Ultrafast molecular dynamics

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Ultrafast molecular dynamics

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

Measure of electronic and nuclear simultaneous dynamics in subfemto timescale

International collaboration

- **Theoretical part**
  - F. Gatti, A. Perveaux, B. Lasorne, D. Lauvergnat, France
  - Á. Vibók, G. Halász, Hungary
  - P. Decleva, Italy
- **Experimental part**
  - R. Kienberger, T. Latka, M. Jobst, F. Krausz, etc., Germany

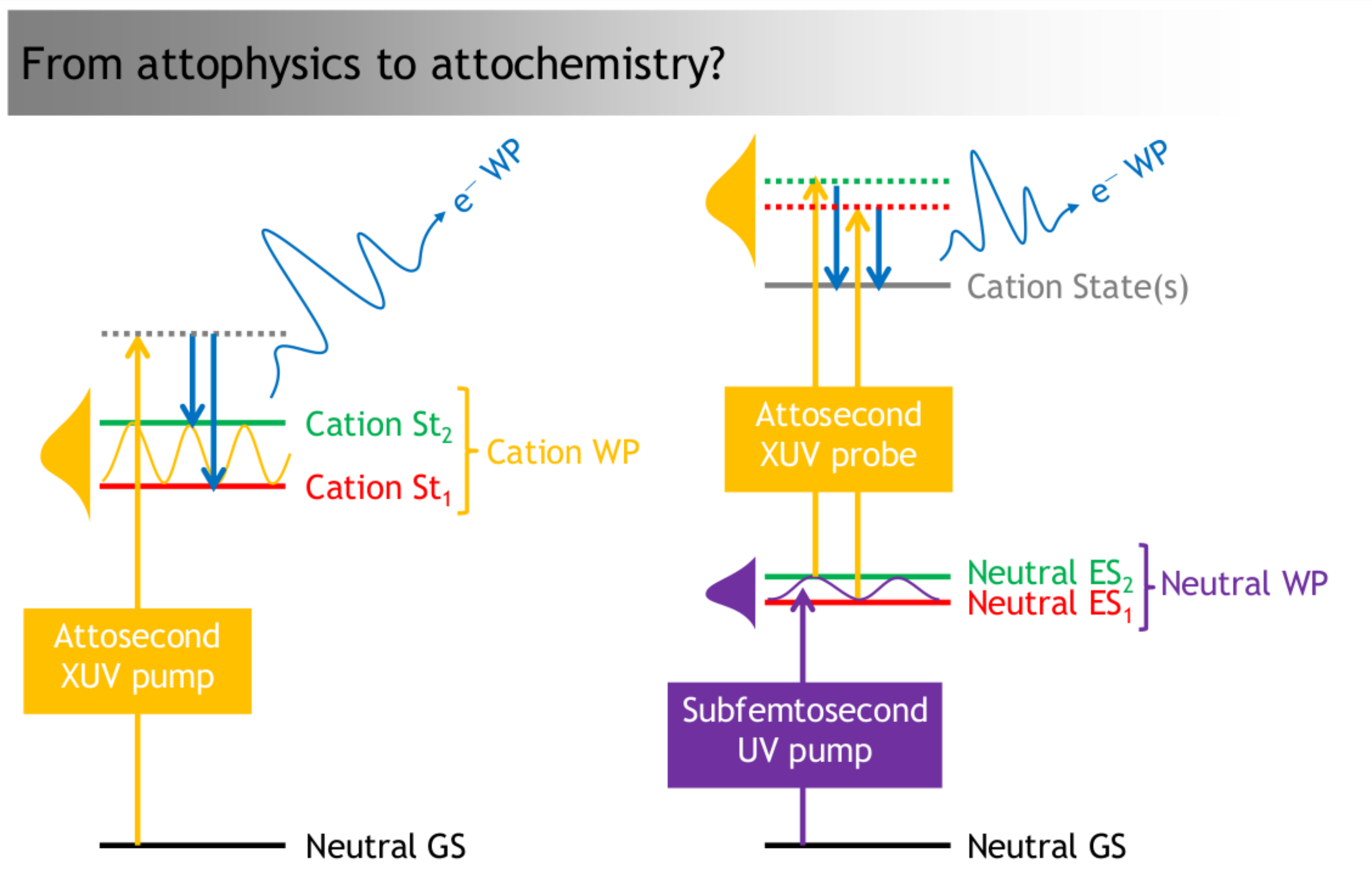
Publications

- G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. Vibók: Simulation of laser-induced quantum dynamics of the electronic and nuclear motion in the ozone molecule on the attosecond time scale. Phys. Rev. A. 86, 043426, (2012).
- G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. Vibók: Coherence revival during the attosecond electronic and nuclear quantum photodynamics of the ozone molecule. Phys. Rev. A. 88, 023425, (2013).
- G. J. Halász, A. Perveaux, B. Lasorne, M. A. Robb, F. Gatti and Á. Vibók: Attosecond electronic and nuclear quantum photodynamics of the ozone molecule. AIP Conference Proceedings 1565, 19 (2013).
- A. Perveaux, D. Lauvergnat, B. Lasorne, F. Gatti, M. A. Robb, G. J. Halász, and Á. Vibók: Attosecond electronic and nuclear quantum photodynamics of ozone: time-dependent Dyson orbitals and dipole. J. Phys. B. 47, 124010 (2014).

Publications (following)

- A. Perveaux, D. Lauvergnat, F. Gatti, G. J. Halàsz, Á. Vibók and B. Lasorne: Monitoring the birth of an electronic wavepacket in a molecule with attosecond time-resolved photoelectron spectroscopy. J. Phys. Chem. A. 118, 8773 (2014).
- P. Decleva, N. Quadri, A. Perveaux, D. Lauvergnat, F. Gatti, B. Lasorne, G. J. Halász and Á. Vibók: Attosecond electronic and nuclear quantum photodynamics of ozone monitored with time and angle resolved photoelectron spectra. Scientific Reports, 6:36613 (2016).
- T. Latka, V. Shirvanyan, M. Ossiander, O. Razskazovskaya, A. Guggenmos, M. Jobst, M. Fiess, S. Holzner, A. Sommer, M. Schultze, C. Jakubeit, J. Riemensberger, B. Bernhardt, W. Helml, F. Gatti, B. Lasorne, D. Lauvergnat, P. Decleva, G. J. Halász, Á. Vibók, R. Kienberger, Femtosecond Wave Packet Revivals in Ozone, 2018, submitted.

Ultrafast molecular dynamics



Ultrafast molecular dynamics

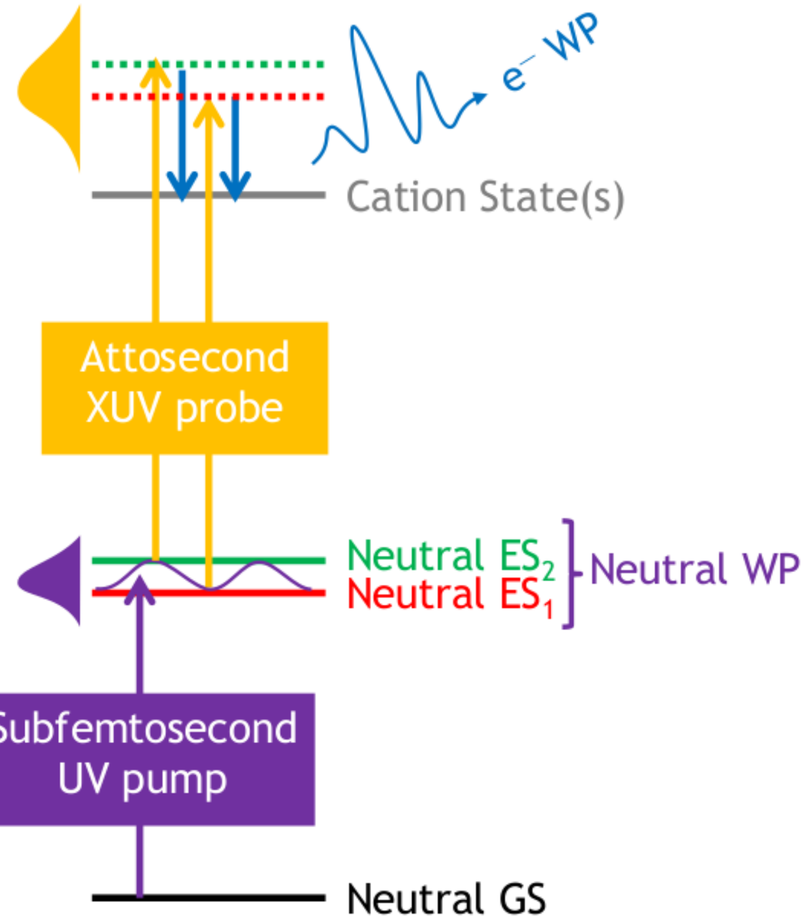
First objective: monitor electronic coherence in the neutral

Pump-probe experiment:

Bandwith of the pump large enough compared to the energy gap

→ electronic wavepacket (coherent mixture of ES_1 and ES_2)

→ probe with time-resolved photoelectron spectrum



Ultrafast molecular dynamics

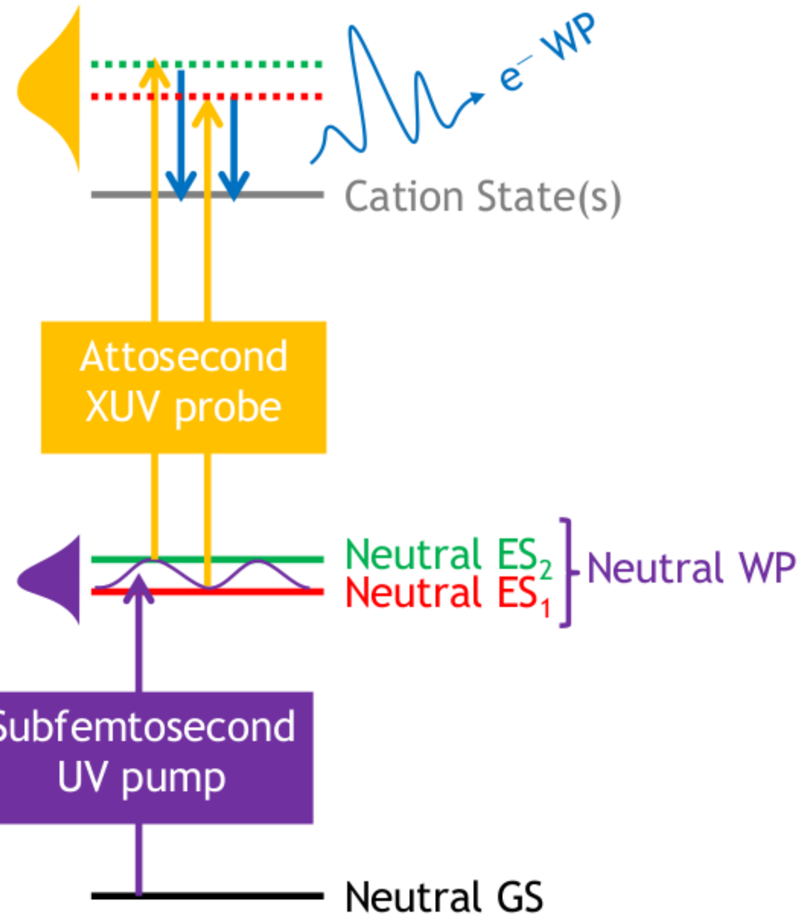
Second objective: control reactivity (electrons → nuclei)

Electronic wavepacket (coherent mixture of ES_1 and ES_2)

→ non-adiabatic transfer to nuclear motion

→ coherently-controlled photoreactivity?

(*Cf*. coherent charge migration *vs*. charge transfer)



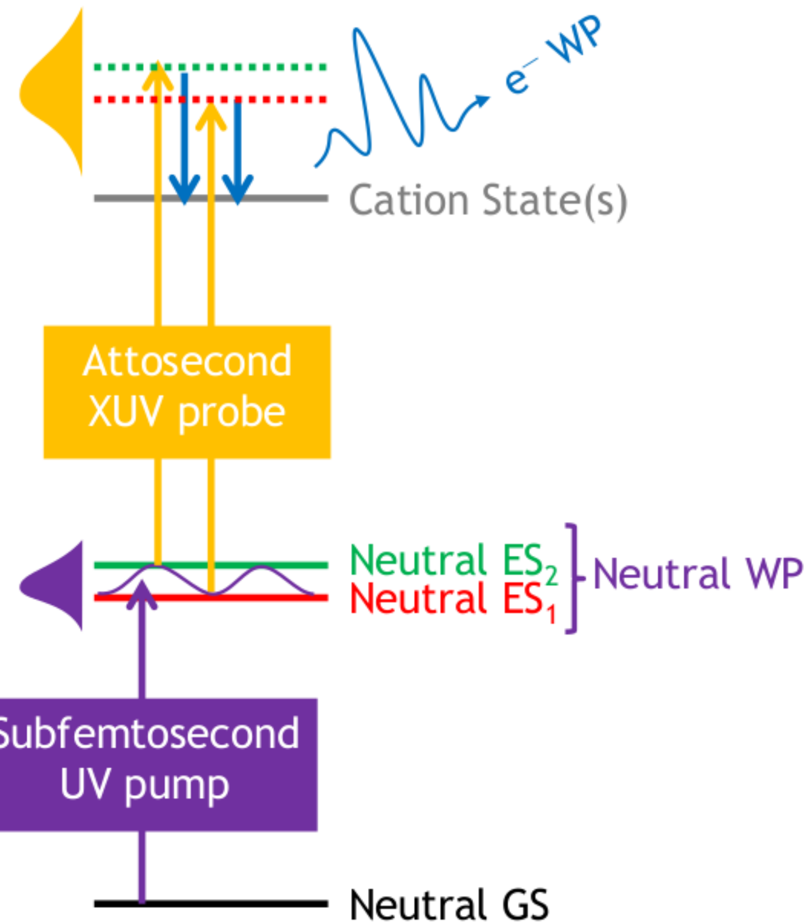
Ultrafast molecular dynamics

Technical constraint

Pump in the UV domain with “subfemtosecond” time resolution (~100 as to 1 fs) and enough cycles

4 eV ↔ 1 fs

(experiments in progress in the group of R. Kienberger and F. Krausz)

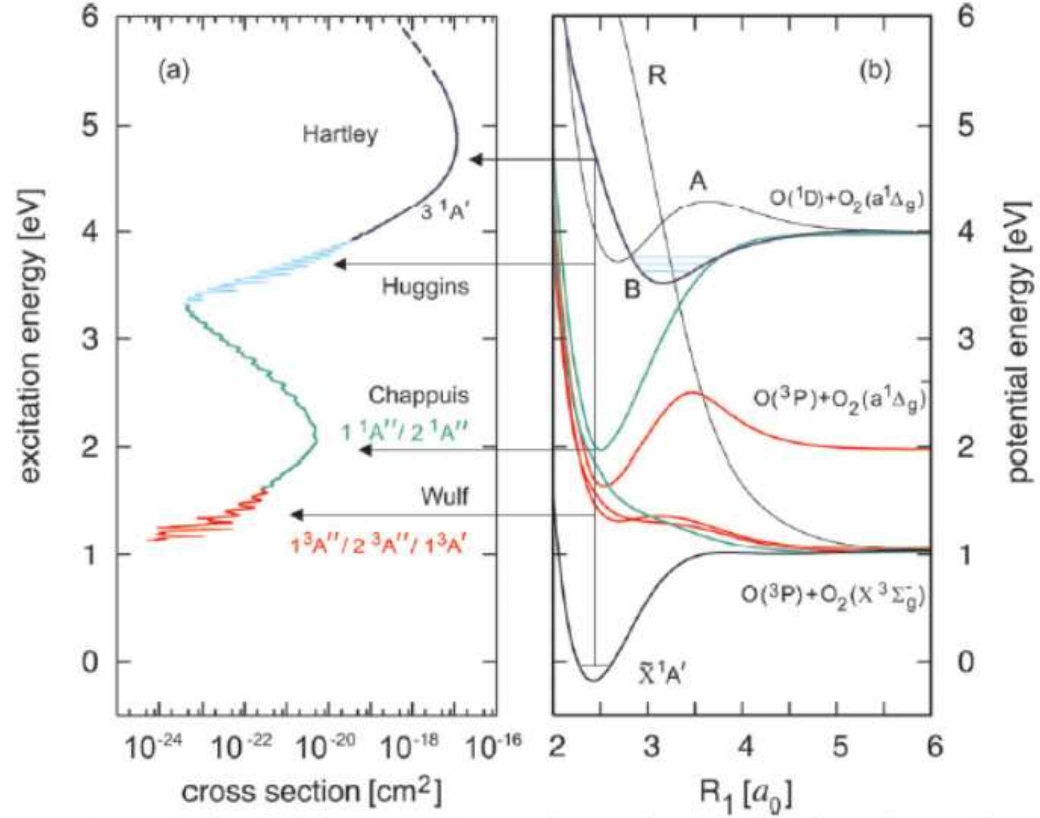


Ultrafast molecular dynamics

First candidate: the ozone molecule

$O_3 + h\nu \rightarrow O_3^* \rightarrow O_2 + O$

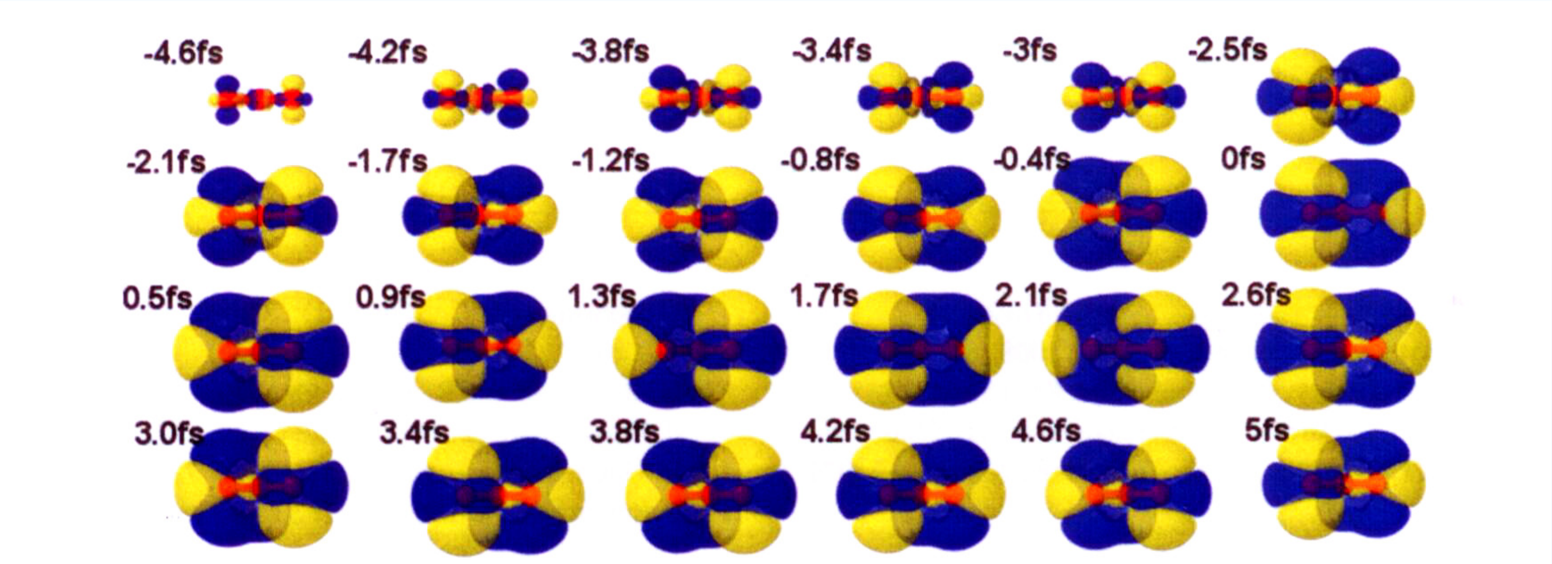
two singlet dissociation channels: GS (X) and Hartley (B)



S. Yu. Grebenshchikov, Z.-W. Qu, H. Zhu, and R. Schinke, Phys. Chem. Chem. Phys. 9 (2007) 2044

Electronic motion

Evolution of differential charge density



Oscillation of the electronic density from one bond to another

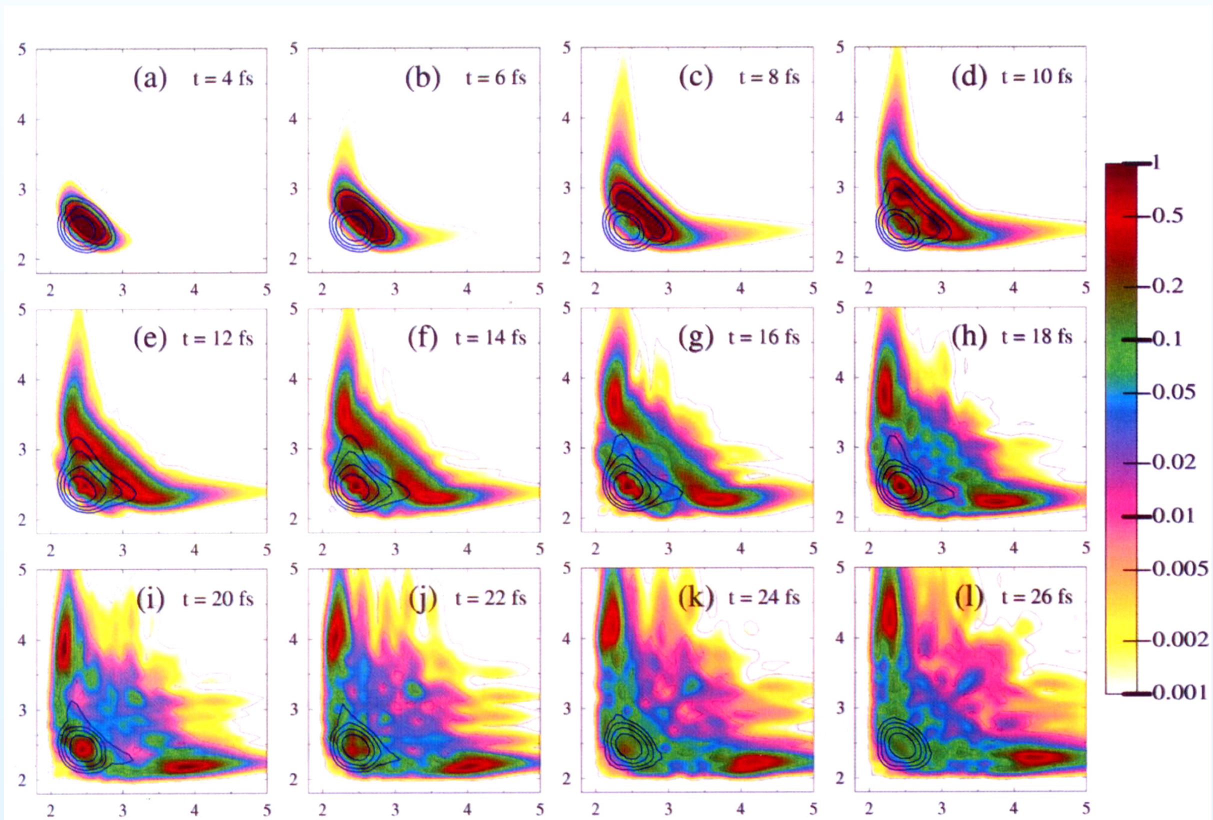
Alternating superposition of two resonant forms:

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

Precursors of the dissociation channels

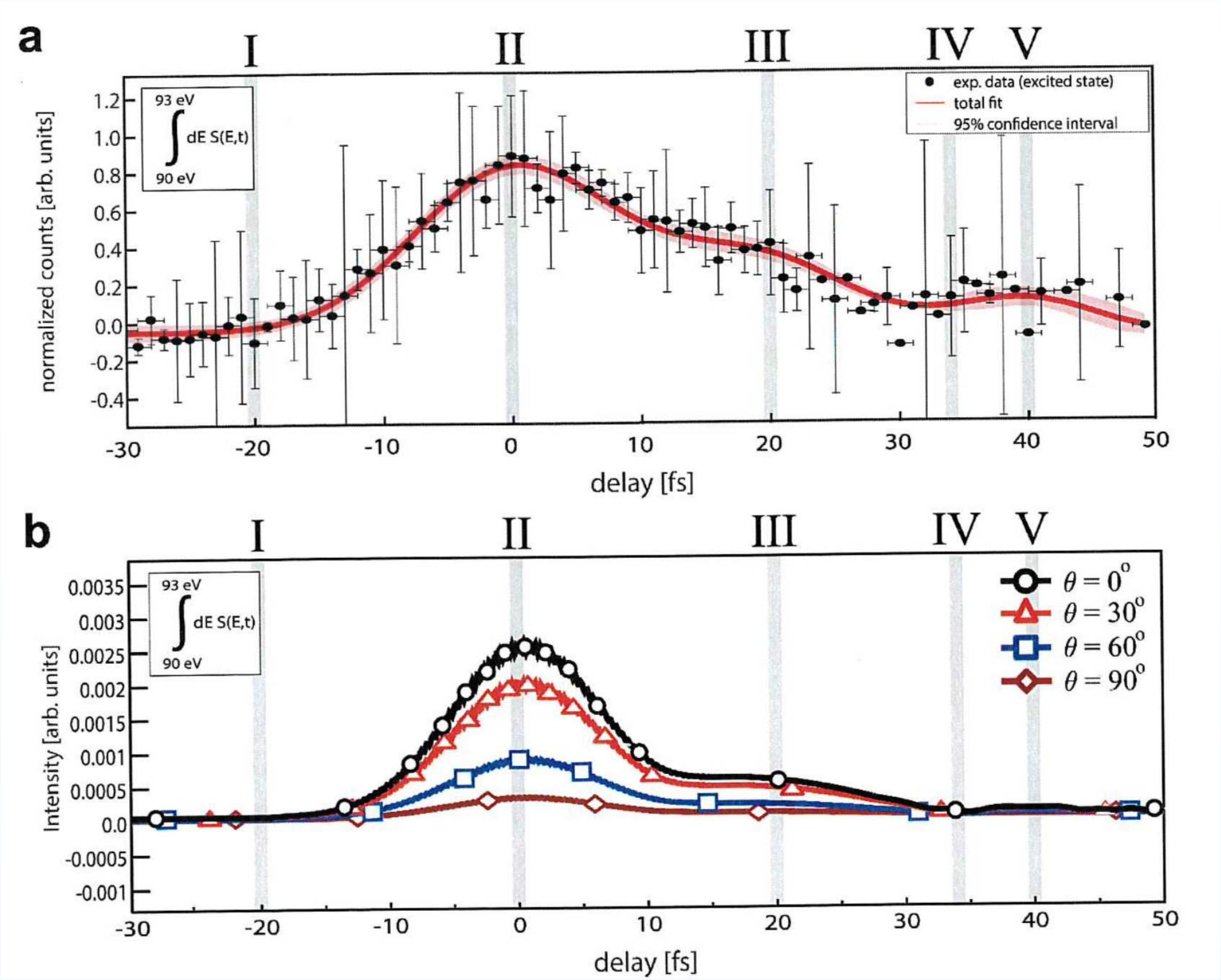
Nuclear motion

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



One part stays trapped

Comparison Theory/Experiment



European Projects

FET open project (resubmitted in January 2019)

ETN project

Tomorrow's chemistry

- Traditional chemistry:
  incoherent superposition of molecular states
  ("mixed state")
  One heats the system: energy consumption
  One creates byproducts: pollution
- Coherent chemistry:
  (1) One deposits the energy in some specific quantum states
  (2) one uses quantum coherence to make the reaction more efficient (optimal control)

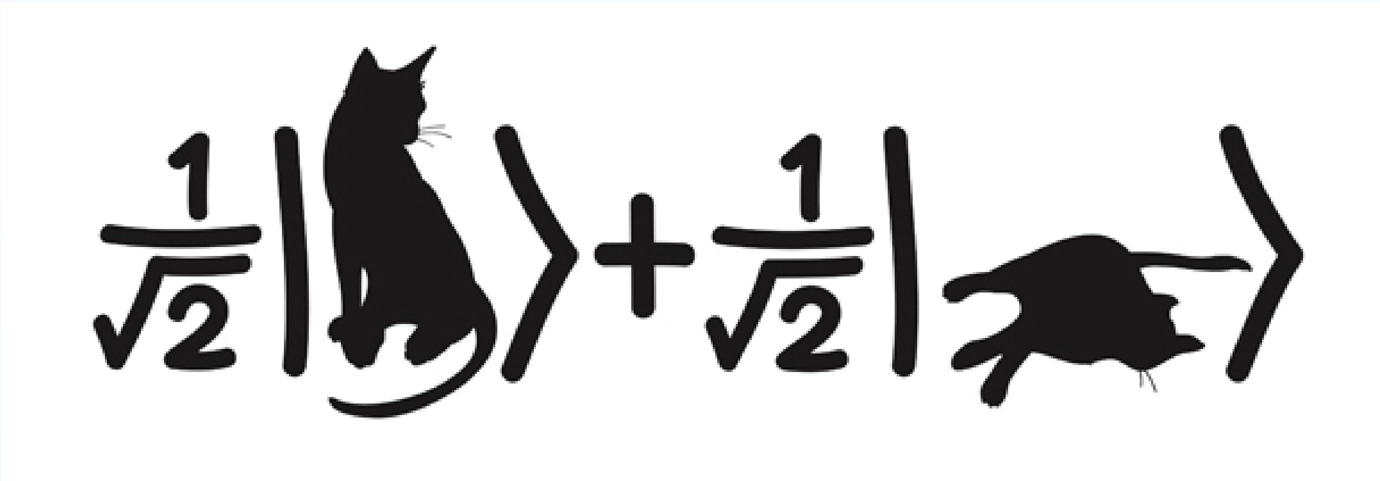
Coherent superposition of quantum states
Like for quantum computers !!!

F. Gatti *Nature* News & Views (2018) 660.

$$c_1\Psi_1(\mathbf{R}) + c_2\Psi_2(\mathbf{R})$$

Schrödinger’s cat

A superposition of two different states



Chemical quantum Surgery

For Chemistry: Lasers

- Vibrational wavepackets: femto lasers
  Activation of CH on a Ni surface: specific excitation of vibrational modes
  Improves the selectivity by several orders of magnitude
  R. Beck, P. Maroni, D. Papageorgopoulos, T. Dang, and T. Rizzo, Science 302 (2003) 98.
- Rotational wave packets: alignment of molecules
  Improves the selectivity of a photodissociation process by one order of magnitude
  Jakob Larsen, I. Wendt-Larsen, and H. Stapelfeldt, Phys. Rev. Lett. 83 (1999) 1123.
- Electronic wavepackets: attospectroscopy

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