Multi-dimensional quantum mechanical treatment of an electronic and nuclear motions in a plant cryptochrome, the ring-opening of spiropyran and the subfemtosecond photodissociation of ozone

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(4) Institute of Physical Chemistry, University of Heidelberg, Germany

ANR CoConics-DYQUMA

Full quantum mechanical approach

Multi-Configuration Time Dependent Hartree

- **MCTDH package of Heidelberg: see http://www.pci.uni-heidelberg.de/tc/usr/mctdh/**

  H.-D. Meyer, U. Manthe, and L.S. Cederbaum, Chem.Phys.Lett. ***165*** *(1990), 73.*

  H.-D. Meyer, F. Gatti, and G. Worth, Multidimensional Quantum Dynamics: MCTDH Theory and Applications Wiley-VCH, 2009, (BOOK).

- A MCSCF algorithm for the nuclear coordinates: "contraction" of the primitive basis set which allows to treat larger systems.

- A Time-Dependent approach : propagation of wave packets

Full quantum mechanical approach (MCTDH)

Propagation of wavepackets, time-dependent basis set optimized by a variational principle

$$\Psi(Q_1,\cdots,Q_f,t) \;=\; \sum_{j_1}^{n_1}\cdots\sum_{j_p}^{n_p} A_{j_1,\cdots,j_p}\prod_{\kappa=1}^{p}\varphi_{j_\kappa}^{(\kappa)}(q_\kappa,t)$$

$$\varphi_{j_\kappa}^{(\kappa)}(Q_\kappa,t) \;=\; \sum_{i_\kappa=1}^{N_\kappa} G_{i_\kappa}^{j_\kappa}(t)\chi_{i_\kappa}^{(\kappa)}(Q_\kappa)\,.$$

Dirac-Frenkel variational principle:

$$\langle\delta\Psi\,|\,H-i\partial_t\,|\,\Psi\rangle = 0\,,$$

Full quantum mechanical approach (ML-MCTDH)

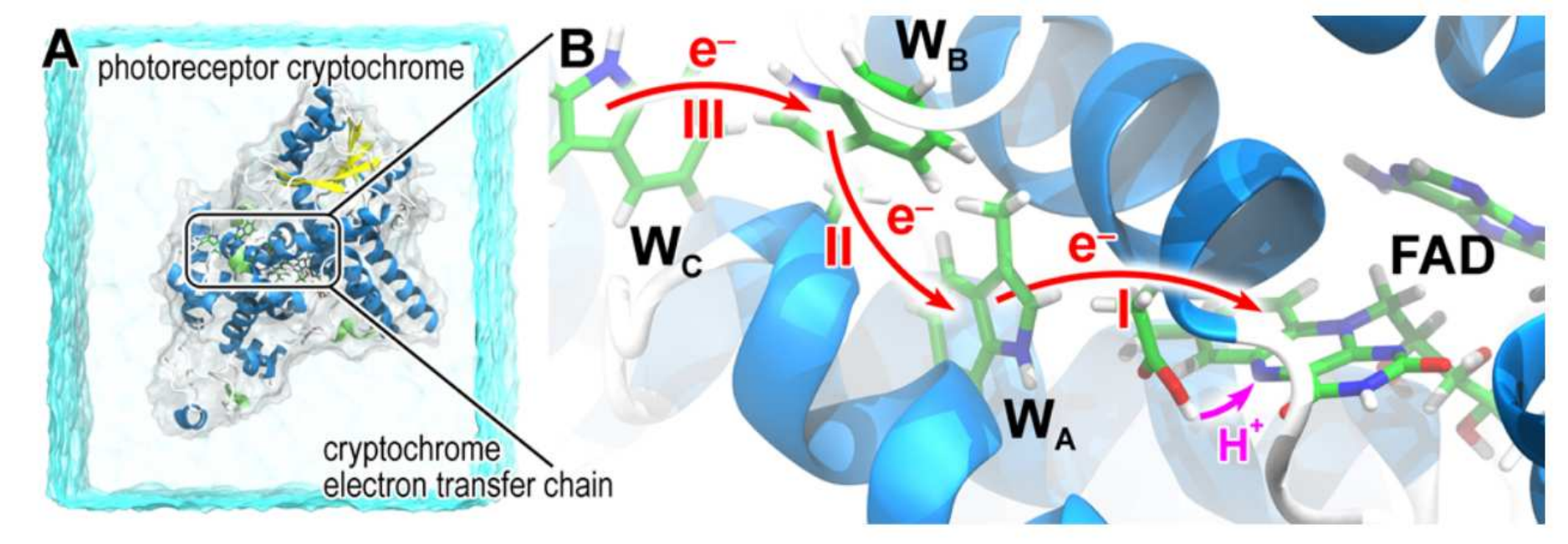
$$\Psi(q_1,q_2,q_3,t) = \sum_{j_{12}=1}^{n_{12}} \sum_{j_3=1}^{n_3} A_{j_{12},j_3}(t)\varphi_{j_{12}}^{(12)}(q_1,q_2,t)\varphi_{j_3}^{(3)}(q_3,t)\,,$$

$$\varphi_{j_{12}}^{(12)}(q_1,q_2,t) = \sum_{k_1=1}^{n_1} \sum_{k_2=1}^{n_2} B_{k_1,k_2}^{(12,j_{12})}(t)\xi_{k_1}^{(1)}(q_1,t)\xi_{k_2}^{(2)}(q_2,t)\,,$$

- Multi-Layer MCTDH approach (H. Wang and M. Thoss)
- Implementation of a procedure to increase on the fly the basis set
- Implementation of the thermalization

  D. Mendive-Tapia, H.-D. Meyer and F. Gatti, Chem. Phys. 482 (2017) 113

Electron transfers (ETs)

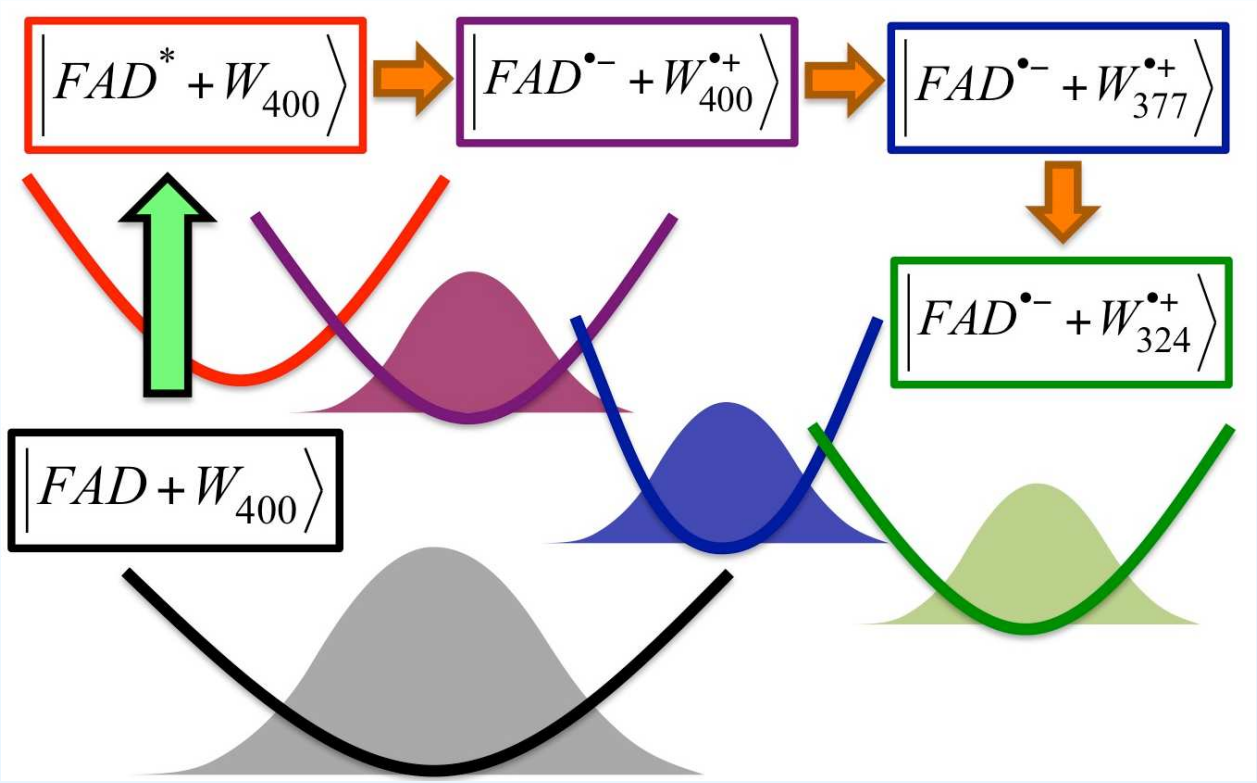


Plant cryptochrome proteins. Creation of radical pairs

Magnetically sensitive radical pairs in the eyes of some birds (orientation during migrations?)

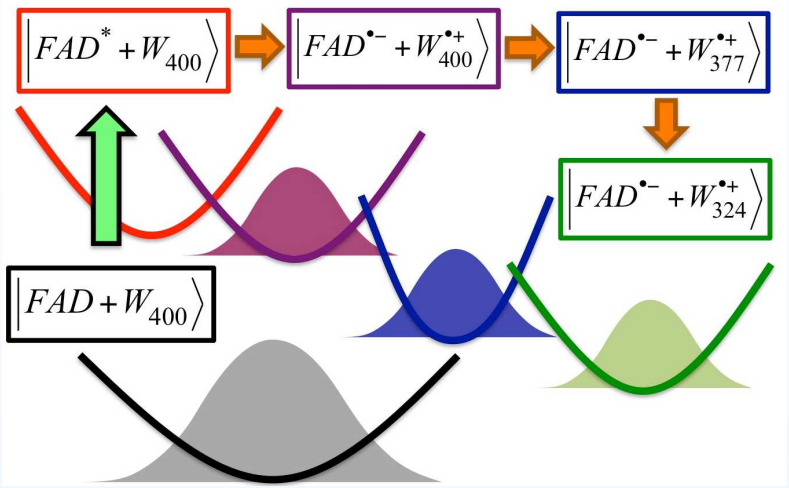
Plant cryptochrome *Arabidopsis thaliana* (AtCry) : available crystal structures

Electron transfers



Absorption of light by the chromophore Flavin Adenine Dinucleotide (FAD) triggers an electron transfer to tryptophan residue

Electron transfers

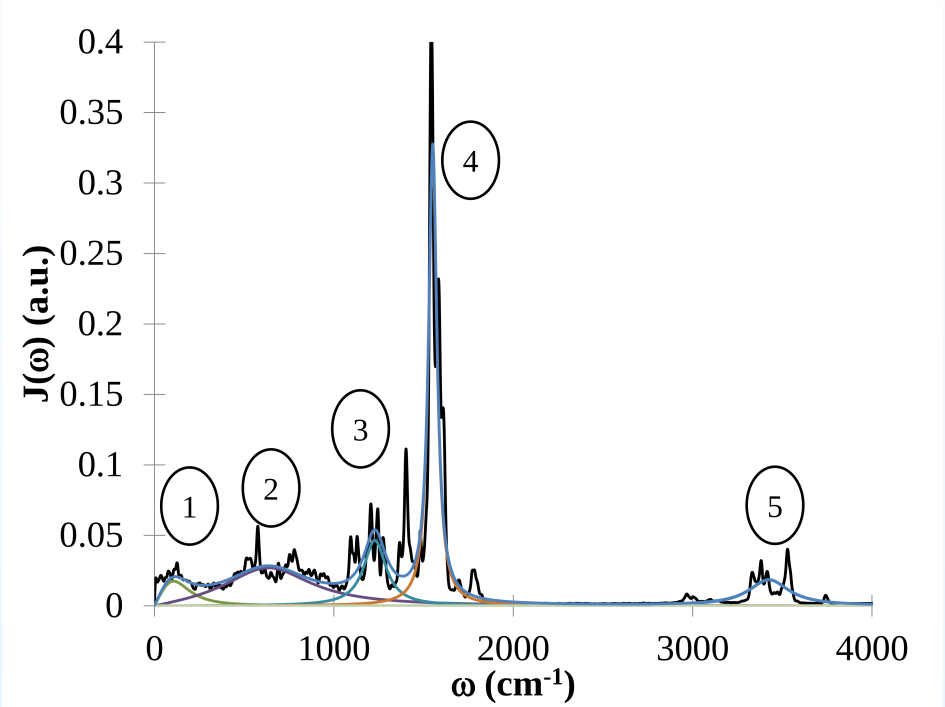


	Time constant τ (ps)
Electron transfer	Experiment [1]
$W_{400} \rightarrow FAD$	0.4
$W_{377} \rightarrow W^{\cdot+}_{400}$	4 - 15
$W_{324} \rightarrow W^{\cdot+}_{377}$	30 - 50

Difficulty to distinguish ET and vibrational cooling in the experiments

[1] Immeln *et al* JACS 134 (2012) 12536

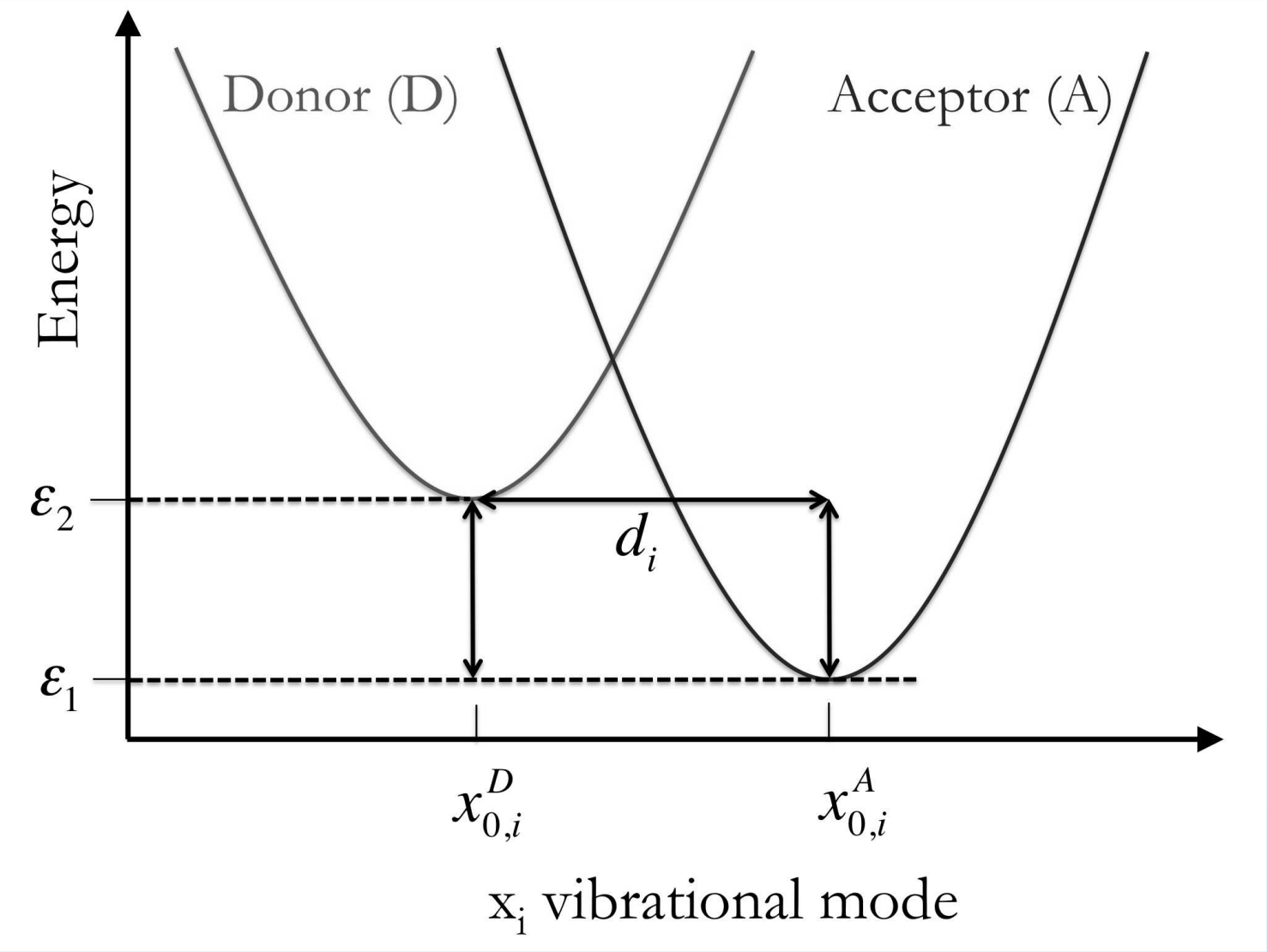
Electron transfers



CDFT QM/MM calculations 110 000 atom including 34 000 water molecules, 298.15 K

PCCP 12 (2016) 21442

Electron transfers



A spin boson model Hamiltonian

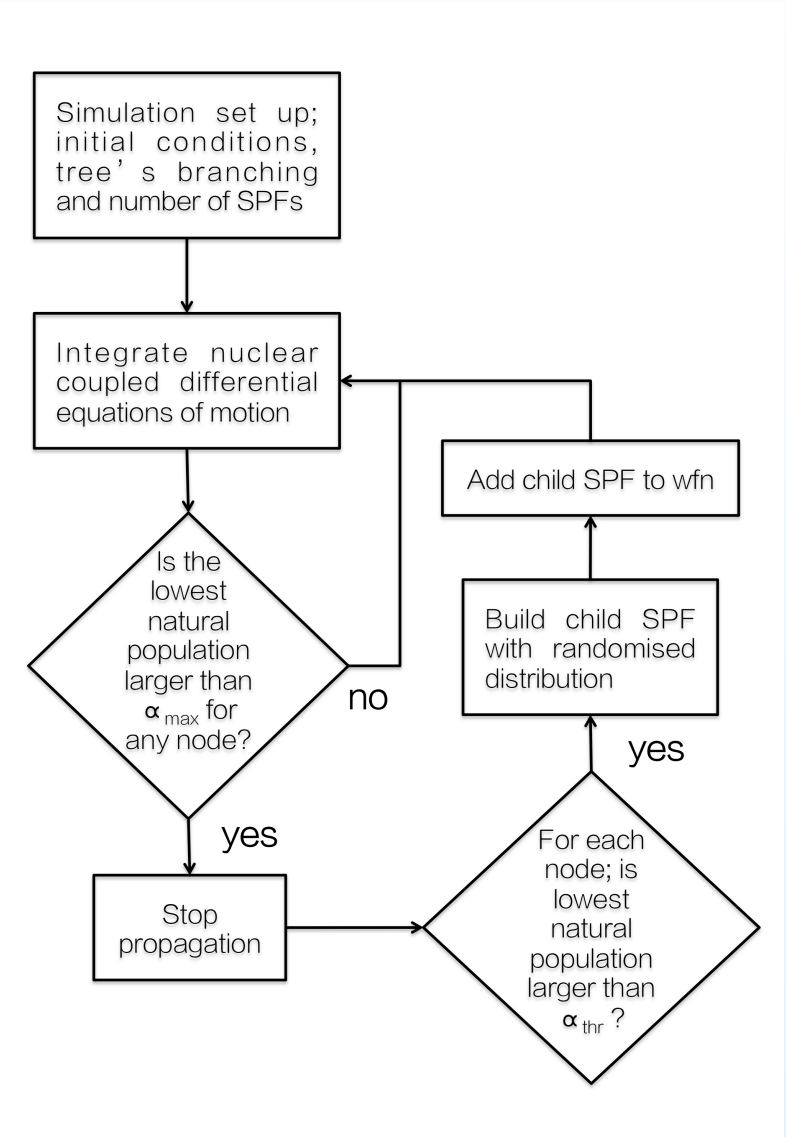
$$\hat{H} = \hat{H}_S + \hat{H}_B + \hat{H}_{BS}$$

$$\hat{H}_S = \begin{bmatrix} \epsilon_1 & H_{12} \\ H_{12} & \epsilon_2 \end{bmatrix} = \epsilon_1 |D\rangle \langle D| + \epsilon_2 |A\rangle \langle A| + H_{12}(|D\rangle \langle A| + |A\rangle \langle D|)$$

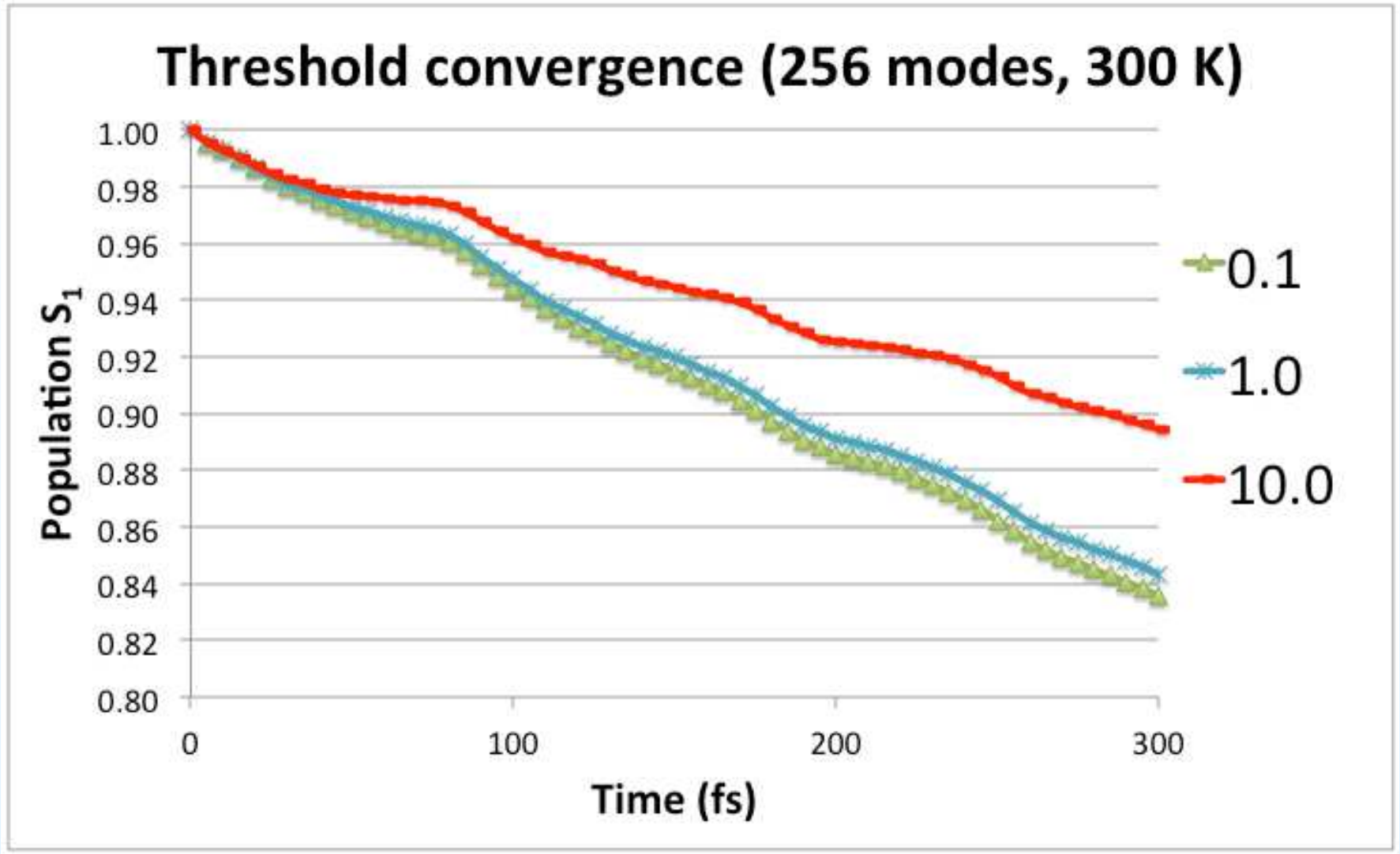
$$\hat{H}_B = \sum_{i=1}^{N} \frac{\hbar w_i^D}{2} (\hat{p}_i^2 + \hat{x}_i^2) |D\rangle \langle D| + \sum_{i=1}^{N} \frac{\hbar w_i^A}{2} (\hat{p}_i^2 + \hat{x}_i^2) |A\rangle \langle A|$$

$$\hat{H}_{BS} = \sum_{i=1}^{N} k_i^D x_i |D\rangle \langle D| + \sum_{i=1}^{N} k_i^A x_i |A\rangle \langle A|$$

On the fly basis set



Electron transfers



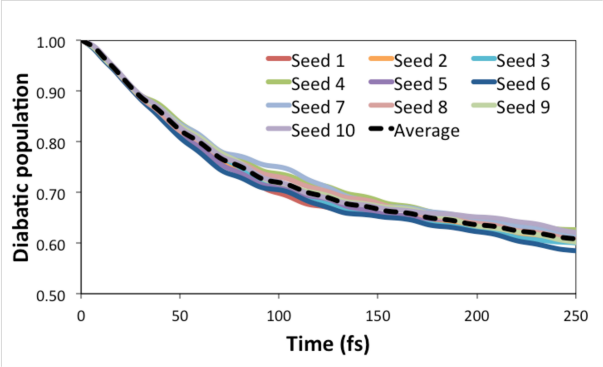
Initial condition

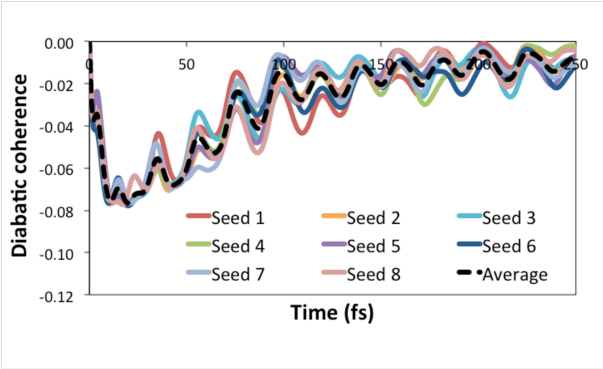
Difficulty to define the initial condition: two extreme cases
This initial state is thermalized

- Slow bath relaxation:
  Vertical instantaneous transition for the electronic degrees of freedom
  Bath Centered on the ground state curve
- Fast bath relaxation:
  Bath relaxed onto the individual ET electronic state

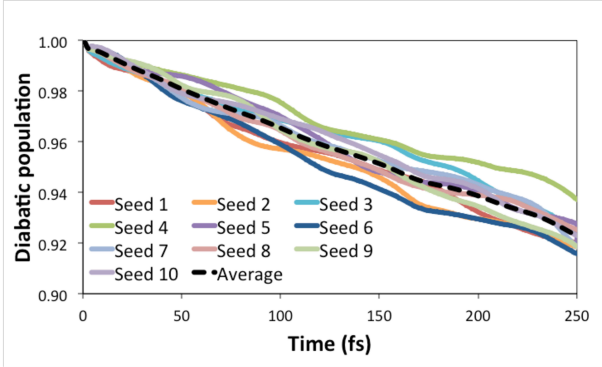
Electron transfers (T = 298.15 K)

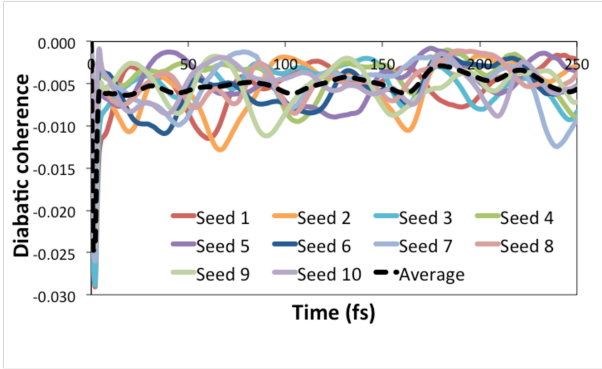
Slow bath relaxation





Fast bath relaxation

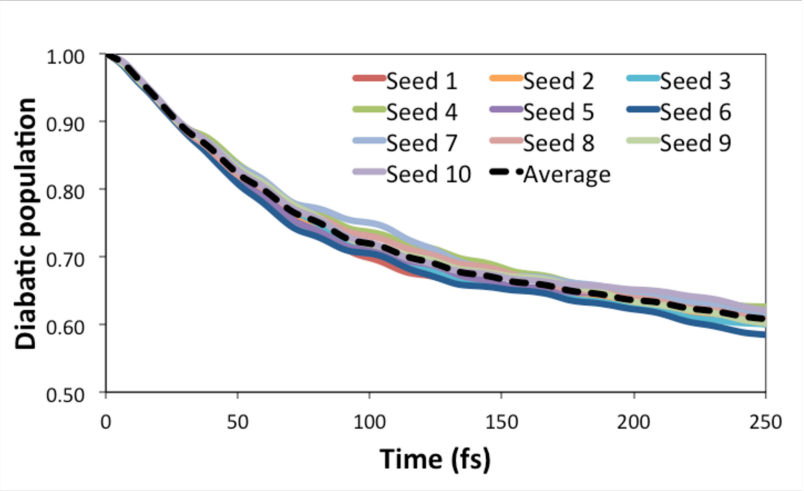


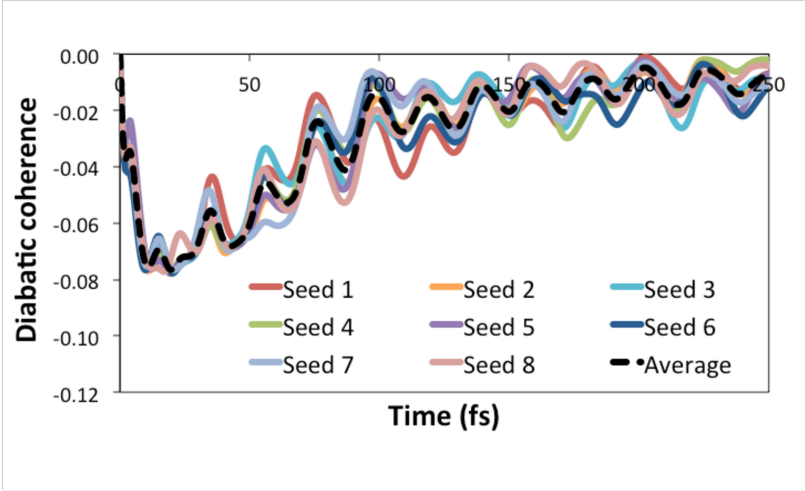


A sum of thermalized wavepackets with random factors (stochastic average)

Electron transfers

Slow bath relaxation:

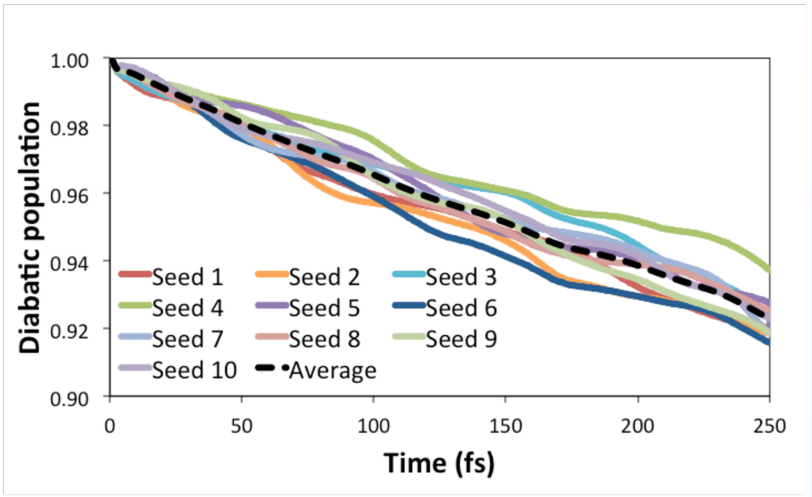


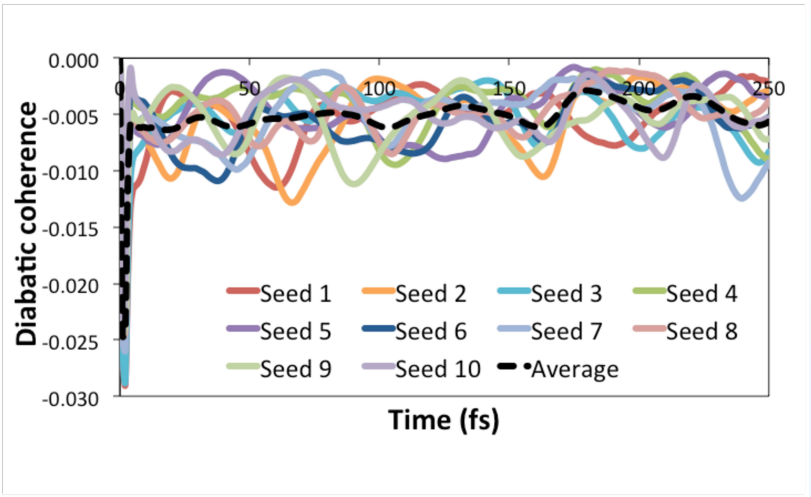


- 256 modes for convergence
- Little temperature dependence
- Process by strong non-equilibrium forces at the crossing region
- Fast decline that saturates around 0.5 ps without full decay

Electron transfers

Fast bath relaxation:





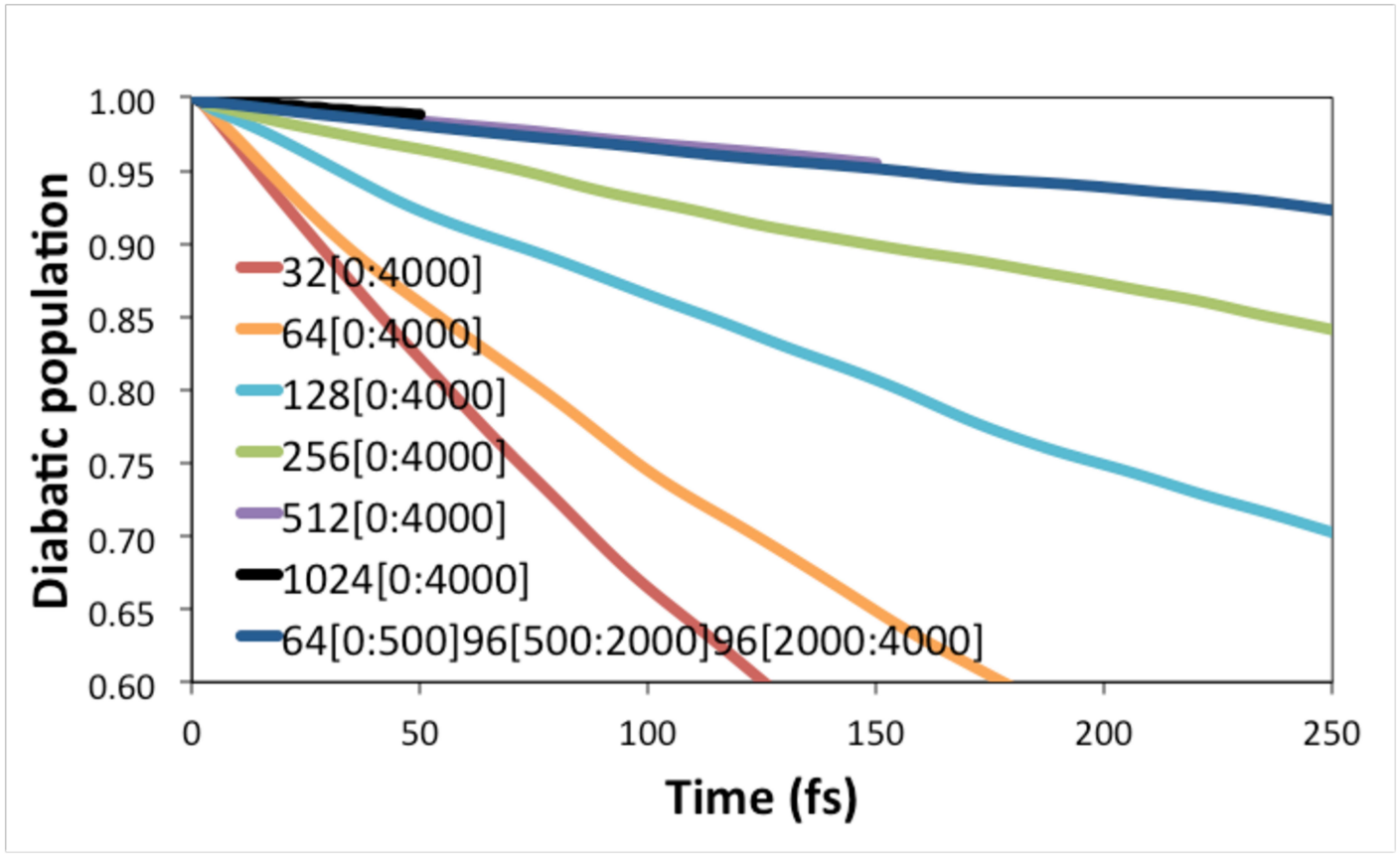
- 512 modes for convergence
- Very strong temperature dependence (no transfer for T = 0 K)
- Thermal averaging destroys the oscillations in the quantum coherence
- Slower decay close to the experimental value

Electron transfers

Fast bath relaxation:

Temperature (K)	τ (ps)
0	-
50	49.9
100	16.7
150	8.7
200	5.6
250	4.1
298.15	3.3

Electron transfers



Conclusion

Experiment (ps)	Marcus Theory	HEOM	This work (fast)
4 - 15	4.97	0.82	3.3

HEOM : Hierarchical Equations of Motions

- Fast and slow bath relaxations: in reality mixed scenario depending on the bath modes
- Process seems to be dominated by low-frequency modes
- Low-frequency modes partly linked to the molecules of water, which can relax fast

Full ab initio approach

The process strongly depends on the differences in the relaxation time-scale between electronic and nuclear (bath) degrees of freedom

Atto spectroscopy of Ozone I

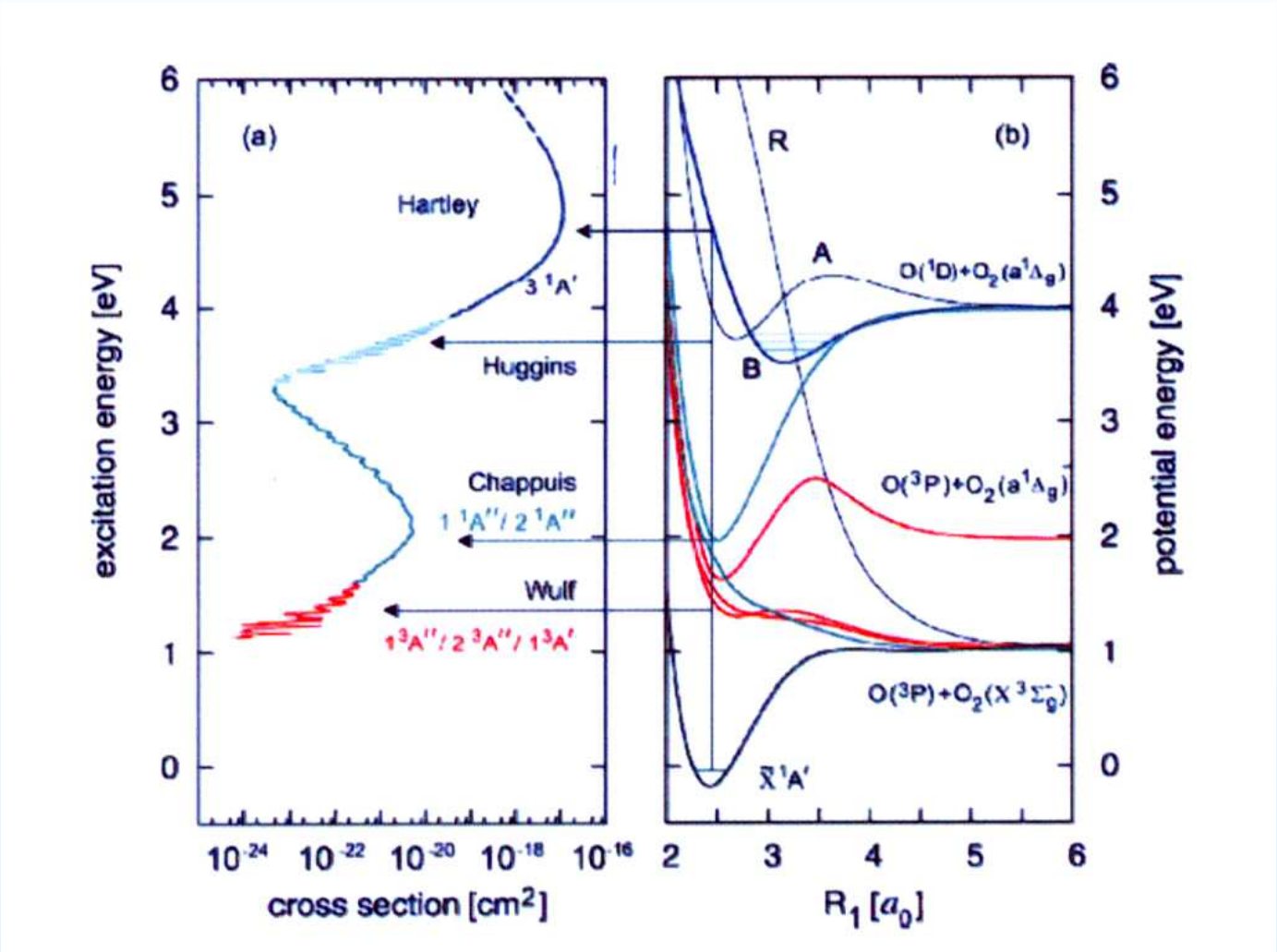
Collaboration with F. Krausz and R. Kienberger, Munich

Objective: creation of a coherent superposition of molecular electronic states in Ozone

Measure of electronic and nuclear simultaneous dynamics in subfemto timescale

Collaboration with G. Halász and Á. Vibók, Debrecen

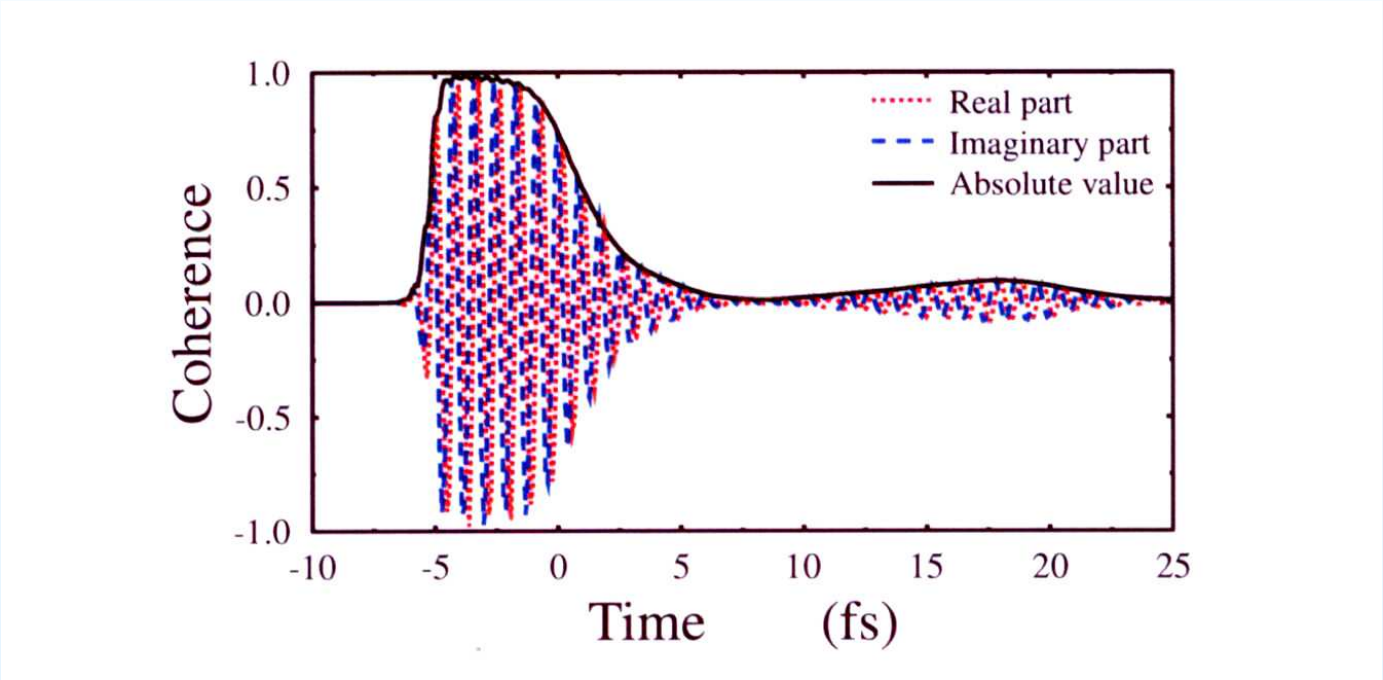
Atto spectroscopy of Ozone II



Atto spectroscopy of Ozone III

Relative electronic coherence

Full width at half maximum: 3 fs; Center wavelength : 260 nm; Intensity : 10^{13} W/cm^2

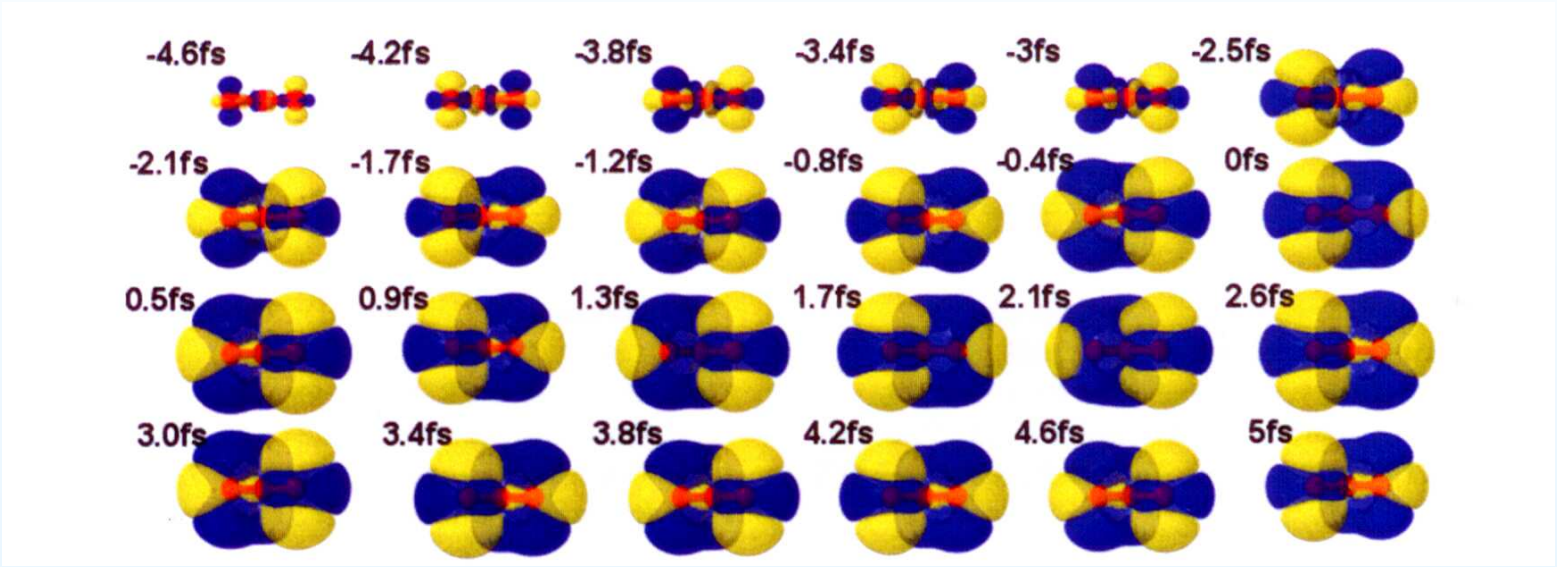


G. Halász, A. Perveaux, B. Lasorne, M. Robb, F. Gatti and A. Vibók,

PRA (2012) **86** 043426.

Atto spectroscopy of Ozone IV

Evolution of differential charge density at the FC geometry



Oscillation of the electronic density from one bond to another

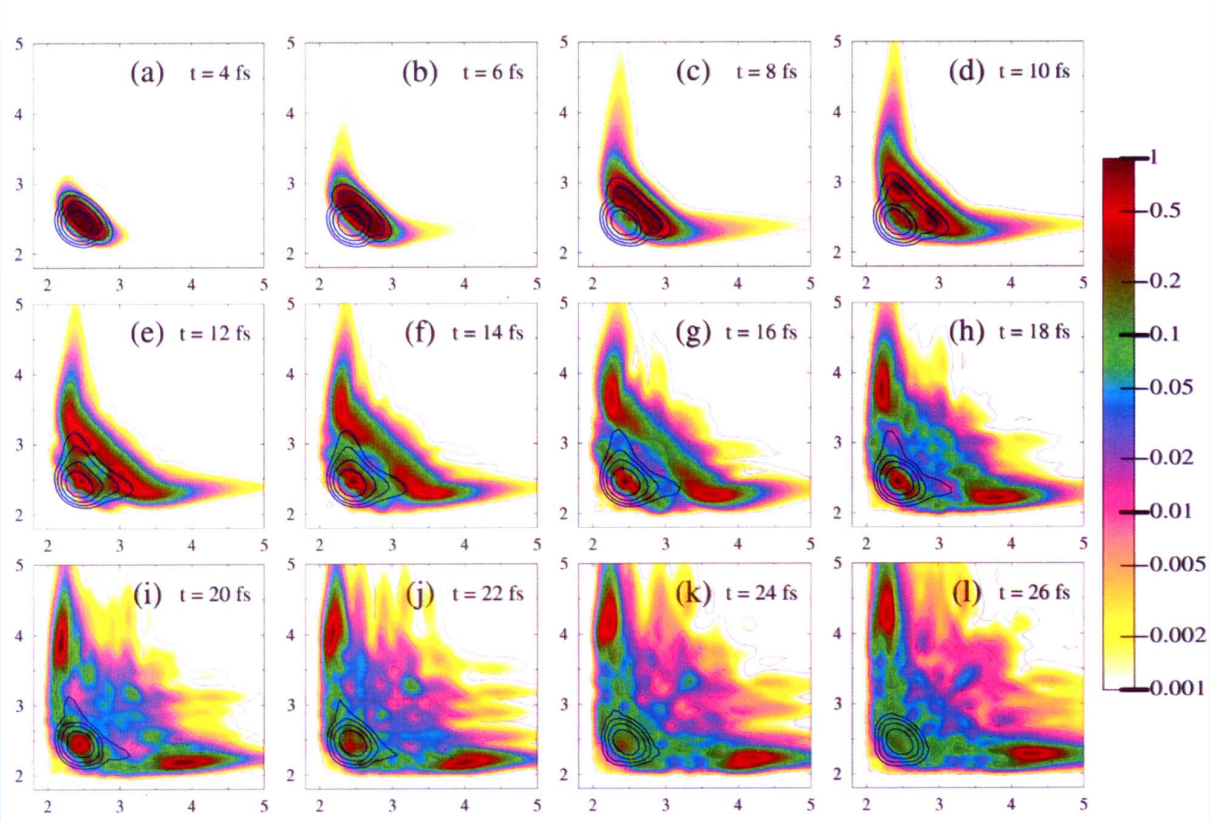
Alternating superposition of two resonant forms:

$$O - - O = O \leftrightarrow O = O - - O$$

Precursors of the dissociation channels

Atto spectroscopy of Ozone V

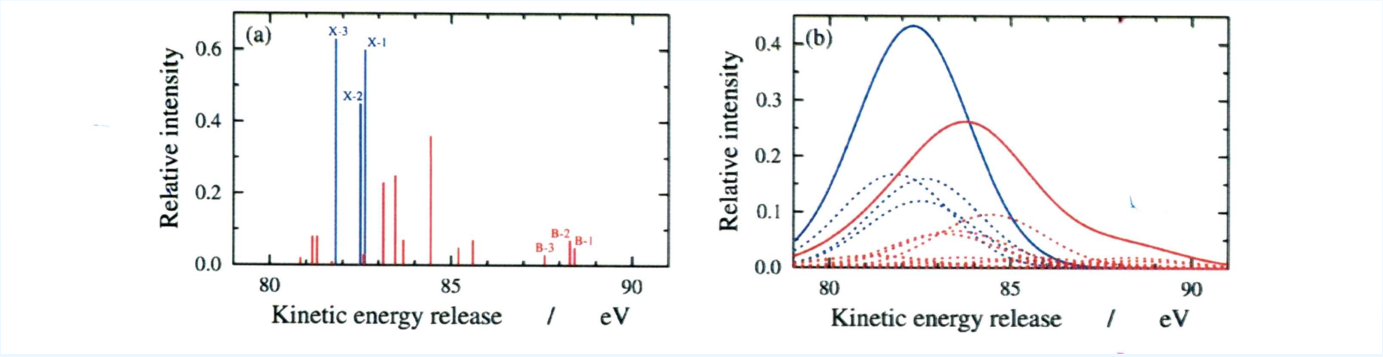
Time evolution of the wave-packet along the O-O bonds



One part stays trapped on the ridge of the “B” PES

Atto spectroscopy of Ozone VI

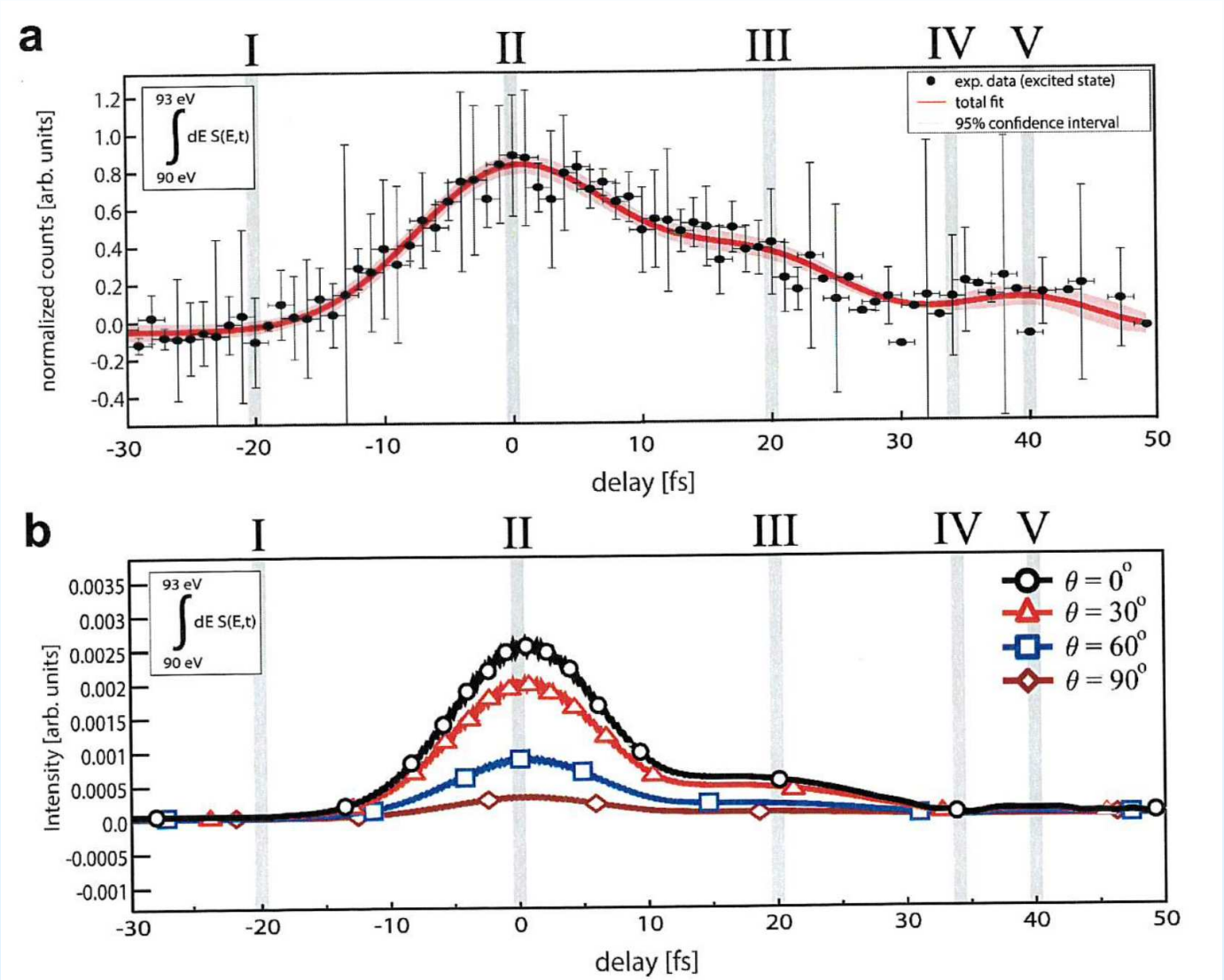
Stick photoelectron Spectra from X (blue) or B (red)
as functions of the kinetic energy release
For a probe photon at 95 eV (sudden approximation)



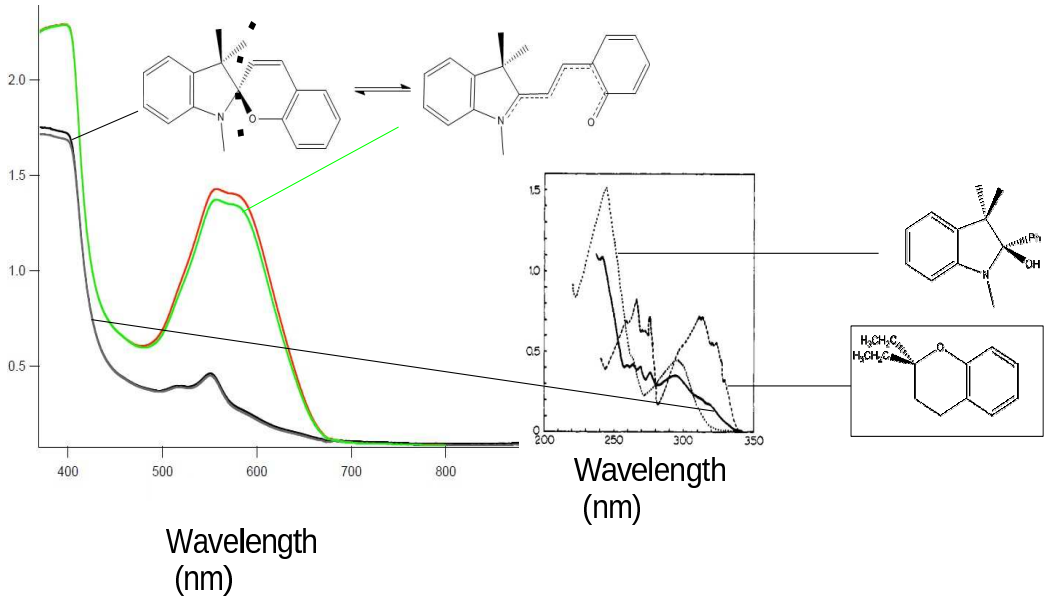
A. Perveaux, D. Lauvergnat, F. Gatti, M. A. Robb, G. J. Halász, Á. Vibók and B. Lasorne,
JPCA 118 (2014) 8773

Photoelectron Angular Distributions (MFPADs)

Atto spectroscopy of Ozone VII



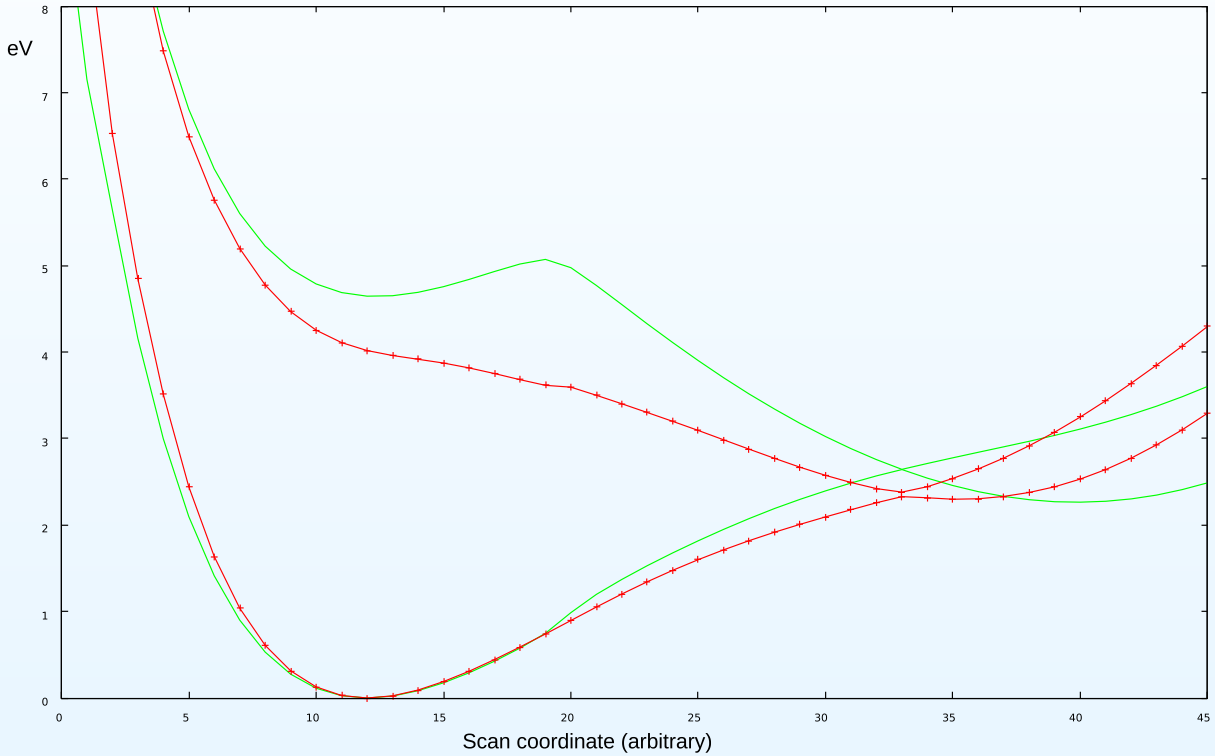
Study of the spiropyran (B. Gonon) : ring-opening



Collaboration with experimentalists from Dijon:

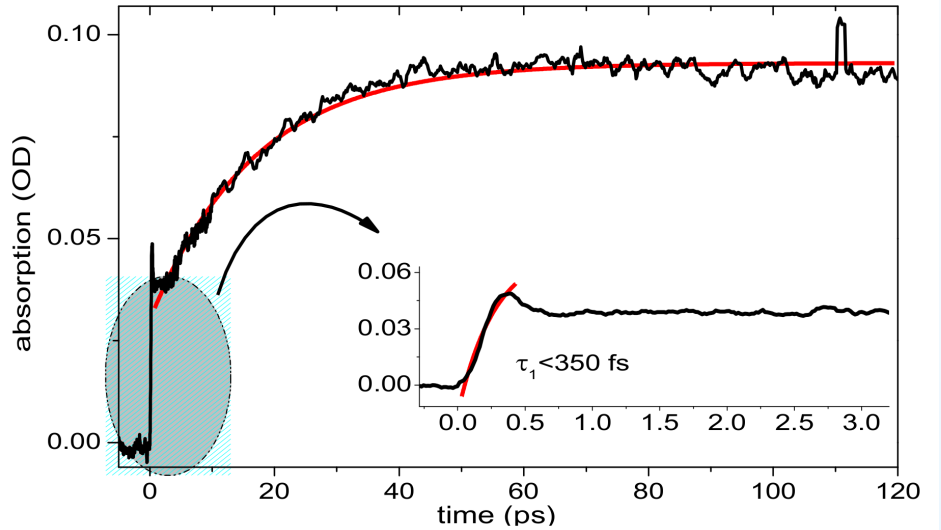
Edouard Hertz, Bruno Lavorel, Olivier Faucher

Post-CASSCF calculations



Very strong impact (XMCQDPT2, firefly)

Experiment

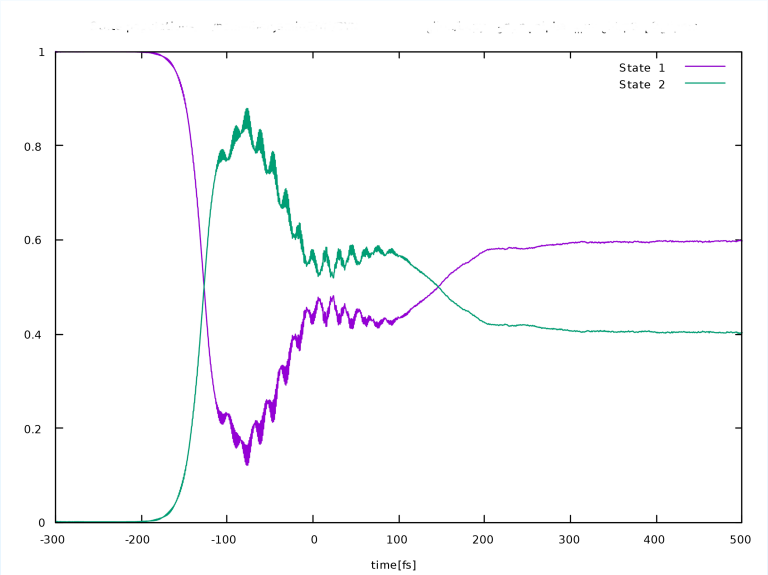


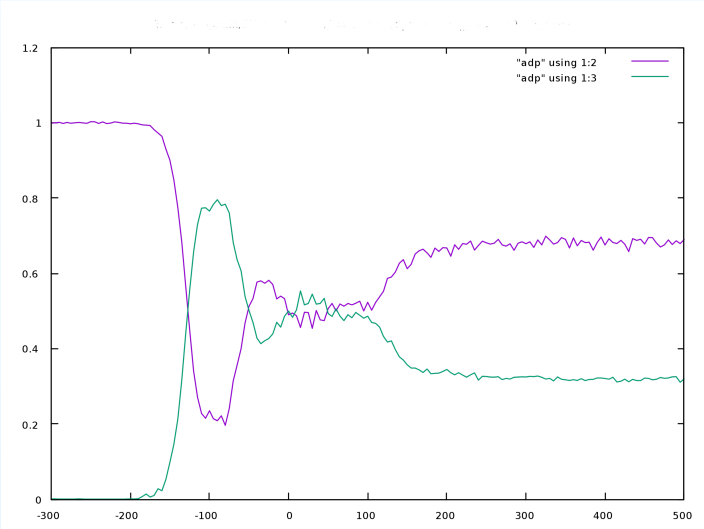
Pump : 400 nm, Probe: 540 nm
Liquid phase (toluene)

A very fast process occurs

Simulations

Diabatic and Adiabatic populations:





Experiment

- We observe a very fast transfer (100 fs), which does not strongly depend on the laser frequency
  As in the experiment
- Due to the presence of the CI
- Use of a chirped pulse. The pulse becomes longer and they observe less reaction
- The simulations lead to the the same trend

Spectral shaping (400 nm)

Chirped pulses : spectral shaping. We change the spectral phase only

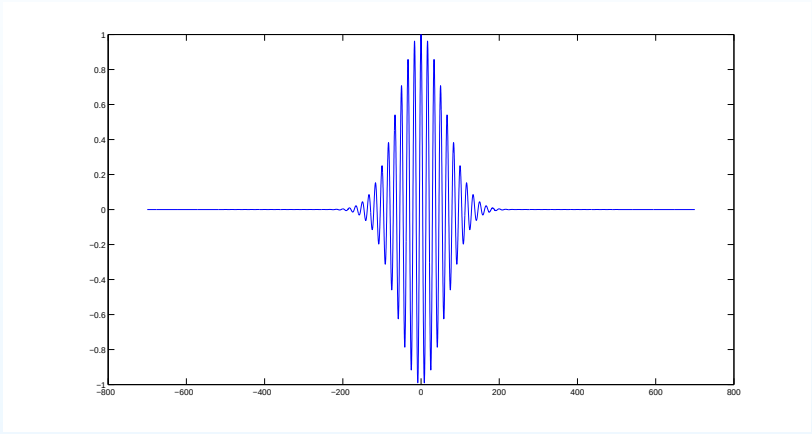
$$\mathcal{E}_{in}(t) \quad = \quad \mathcal{E}_{0in}\Lambda_{in}(t)e^{i(\omega_0 t-\theta)} \ , \ \Lambda_{in}(t) = e^{-(t/T_{in})^2}$$

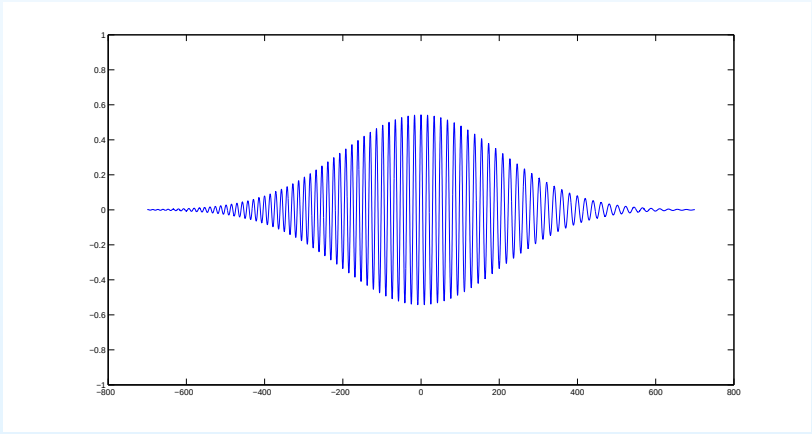
$$\tilde{\mathcal{E}}(\omega) = \tilde{\mathcal{E}}_{in}(\omega)e^{i\varphi(\omega)}$$

Spectral shaping (400 nm)

$$
\begin{aligned}
\mathcal{E}_{out}(t) &= \mathcal{E}_{0out}\Lambda_{out}(t)e^{i(\omega_0 t+\phi(t)-\theta)} \\
\varphi(\omega) &= \gamma(\omega-\omega_0)^2 \\
\Lambda_{out}(t) &= \sqrt{\frac{T_{in}}{T}}e^{-(t/T)^2} \\
\phi(t) &= \alpha t^2\ ,\ \alpha = -\frac{4\gamma}{T_{in}^4+16\gamma^2} \\
T &= \frac{4\gamma}{T_{in}}\sqrt{1+\left(\frac{T_{in}^2}{4\gamma}\right)^2} = \frac{1}{T_{in}}\sqrt{16\gamma^2+Tin^4}
\end{aligned}
$$

Pulse shaping (400 nm)

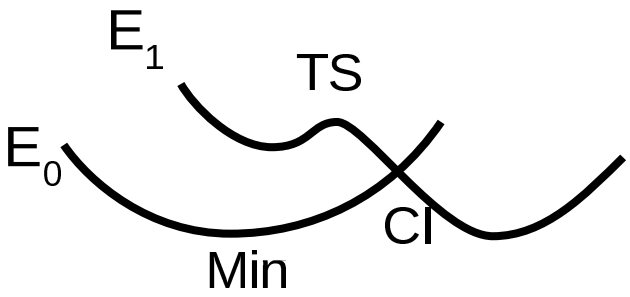


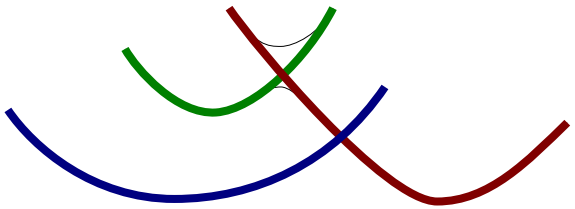


Less reaction in experiment and theory

Study of the spiropyran molecule

Polynomials : sixth order for x_0, fourth order for x_1, harmonic for x_2, linear coupling.





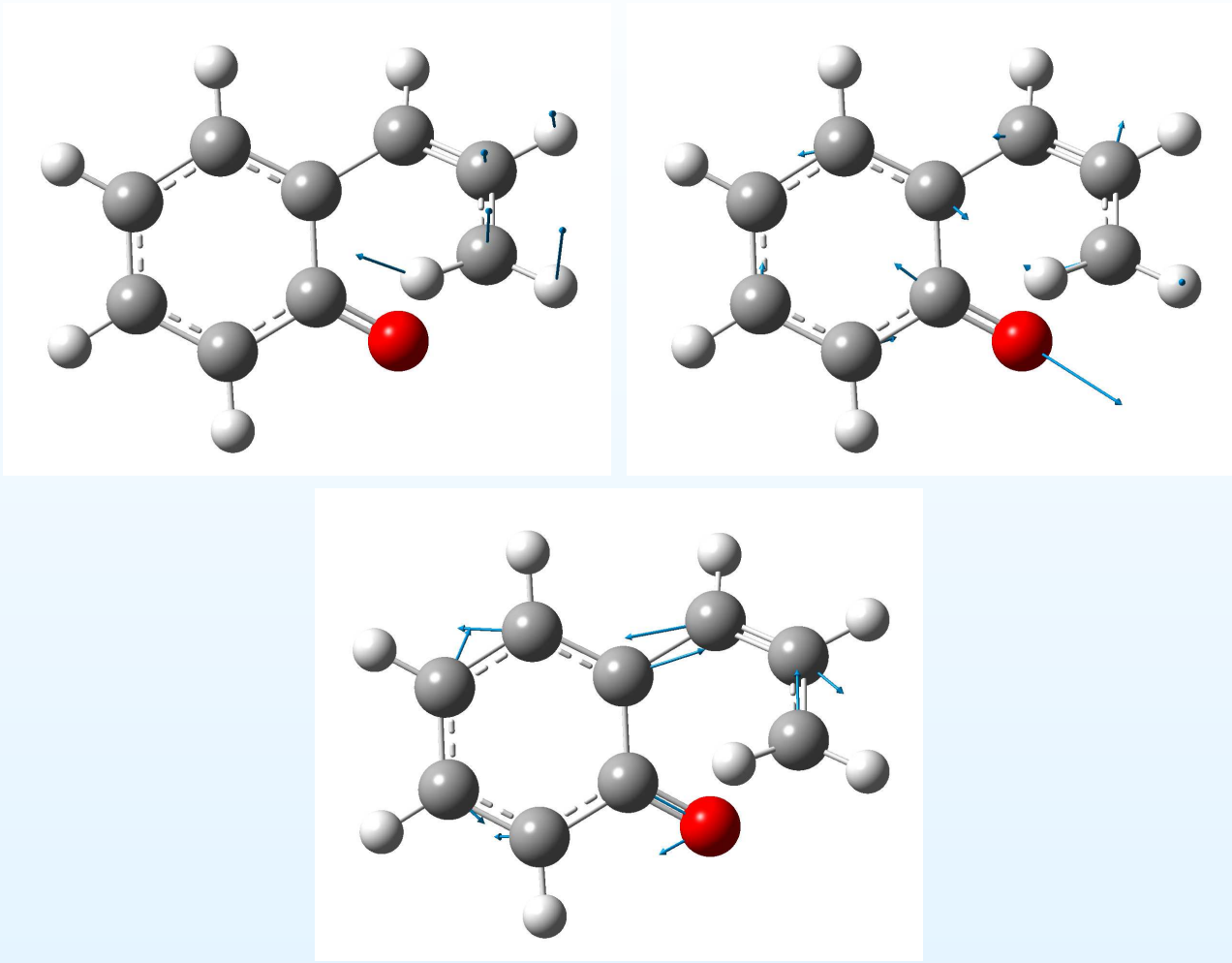
$$\mathbf{H}=\begin{pmatrix} H_{11} & H_{12} & H_{13} \\ H_{21} & H_{22} & H_{23} \\ H_{31} & H_{32} & H_{33} \end{pmatrix} \longrightarrow \text{Diagonalisation} \quad E_i$$

3D Model

3 dimensional model

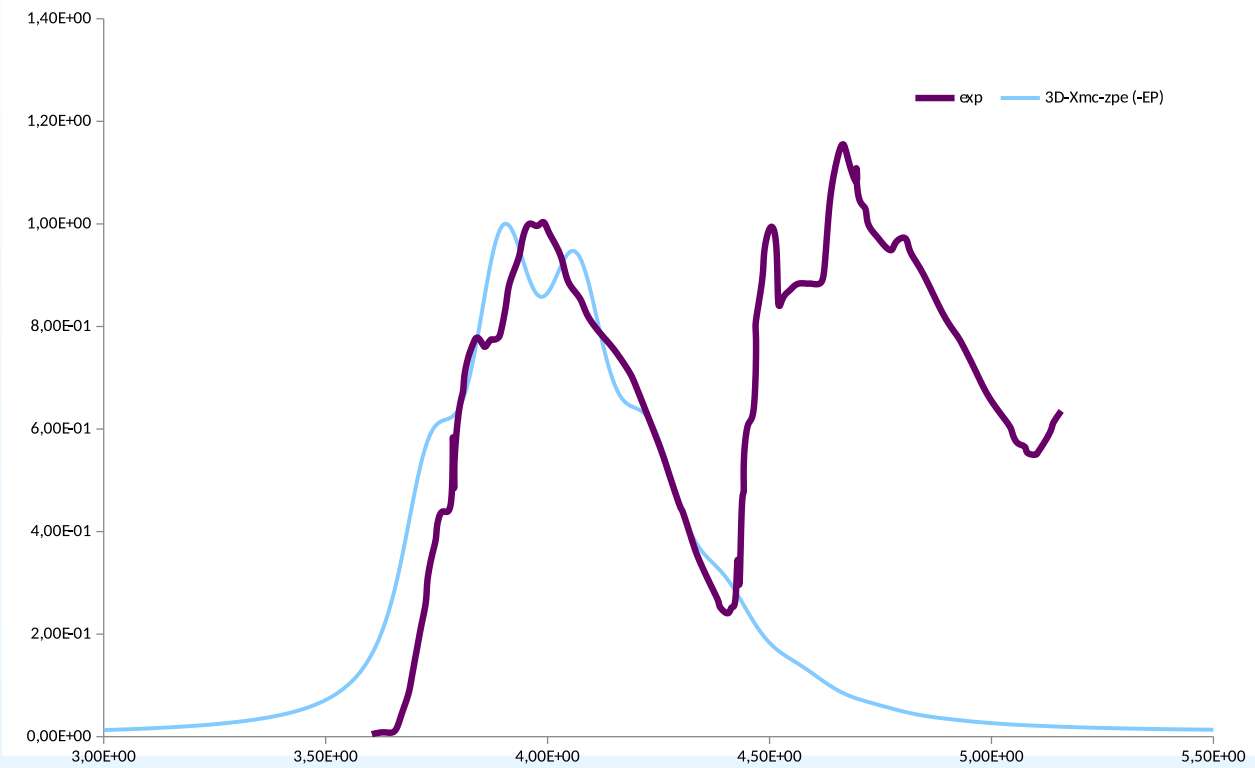
- The direction from the equilibrium geometry to the CI
- Two directions calculated to include the branching space at the CI, which has been calculated numerically at the XMCQDPT2 level of theory

3D Model

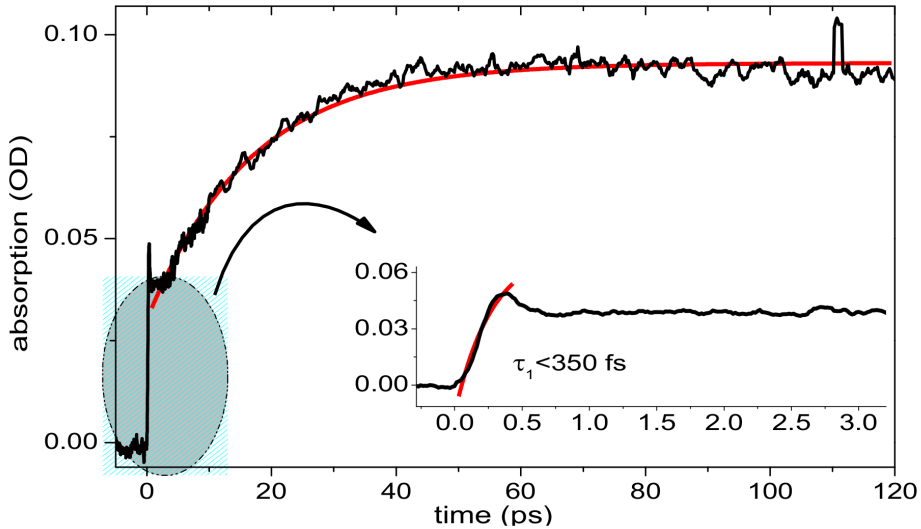


Branching space calculated numerically at the XMCQDPT2 level of theory

3D Model


1,40E+00
1,20E+00
1,00E+00
8,00E-01
6,00E-01
4,00E-01
2,00E-01
0,00E+00
3,00E+00
3,50E+00
4,00E+00
4,50E+00
5,00E+00
5,50E+00
exp
3D-Xmc-zpe (-EP)

Experiment



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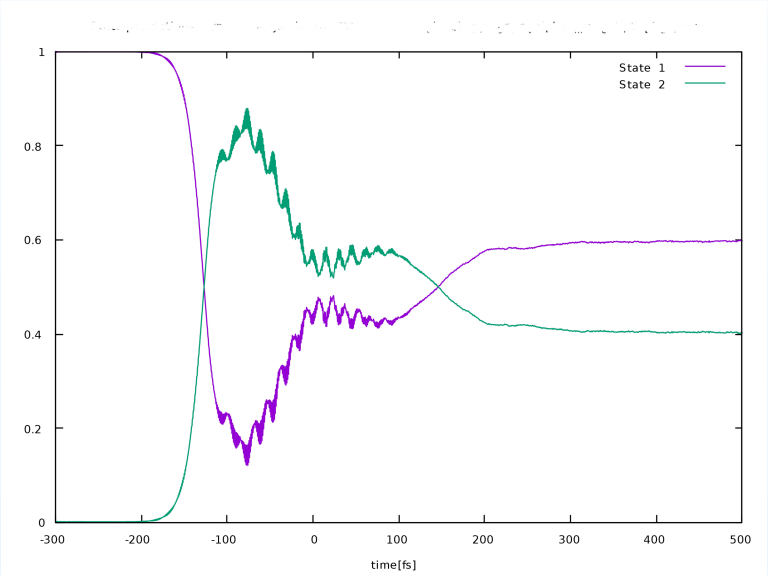
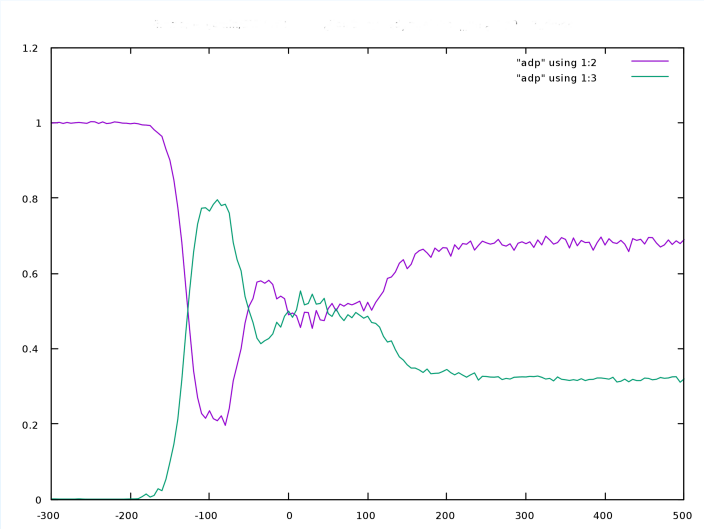
Diabatic and Adiabatic populations:





Experiment

- We observe a very fast transfer (100 fs), which does not strongly depend on the laser frequency
  As in the experiment
- Due to the presence of the CI
- Use of a chirped pulse. The pulse becomes longer and they observe less reaction
- The simulations lead to the the same trend

Spectral shaping (400 nm)

Chirped pulses : spectral shaping. We change the spectral phase only

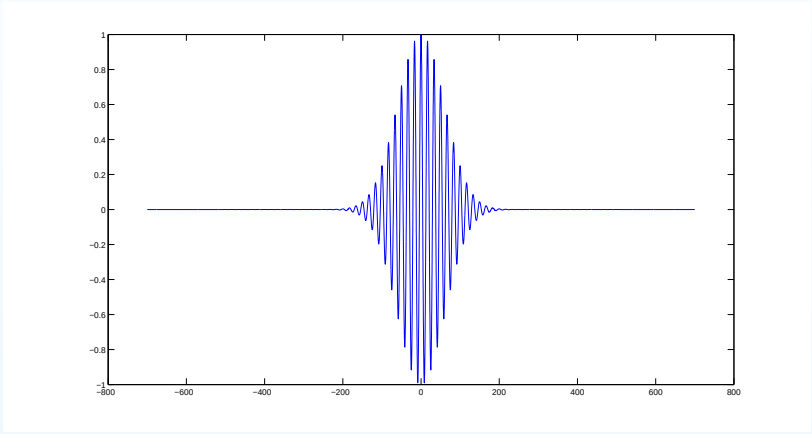
$$\mathcal{E}_{in}(t) \quad = \quad \mathcal{E}_{0in}\Lambda_{in}(t)e^{i(\omega_0 t-\theta)} \ , \ \Lambda_{in}(t) = e^{-(t/T_{in})^2}$$

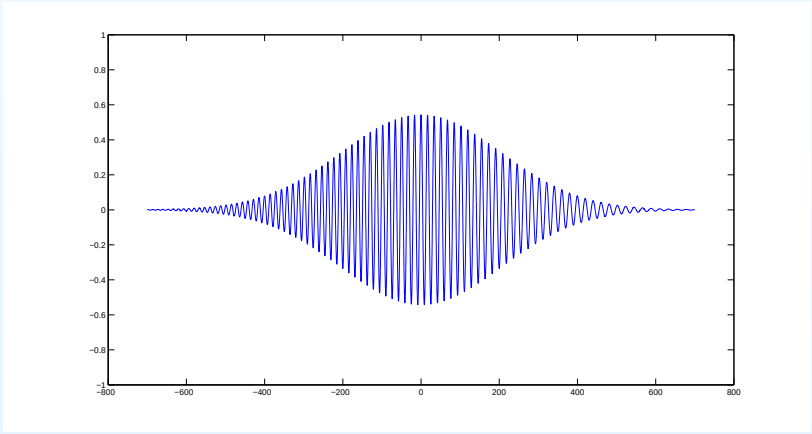
$$\tilde{\mathcal{E}}(\omega) = \tilde{\mathcal{E}}_{in}(\omega)e^{i\varphi(\omega)}$$

Spectral shaping (400 nm)

$$
\begin{aligned}
\mathcal{E}_{out}(t) &= \mathcal{E}_{0out}\Lambda_{out}(t)e^{i(\omega_0 t+\phi(t)-\theta)} \\
\varphi(\omega) &= \gamma(\omega-\omega_0)^2 \\
\Lambda_{out}(t) &= \sqrt{\frac{T_{in}}{T}}e^{-(t/T)^2} \\
\phi(t) &= \alpha t^2 \ , \ \alpha = -\frac{4\gamma}{T_{in}^4+16\gamma^2} \\
T &= \frac{4\gamma}{T_{in}}\sqrt{1+\left(\frac{T_{in}^2}{4\gamma}\right)^2} = \frac{1}{T_{in}}\sqrt{16\gamma^2+Tin^4}
\end{aligned}
$$

Pulse shaping (400 nm)





Less reaction in experiment and theory

Towards the Chemistry of the Future ?

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