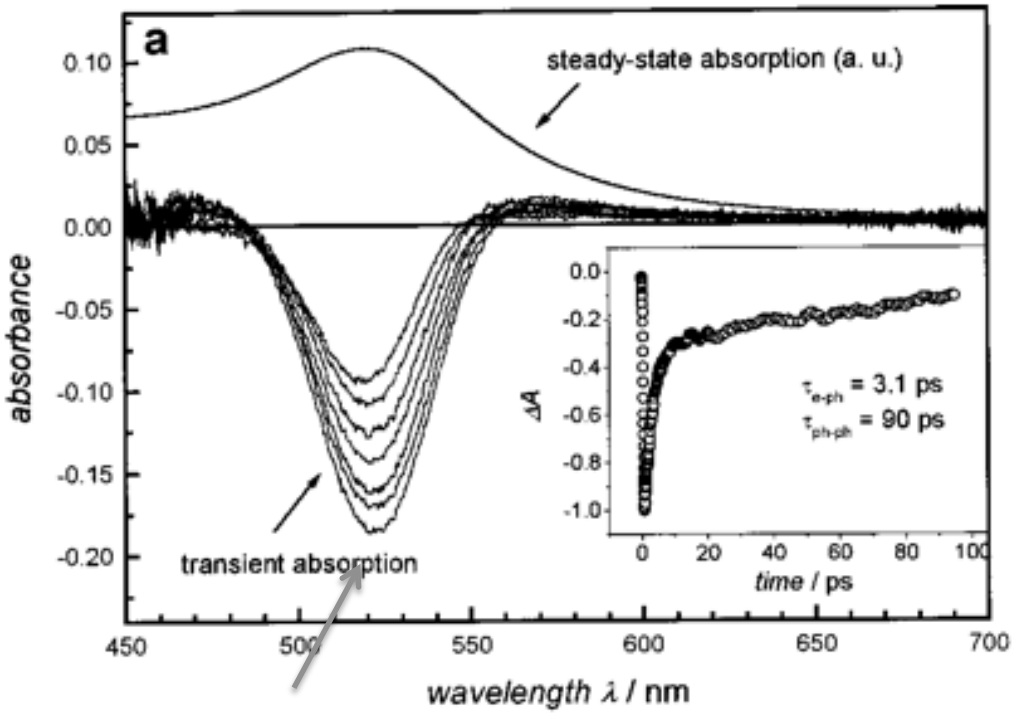
Adachi, Kobryanskii and Kobayashi Phys. Rev. Lett. 89 027401 (2002)

Vibronic effects: Electronic Relaxation

E.g. pump-probe experiment in 15 nm spherical gold nanoparticles



Nonradiative relaxation dynamics

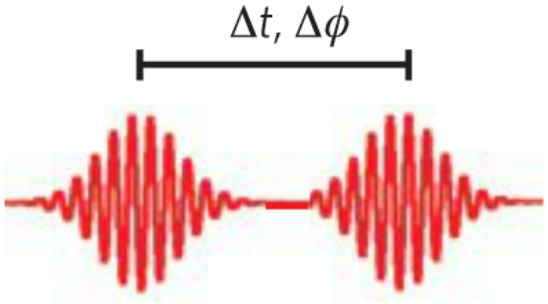


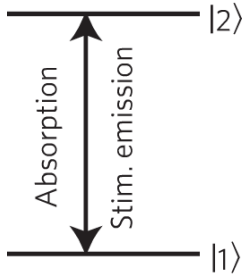
surface-plasmon resonance

S. Link and M. A. El-Sayed, J. Phys. Chem. B **103**, 8410-8426 (1999)

Vibronic effects: Electronic Decoherence

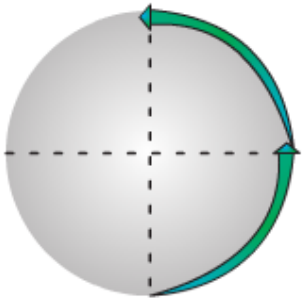
Near-resonant two pulse excitation scheme

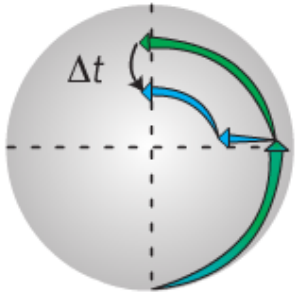


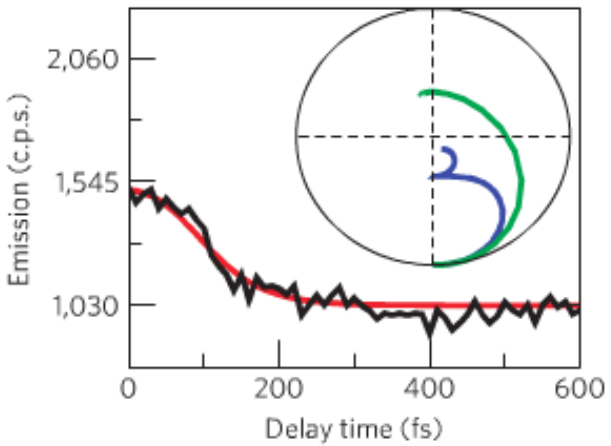


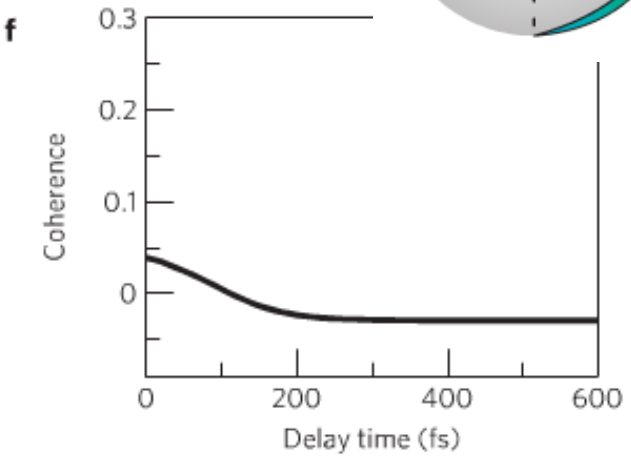
Terrylenediimide

Decoherence reconstructed from spontaneous emission measurements through optical Bloch equations







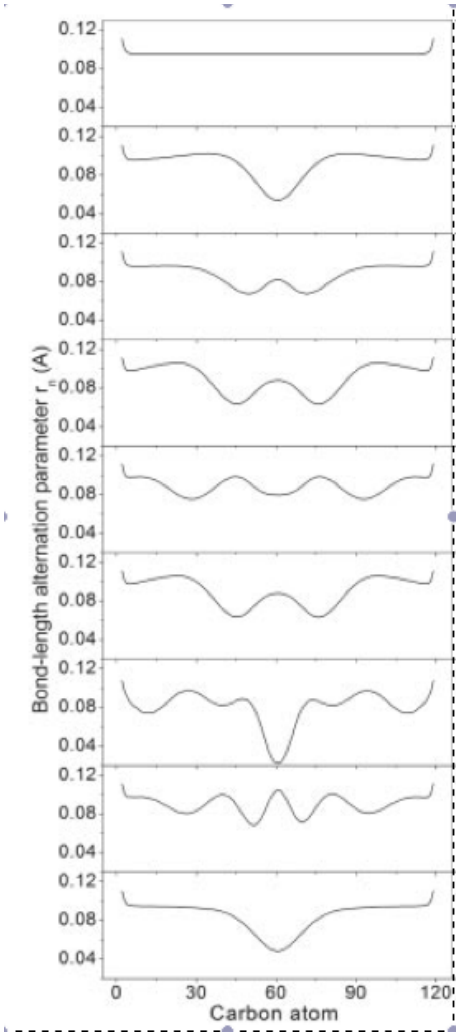


Hildner, Brinks and van Hulst, Nature Phys. **7**,172-177 (2011)

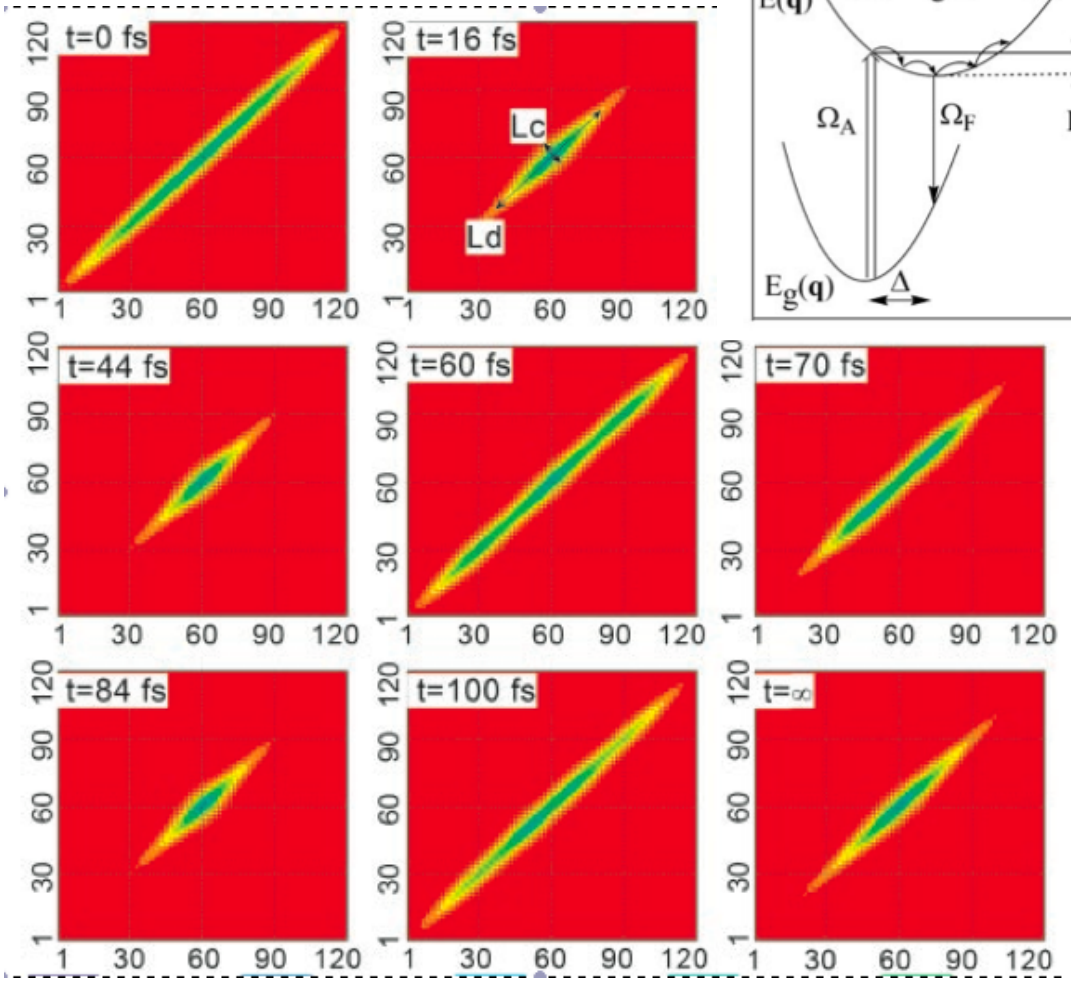
Exciton self-trapping

Adiabatic Excited State Molecular Dynamics in *cis*-polyacetylene

BLA



Transition densities



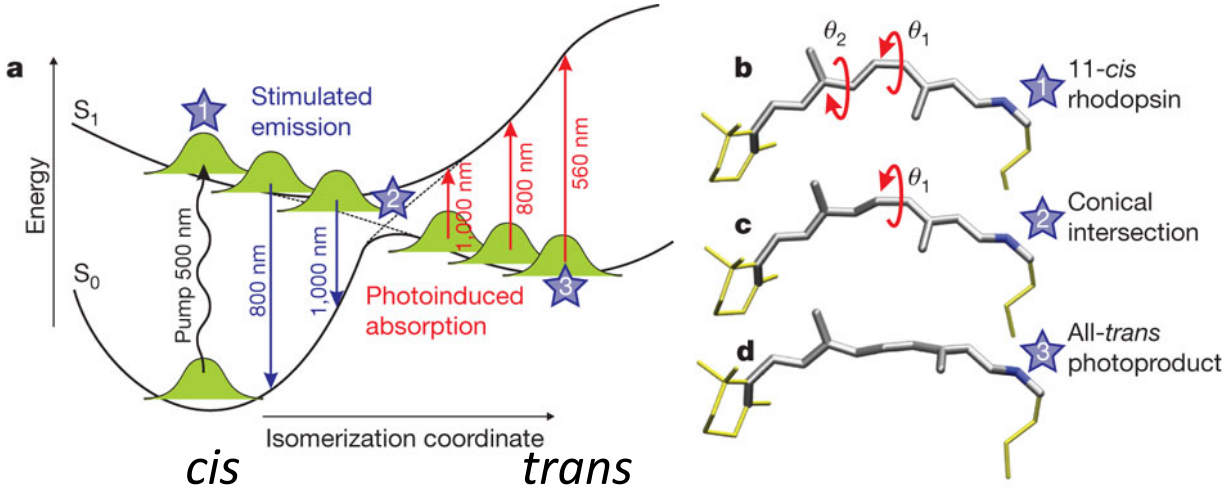
S. Tretiak, et al. PNAS **100**, 2185 (2003)

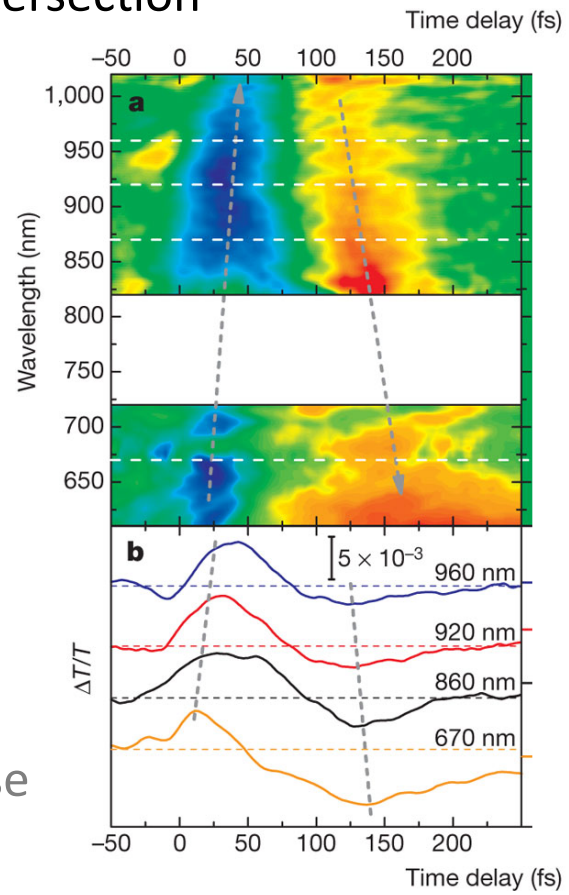
Vibronic effects: Chemical Reaction

Measurements on the conical intersection dynamics of the primary photoisomerization event in vision

cis-retinal ⟶ *trans*-retinal

Wave-packet dynamics through the rhodopsin conical intersection





Isomerization potential energy surfaces of rhodopsin

Pump with a 10 fs 500nm pulse, probe with 15fs NIR pulse

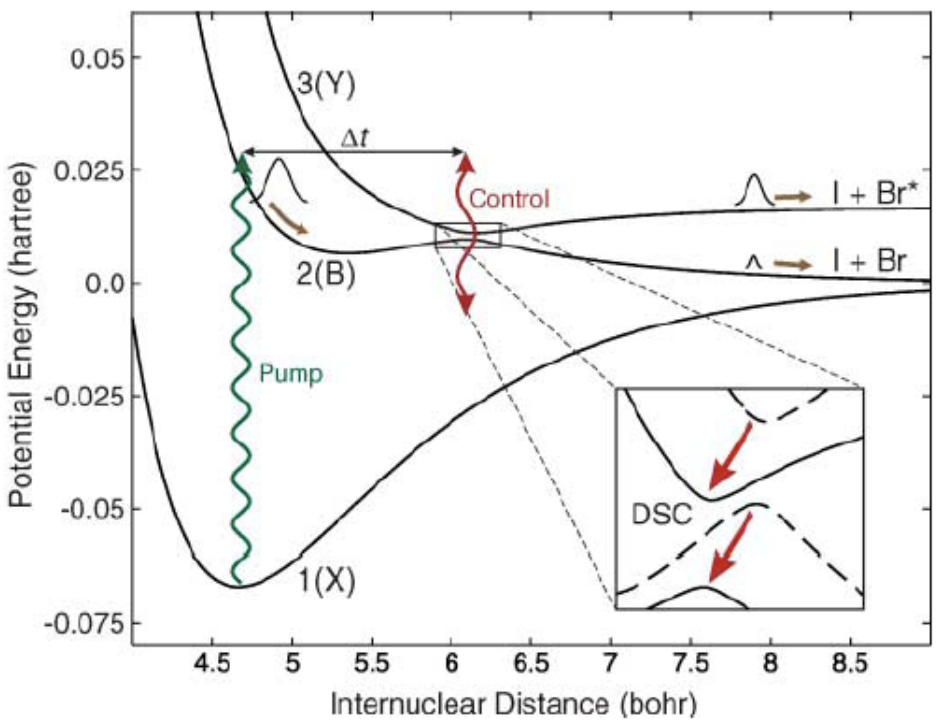
D. Polli, G. Cerullo et al. Nature **467**, 440-443 (2010)

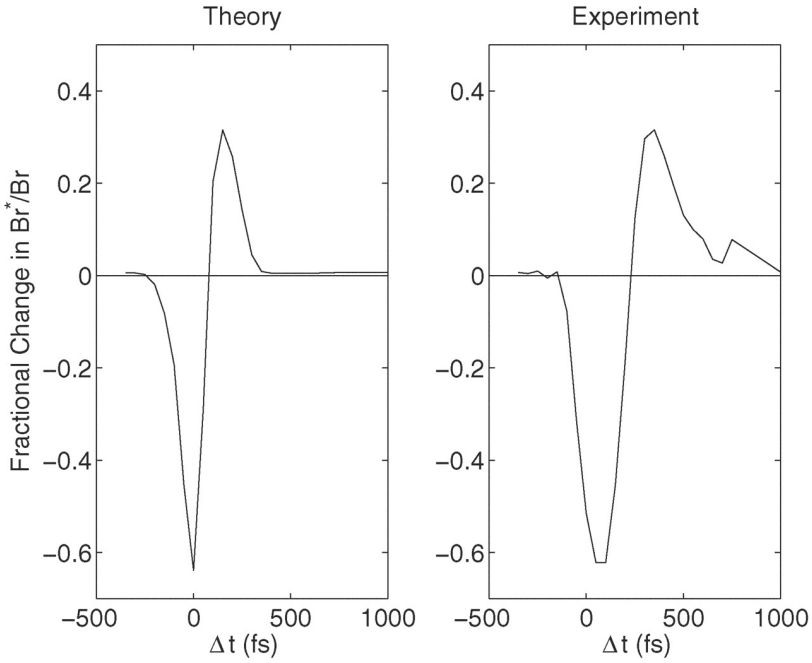
Control of nonadiabatic dynamics

Dynamic Stark Control of Photochemical Processes

Benjamin J. Sussman,[1,2] Dave Townsend,[1] Misha Yu. Ivanov,[1] Albert Stolow[1,2*]

Science 314, 278 (2006)





Approximation schemes

Implicit modeling

Nuclei as a bath: Vibronic couplings generate electronic decoherence and relaxation. Effects modeled through phenomenological models or master equations

A whole gradient of approximations and techniques
e.g. surrogate hamiltonians, mixed quantum-classical, semiclassical, QM-MM, non-Markovian master equations, …

Nuclei as an essential part of the system: Vibronic effects described explicitely via time-domain quantum simulation of the electron-vibrational dynamics.

Explicit modeling

Schedule of this session

From Yesterday	Martin Glässl, University of Bayreuth Real-Time Path Integrals for Laser Driven Carrier-Phonon Dynamics in Quantum Dots
09:20 to 10:00	Oleg Prezhdo , University of Rochester Elastic and Inelastic Electron-Phonon Scattering in Nanoscale Materials
10:00 to 10:20	Discussion
10:20 to 10:40	Coffee Break
10:40 to 11:20	Ermin Malic , TU Berlin Ultrafast relaxation dynamics in graphene - Impact of carrier-phonon and carrier-carrier scattering
11:20 to 11:40	Discussion
11:40 to 12:20	Robert van Leeuwen , University of Jyväskylä Electron-electron and electron-phonon interactions in time-dependent quantum transport using non-equilibrium many-body theory
12:20 to 12:40	Discussion

Challenges proposed by the speakers

1. When can vibrations be described classically and when do they require quantum or semiclassical treatments? E.g., does the classical treatment of C-C stretching vibrations in nanoscale carbon materials make sense?

OP

2. Can one consider electron-light and electron-phonon interactions independently (e.g. sequentially in time-domain) or are they coupled?
3. How to go beyond the Markov approximation by considering quantum-kinetic memory effects in density matrix formulations of carrier relaxation dynamics?

EM

4. How to consider impurity-induced carrier-phonon relaxation channels close to the Dirac point?
5. The self-consistent Born approximation is said only to work in the weak coupling regime. What is needed to go beyond? More generally, what is the importance of higher order terms in the electron-phonon interaction?

RvL

6. What is the interplay between electron-electron and electron-phonon interactions? (mixed Feynman diagrams containing electron interaction and phonon propagators in a many-body theory language).

7. IF's wish: Quantum-classical method beyond Ehrenfest that can be used to follow nonperturbative laser-induced dynamics