Resonant Strong Field Control of Molecules in the Gas and Liquid Phase

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Kassel, dOCUMENTA (13) 2012:
Guiseppe Penone, Idee di Pietra

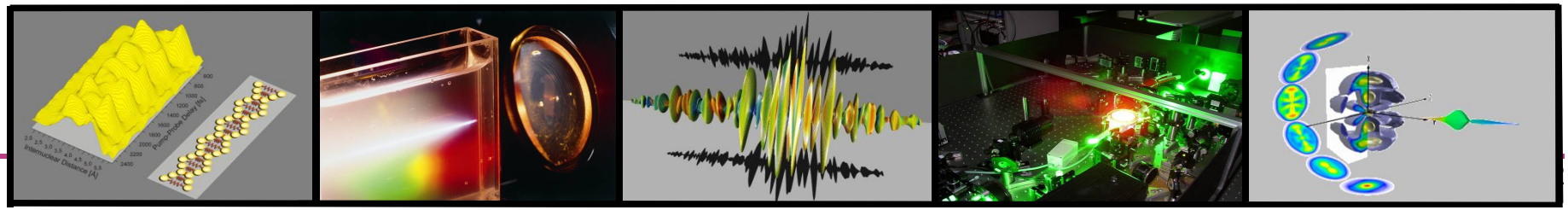
Strong field:

- **Ionization probability << 1**
- **Regime of EFFICIENT coherent population transfer (Rabi oscillations, chirped rapid adiabatic passage)**

Outline

- Introduction to Ultrafast Laser Control and Current Status of our Pulse Shaping Device **Polarization Shaping and Zeptosecond Temporal Resolution**
- **Efficient Sub-cycle Control** of the Coupled Electron and Nuclear Dynamics in **Molecules (K_2)***
- Strong Field Control on Molecules in the Liquid Phase: **Joint Wave Packet Motion and Adiabatic Population Transfer**

* In coop. with Regina de Vivie-Riedle



THANKS to the Current Group…

…and

Deutsche Forschungsgemeinschaft DFG

MARIE CURIE ACTIONS

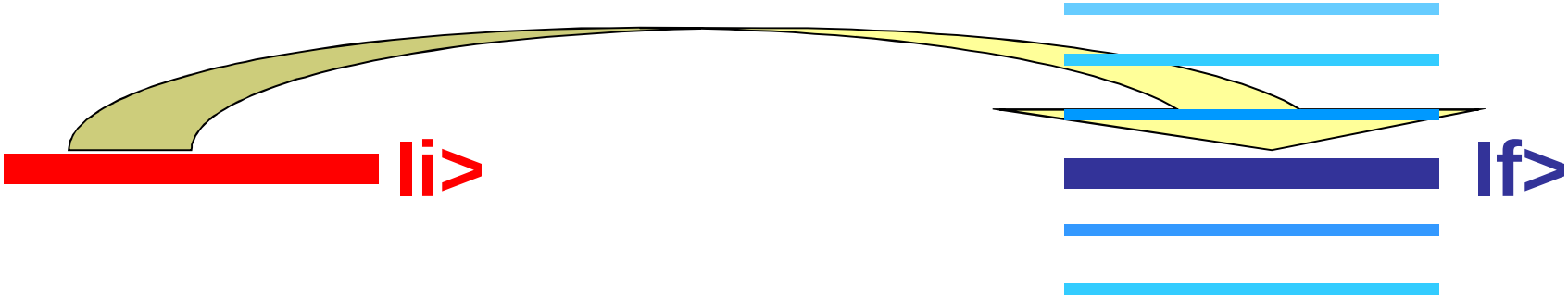
Prof. Dr. M. Wollenhaupt

T. Bayer
H. Braun
C. Gerbig
N. Götte
T. Kalas
J. Köhler
C. Lux
J. Mildner
S. Morgenstern
M. Ruge
C. Sarpe-Tudoran
(J. Schneider)
T. Blumenstein
V. Brandenstein
T. Bolze
D. Otto
V. Sporleder
T. Winkler
B. Zielinski

UNIKASSEL VERSITÄT

Ultrafast Laser Control

General Idea: steer photophysical system from initial state to final state by adapting (tailoring) light field to primary photophysical processes

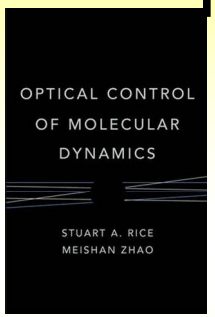


Origine: coherent control of chemical reactions

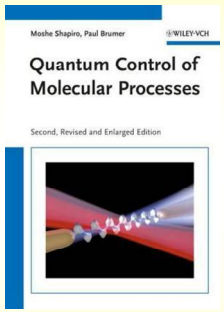
Our experimental Reviews

- **Wollenhaupt, TB, Faraday Discussions 153 (2011) 9-26.**
- **Stoian, Wollenhaupt, TB, Hertel in "Laser Precision Microfabrication" Springer (2010) ch. 5.**
- **Wollenhaupt, Engel, TB, Annu. Rev. Phys. Chem. 56 (2005) 25-56.**
- **Brixner, Pfeifer, Gerber, Wollenhaupt, TB in "Femtosecond Laser Spectroscopy" Springer (2005) 225-266.**
- **TB, Helbing, Gerber, in "Advances: Chemical Reactions and their Control on the Femtosecond Time Scale" John Wiley & Sons, Inc. New York; (1997) 47-77.**

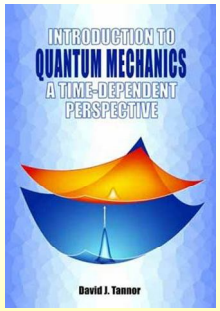
Textbooks



Rice / Zhao (2000)



Brumer Shapiro (2003, 2011)

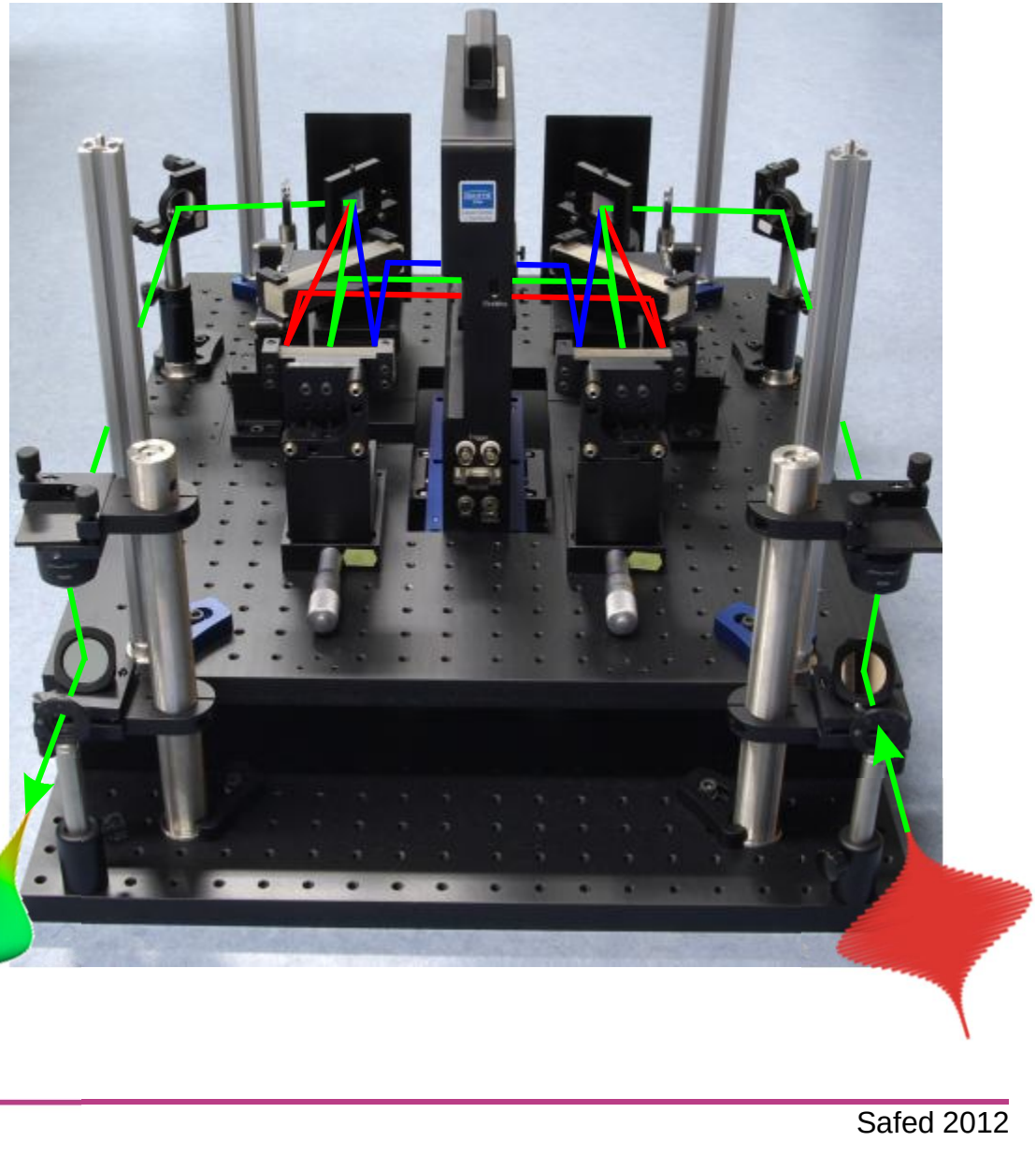


Tannor (2008)

Our Polarization Pulse Shaper Setup

Key features:

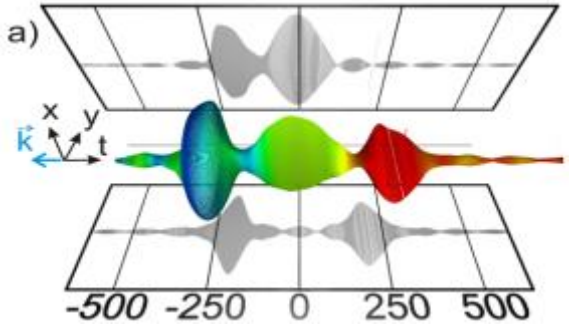
- 2 x 640 pixel LC modulator
  (Jenoptik)
- Polarization pulse shaping
  or Phase & Amplitude shaping
- High spectral resolution:
  0.16 nm/pixel @ 800 nm
- Large temporal window:
  > 10 ps
- Volume Phase Holographic Gratings
  1840 lines/mm



Shaping Capabilities of our Current Set Up

Polarization*

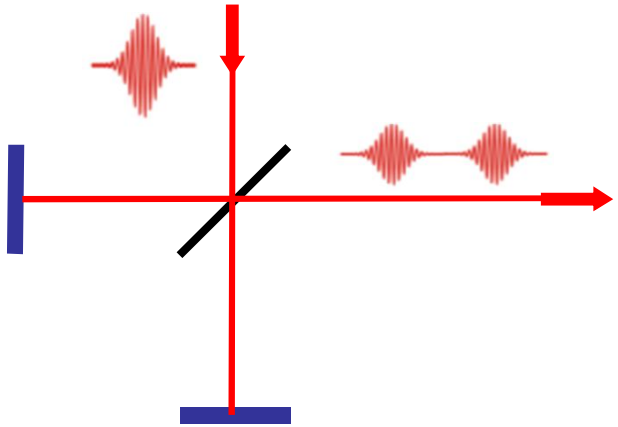
Example for designed and characterized pulse in interaction region

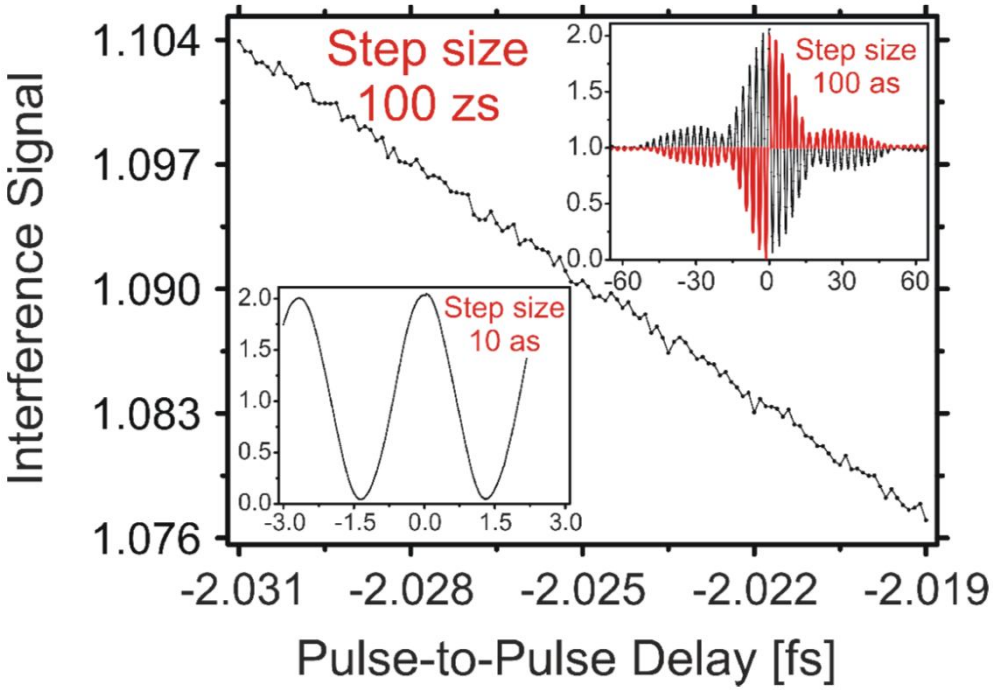


Time [fs]

Amplitude and Phase**

Mimicking a Michelson interferometer to create temporal delay with zeptosecond precision





*Appl. Phys. B **95** (2009) 245 ** Optics Express 19 (2011) 11654

Shaping Capabilities of our Current Set Up

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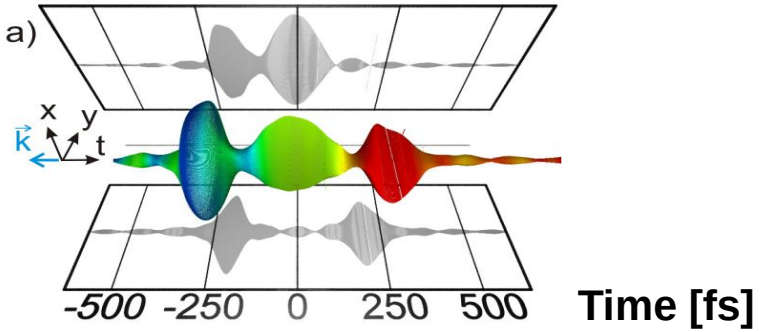

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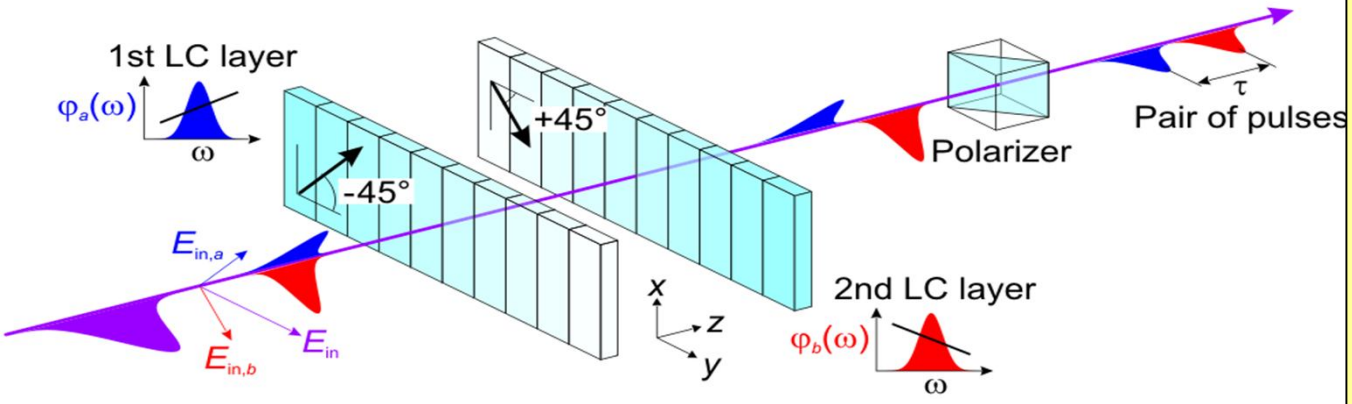
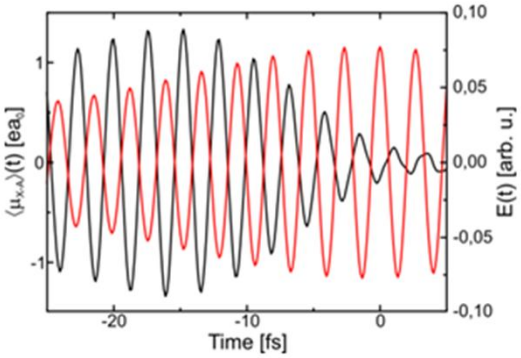
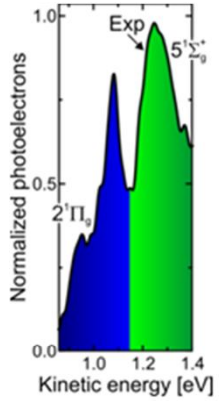


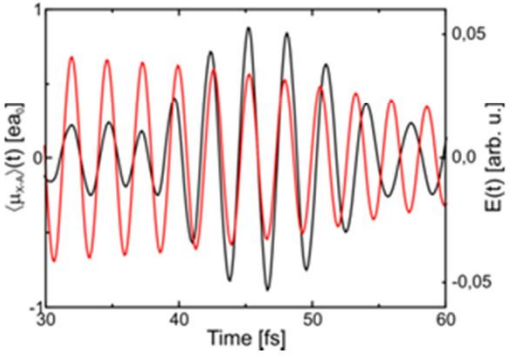
- **2σ-precision: 300 zs = 0.3 as**
- **"Mirror movement": 0.45 Å**
- **Unprecedented resolution to control valence bond electron dynamics (order of fs)**

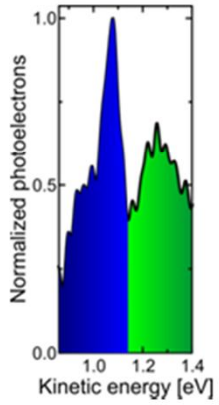
*Appl. Phys. B **95** (2009) 245 ** Optics Express **19** (2011) 11654

Efficient Sub-Cycle Control of the Coupled Electron and Nuclear Dynamics in Molecules*

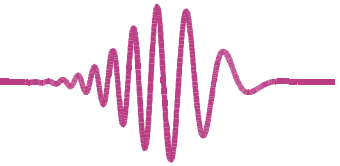








*** In coop. Regina de Vivie-Riedle**



Strong Field Interaction can be

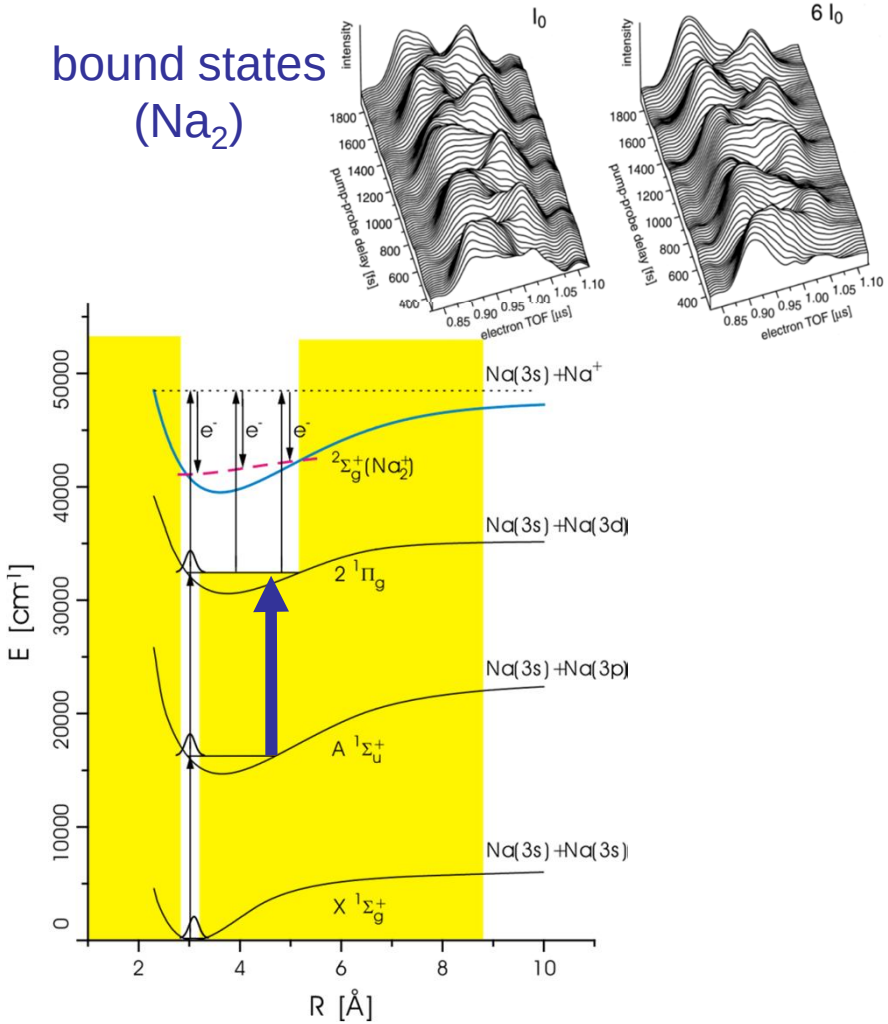
NON RESONANT

or

RESONANT

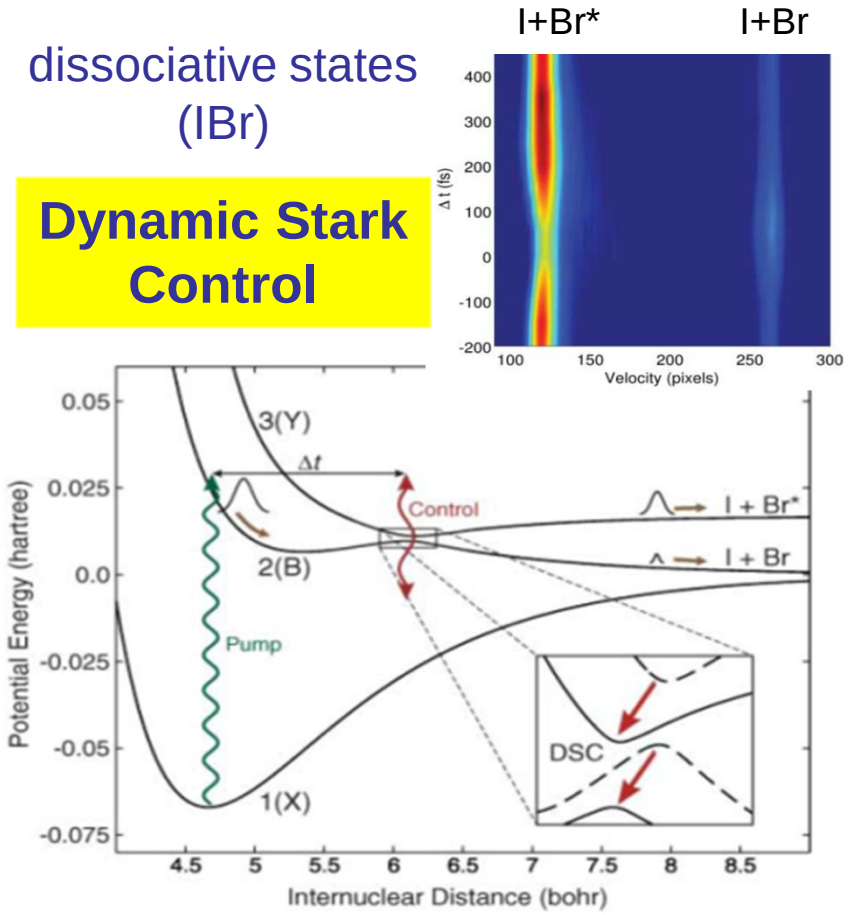
NON RESONANT Strong Field Switching

bound states
(Na_2)



dissociative states
(IBr)

Dynamic Stark Control

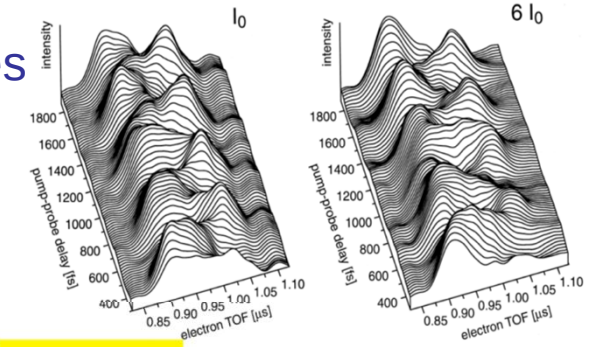


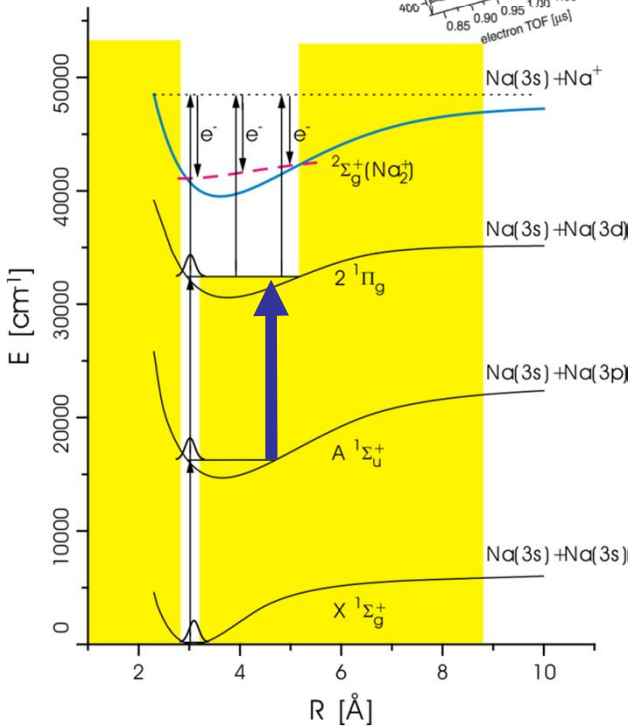
Sussmann / Stolow et al. Science **314** (2006) 278

CPL **312** (1999) 447

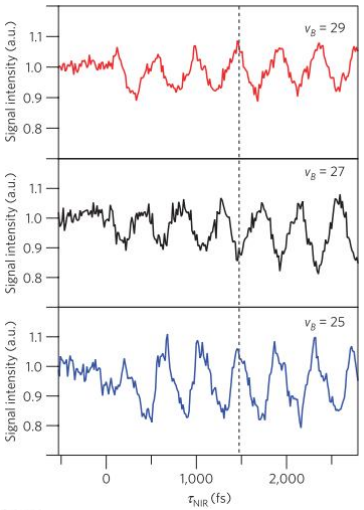
NON RESONANT Strong Field Switching

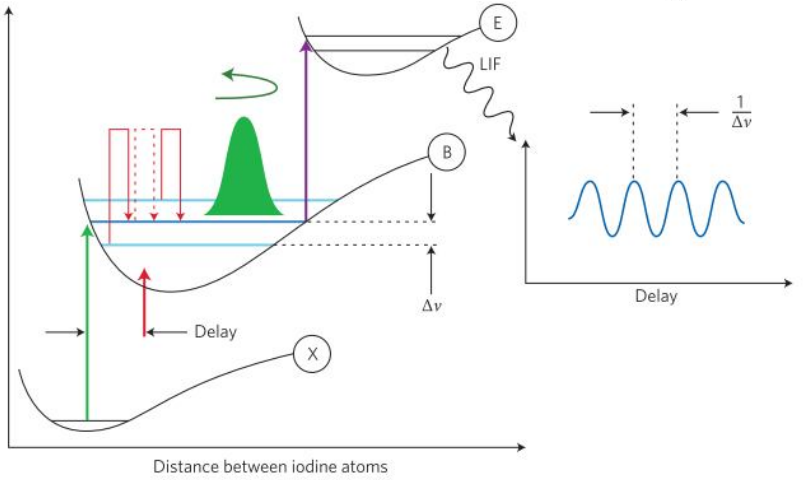
bound states
(Na_2)





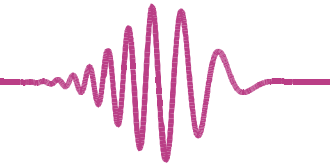
bound states
(I_2)
(Raman Process)





Goto / Ohmori et al. Nature **7** (2011) 383

CPL **312** (1999) 447



Why Investigate Resonant Processes?

Shorter and shorter pulses with ultrabroadband spectra become available

In the context of closed loop experiments this opens the door to exploit the complete electronic and rovibrational manifold for control of chemical reactions

Resonances will dominate the control scenarios

Understanding control mechanisms induced by shaped pulses will increase in importance

ADVANTAGES:

- **on time scale of electron dynamics (fast)**
- **positive and negative Stark shift in order of 100 meV (switching) population to different electronic states with attosecond precision)**
- **efficient and (if adiabatic) robust population transfer**

Difference
Non Resonant and Resonant Stark Control

Five ways to the nonresonant dynamic Stark effect

Benjamin J. Sussman

Am.J.Phys. **79** (2011) 477

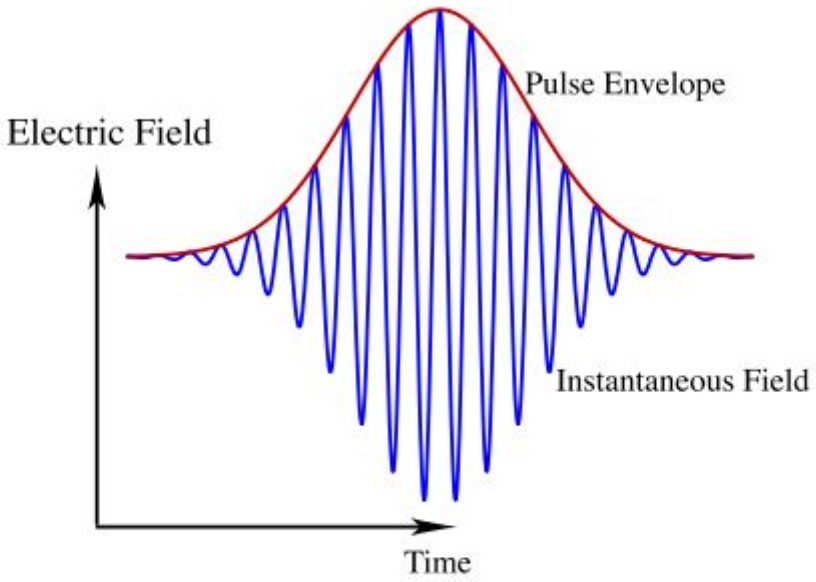


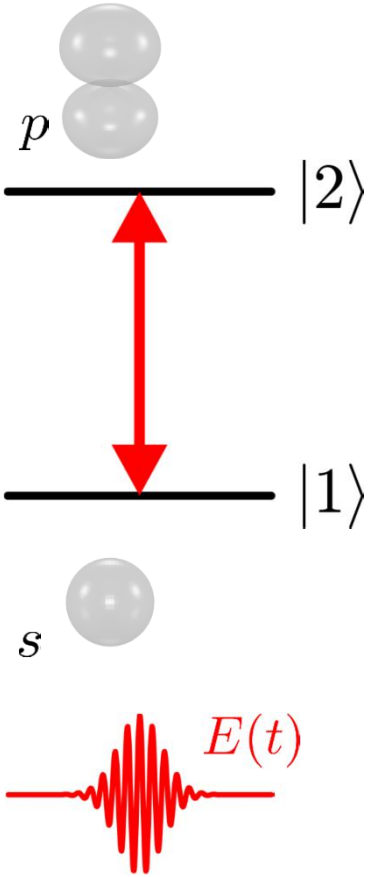
Fig. 1. The electric field of a laser pulse and its envelope. In the static Stark effect, the system responds to the instantaneous electric field. In the nonresonant dynamic Stark effect, the system responds only to the pulse envelope.

$$V \approx -\boldsymbol{\mu}_0 \cdot \mathbf{E}(t) - \tfrac{1}{4}\boldsymbol{\mathcal{E}}^*(t) \cdot \boldsymbol{\alpha} \cdot \boldsymbol{\mathcal{E}}(t).$$

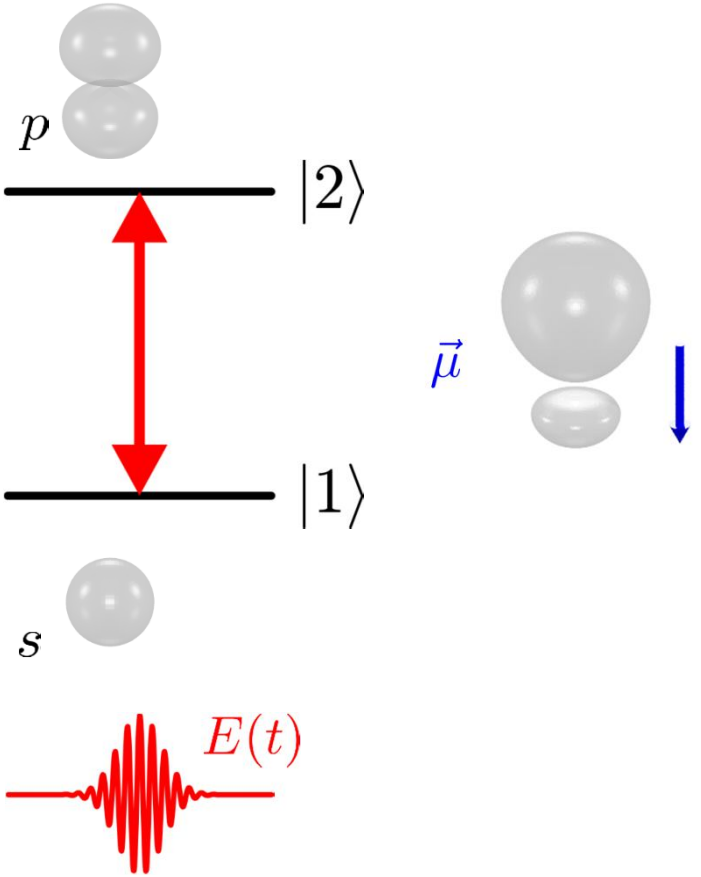
Resonant dipole coupling
Stark shift follows
intantaneous field (fast!)
Stark **shift in both directions**

Nonresonant coupling
Dynamic Stark shift follows only **pulse envelope**
Stark **shift in one direction**

Reminder: Coherent Excitation of Two Level System



Reminder: Coherent Excitation of Two Level System



Interaction energy of induced dipole with electric field:

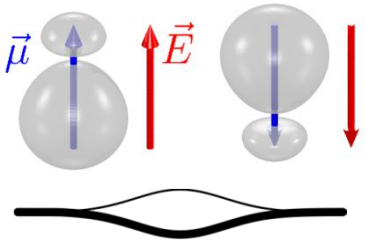
$$-\vec{\mu}(t)\cdot\vec{E}(t) \propto \hbar\Omega(t)\left\{|a_2(t)|^2 - |a_1(t)|^2\right\}$$

Rabi-Frequency

Population of Dessed States

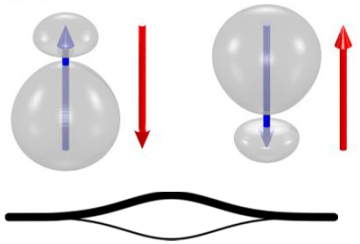
In phase:

Lower Dressed state



Out of phase:

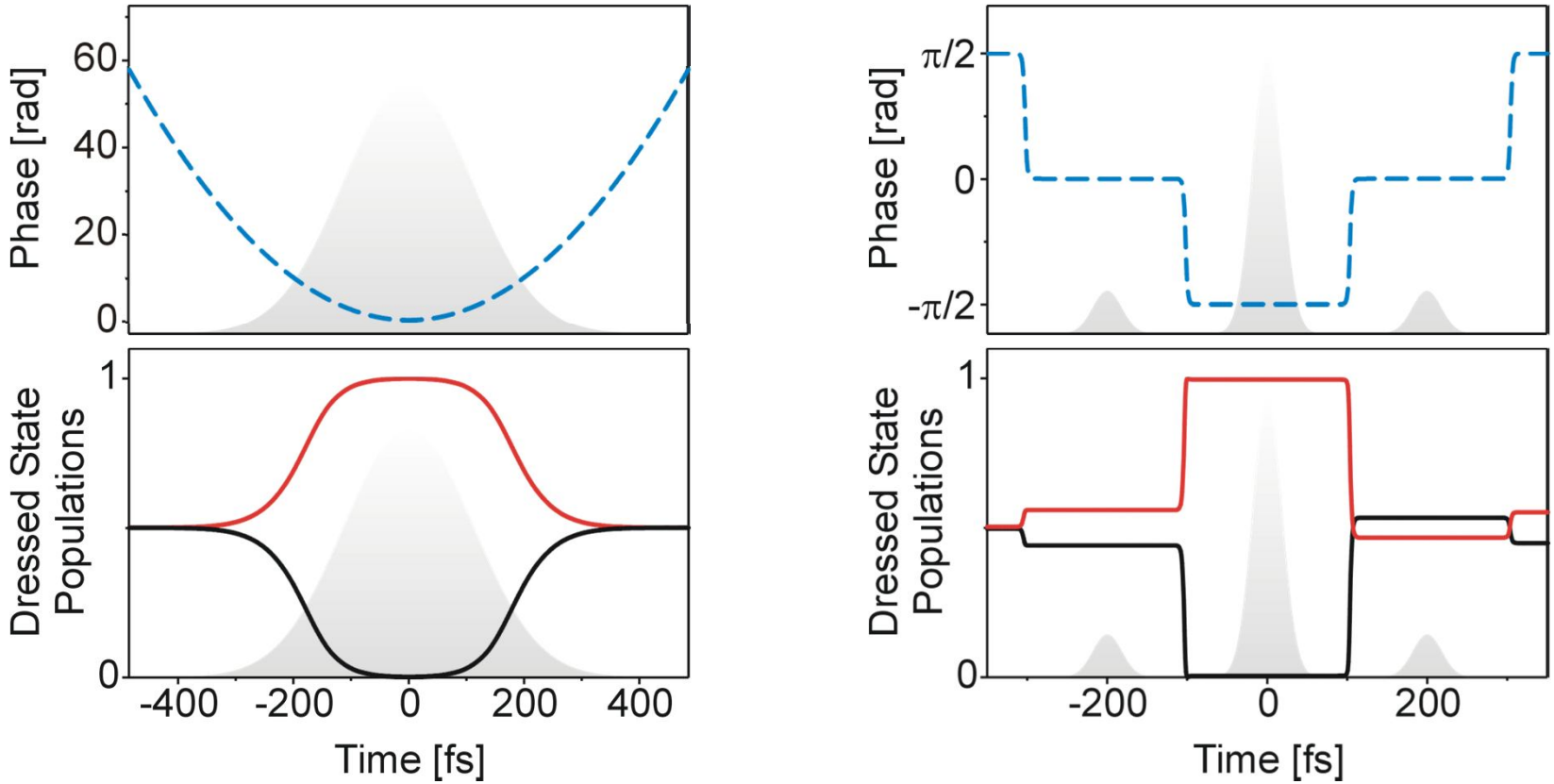
Upper Dressed state



SPODS = Selective Population of Dressed States

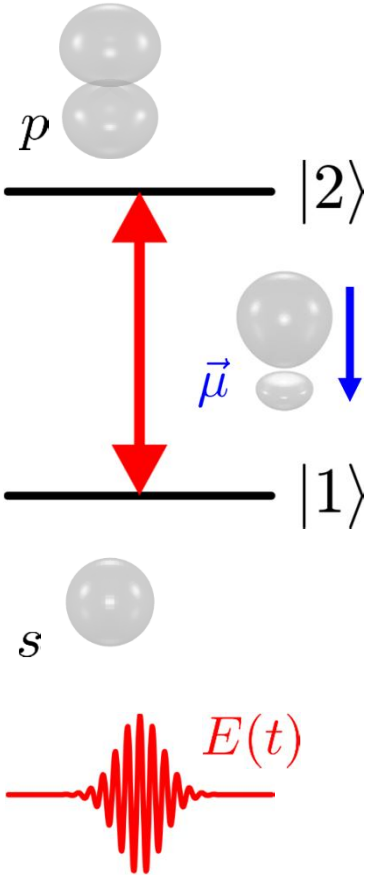
Complementary Approaches to Change the Temporal Phase and Achieve SPODS

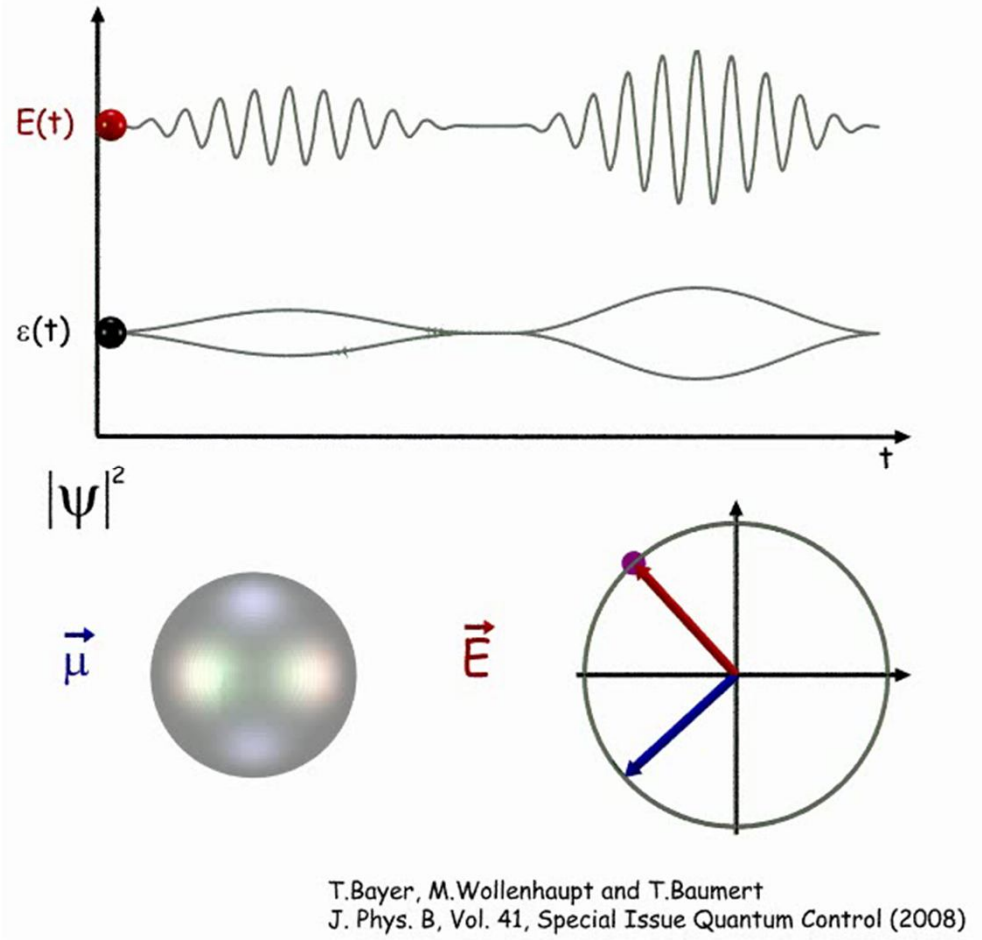
***continuous* variations** ⟷ ***discrete* variations**



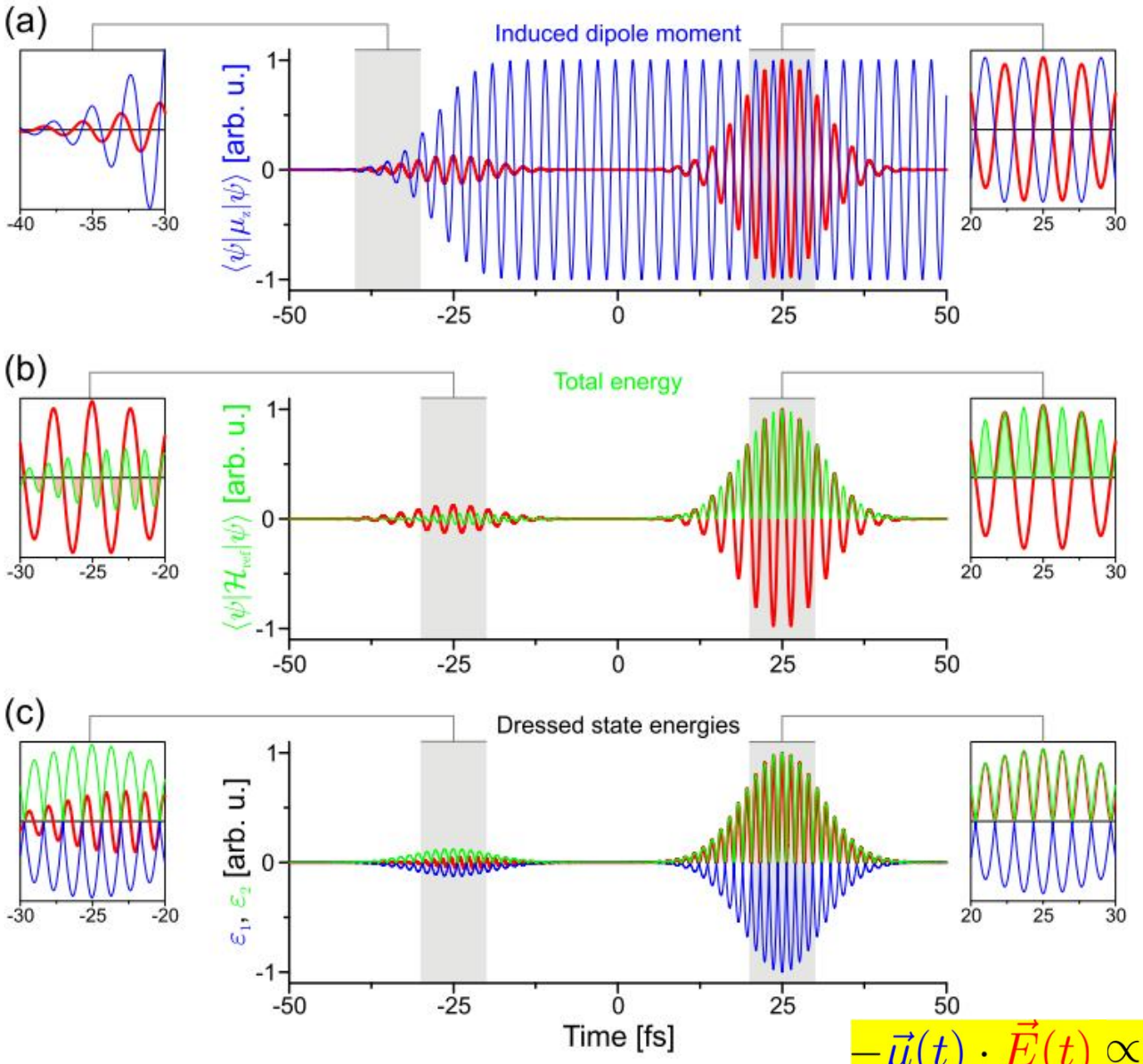
SPODS is the rule and not the exception in resonant strong field control

Example: Discrete Phase Jumps (Photon Locking)





*Photon Locking Exp. ns-scale: Zewail, Mossberg (1985)
Robust Photon Locking fs-time scale PRL (2009)
Theory Coherent Control: Kosloff, Tannor (1992)



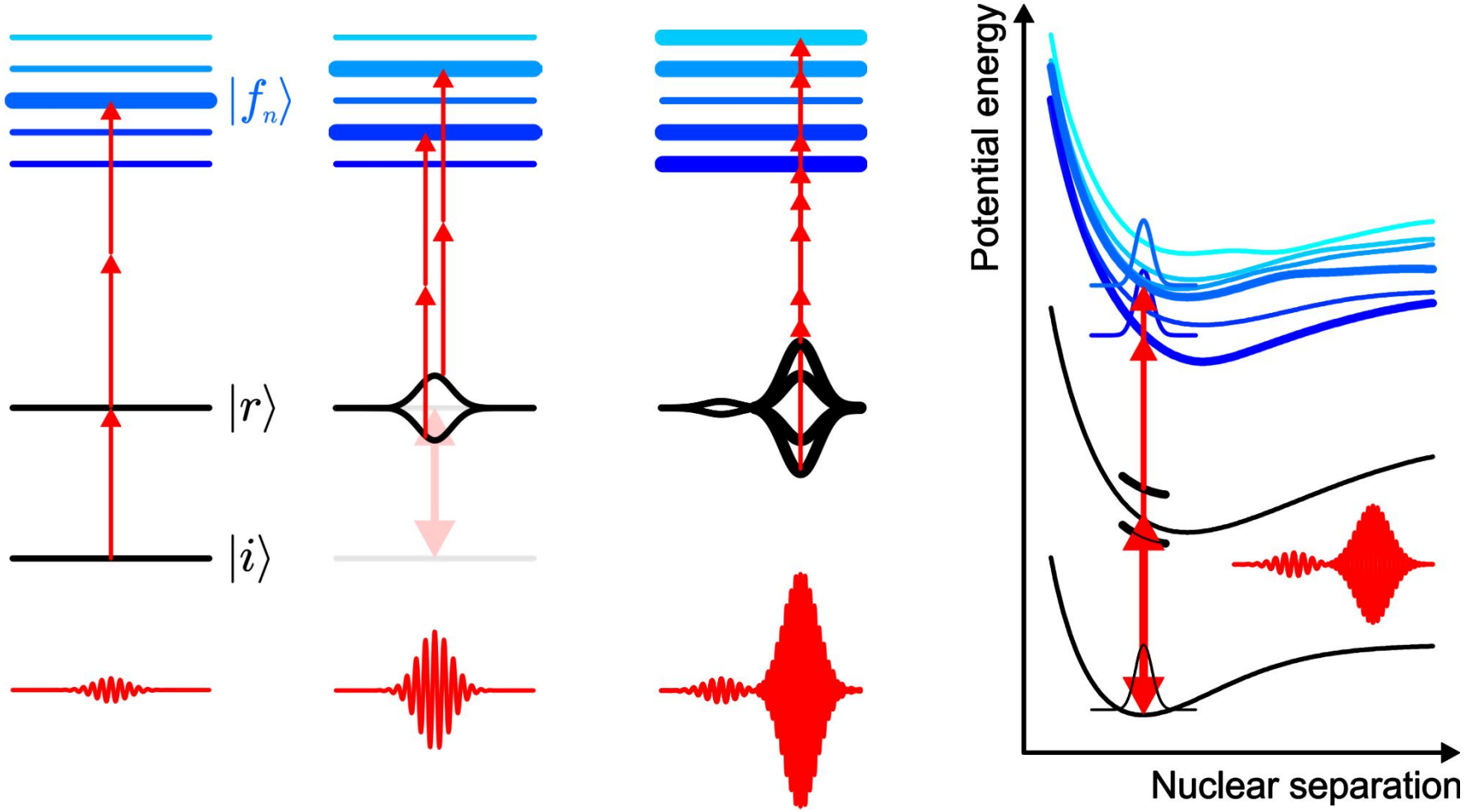
Electric Field
Induced Dipol

Electric Field
Total Energy

Total Energy
Energy Upper DS
Energy Lower DS

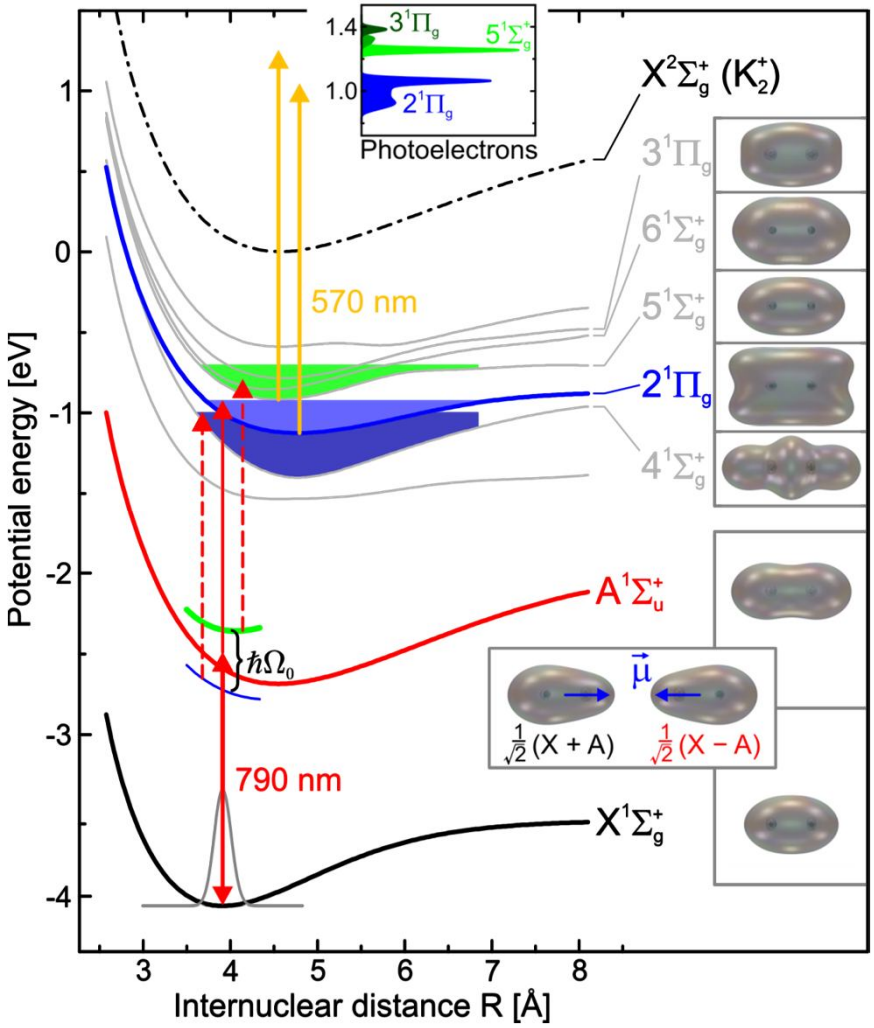
$$-\vec{\mu}(t)\cdot\vec{E}(t) \propto \hbar\Omega(t)\left\{|a_2(t)|^2 - |a_1(t)|^2\right\}$$

Resonant Strong Field Control via SPODS – General Picture



weak-field **strong-field** **selectivity** **molecules**

The Potassium Dimer



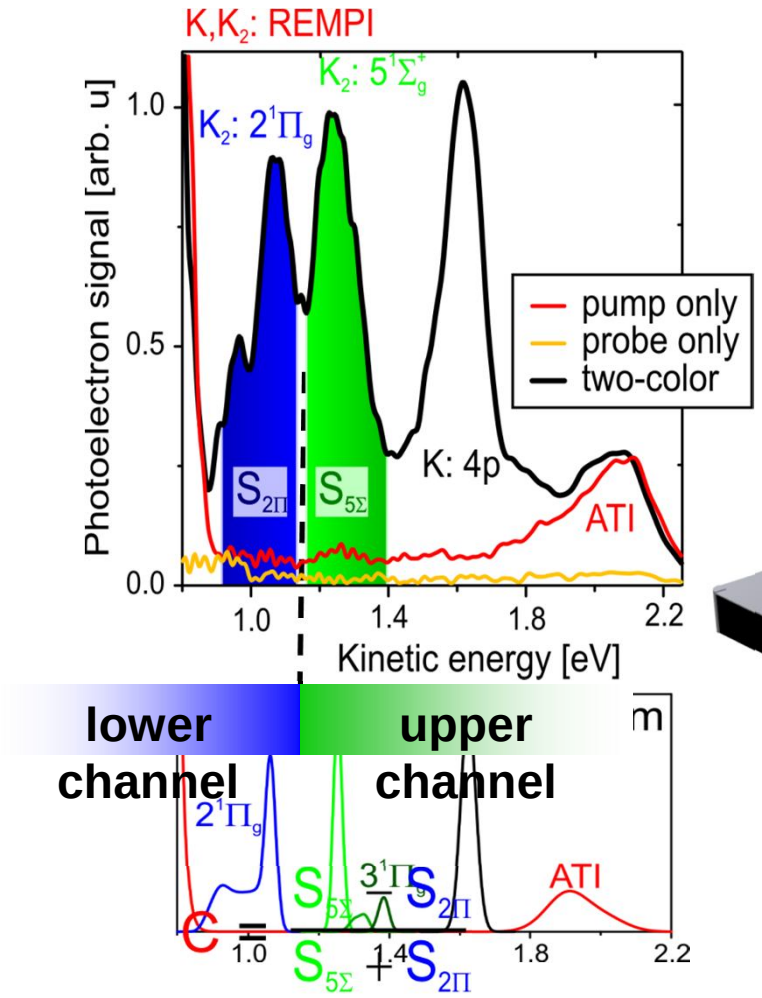
coupled nuclear–electron-motion!

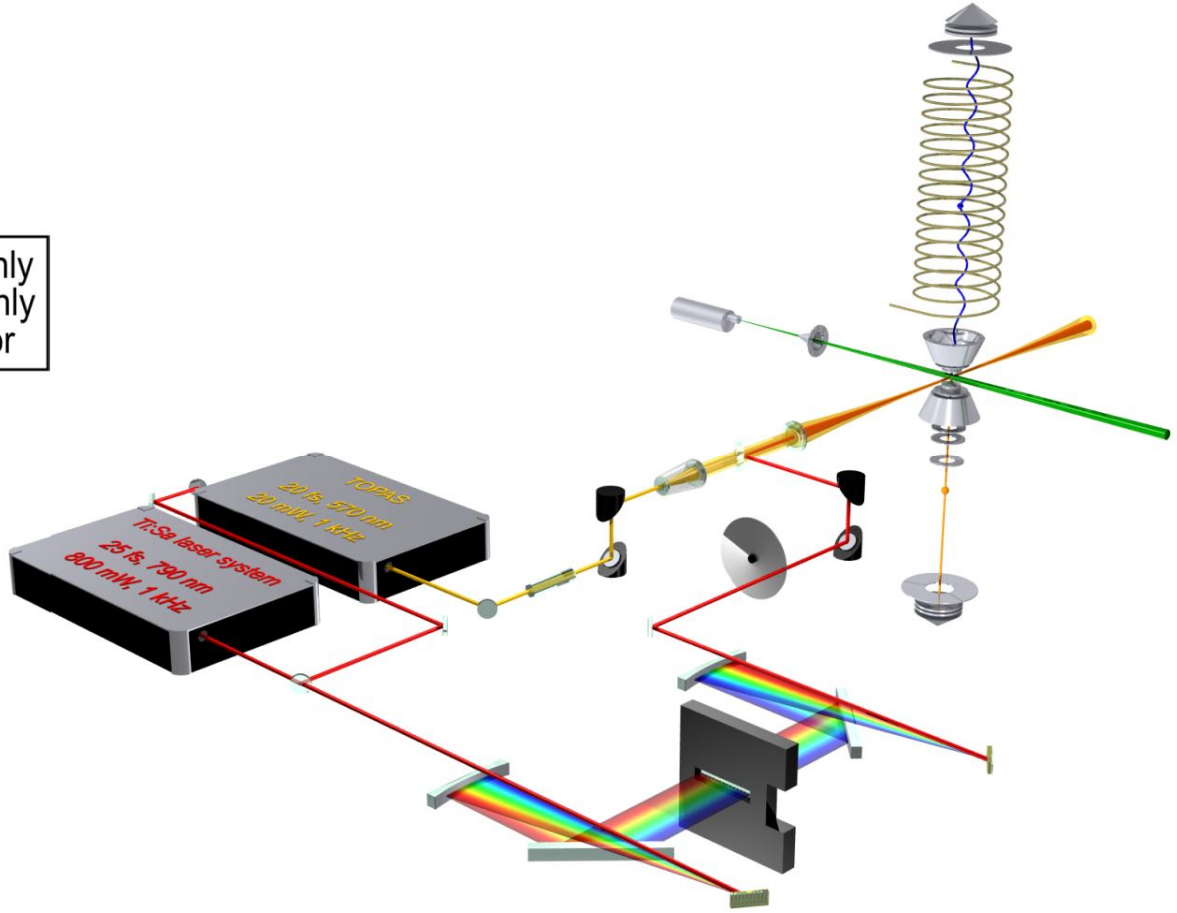
⇨ **Adapt the temporal phase of** $\vec{E}(t)$

for flexiblity we use sinusoidal spectral phase modulation

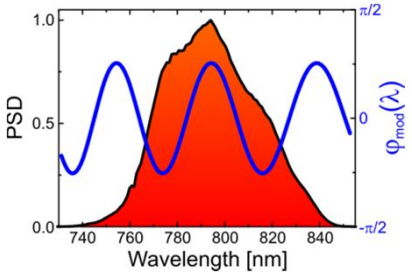
$$\varphi_{\mathrm{mod}}(\omega) = A \cdot \sin(\omega T + \phi)$$

Experimental Two-Colour Setup

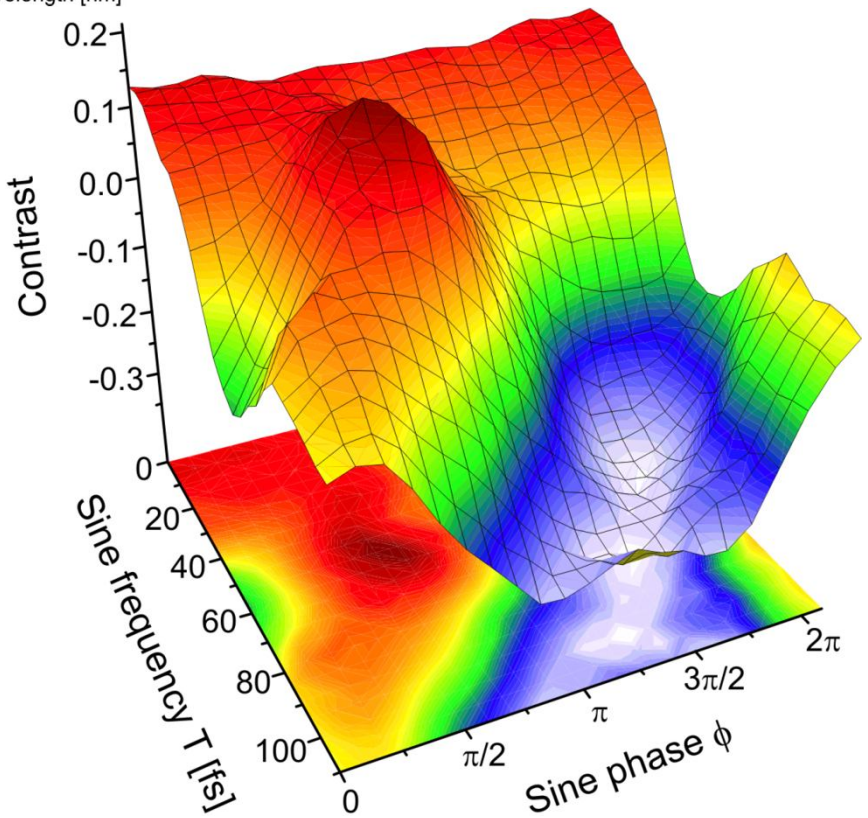




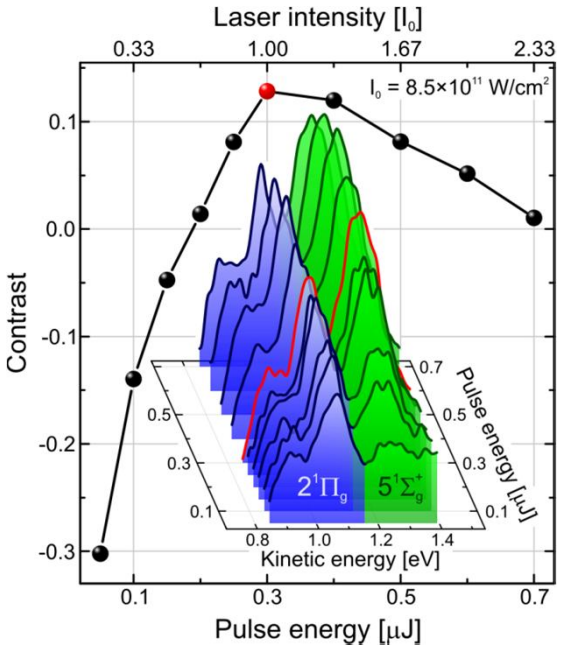
Results



$$\varphi_{\mathrm{mod}}(\omega) = A \cdot \sin(\omega T + \phi)$$



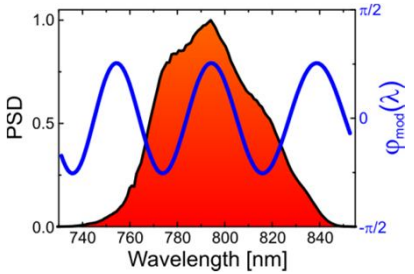
Intensity Scan



Bandwidth-limited Pulse

Strong-Field Effect

A=0.8



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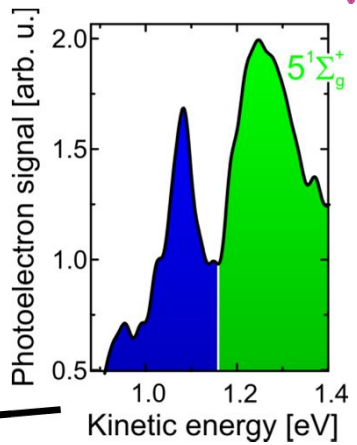
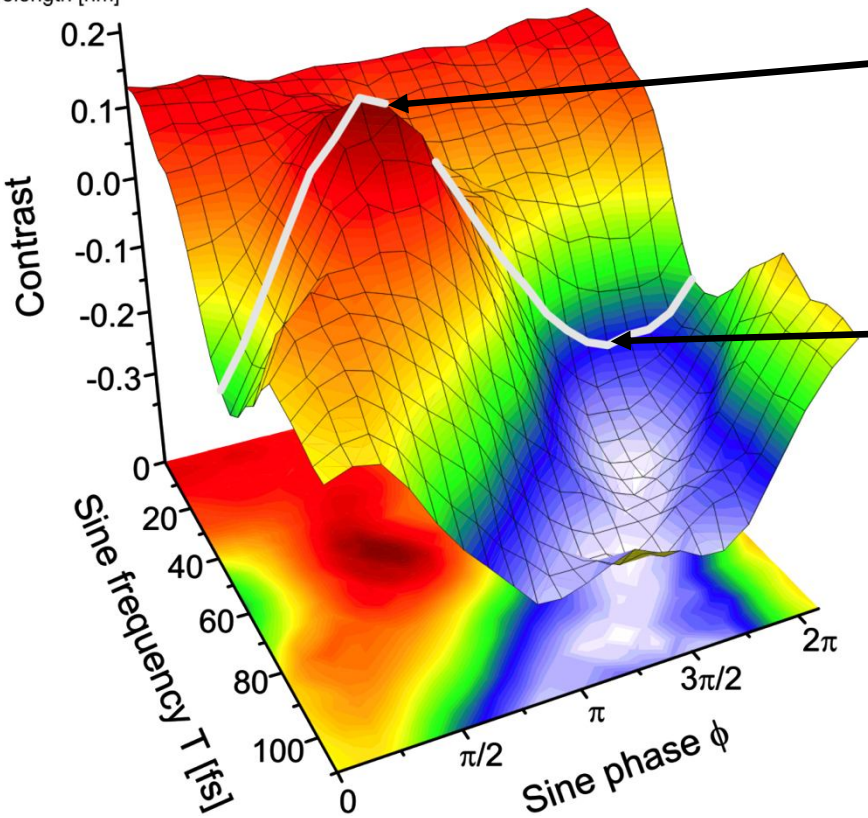
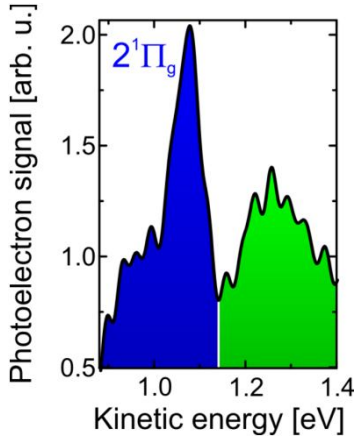
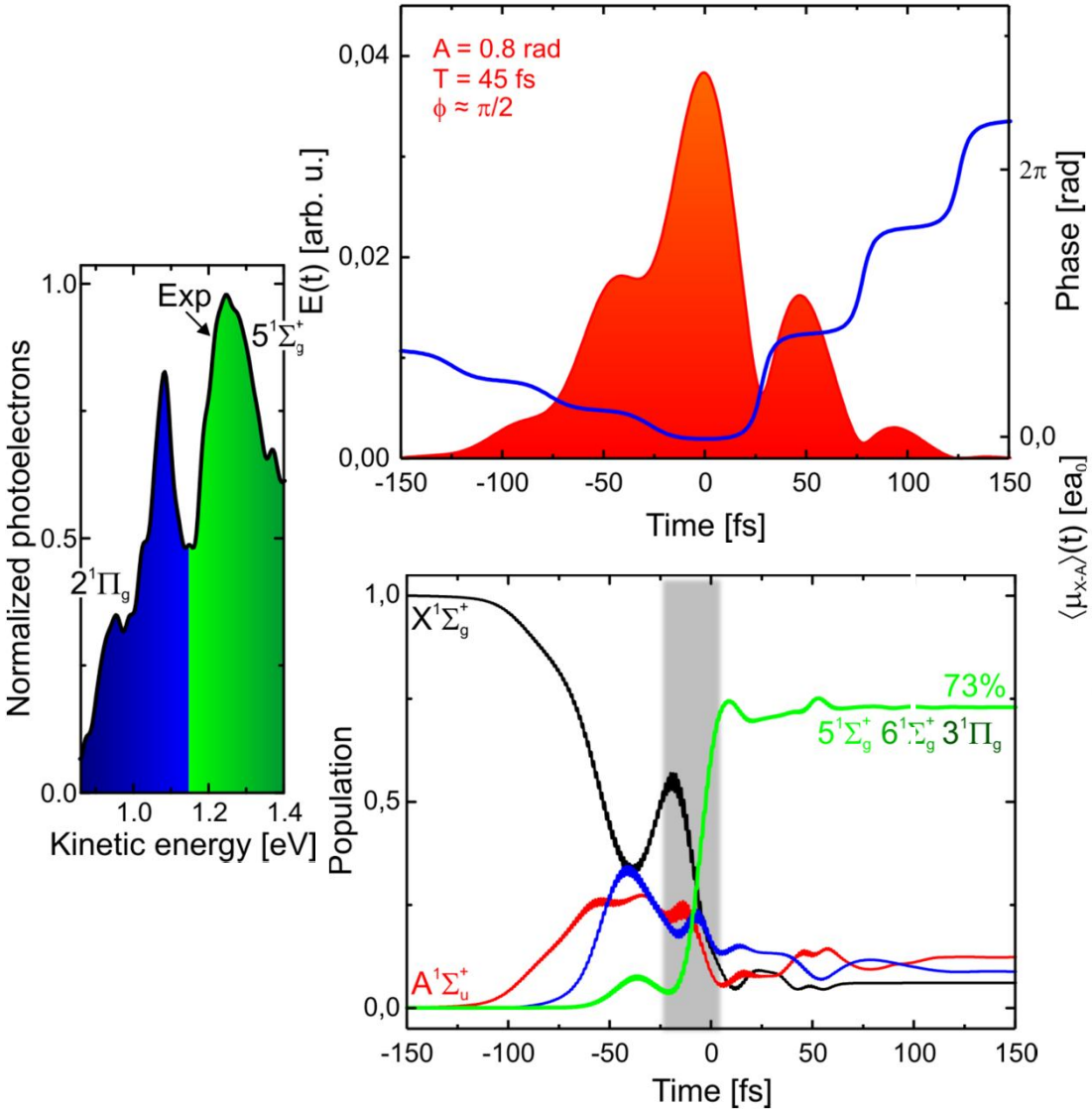


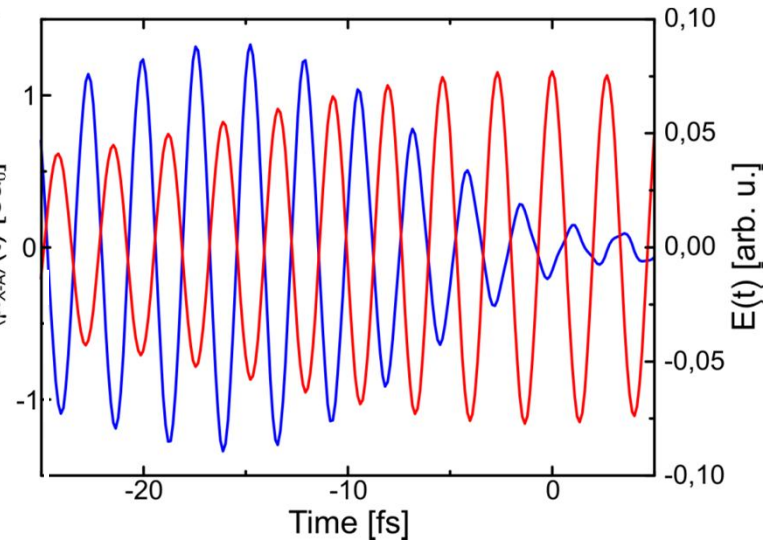


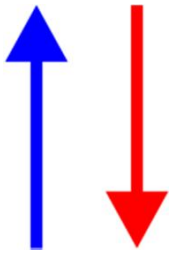


Discussion: Maximum

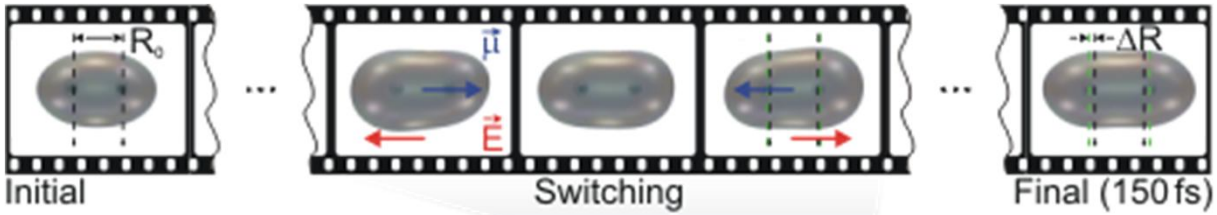


Dipole-Dynamics

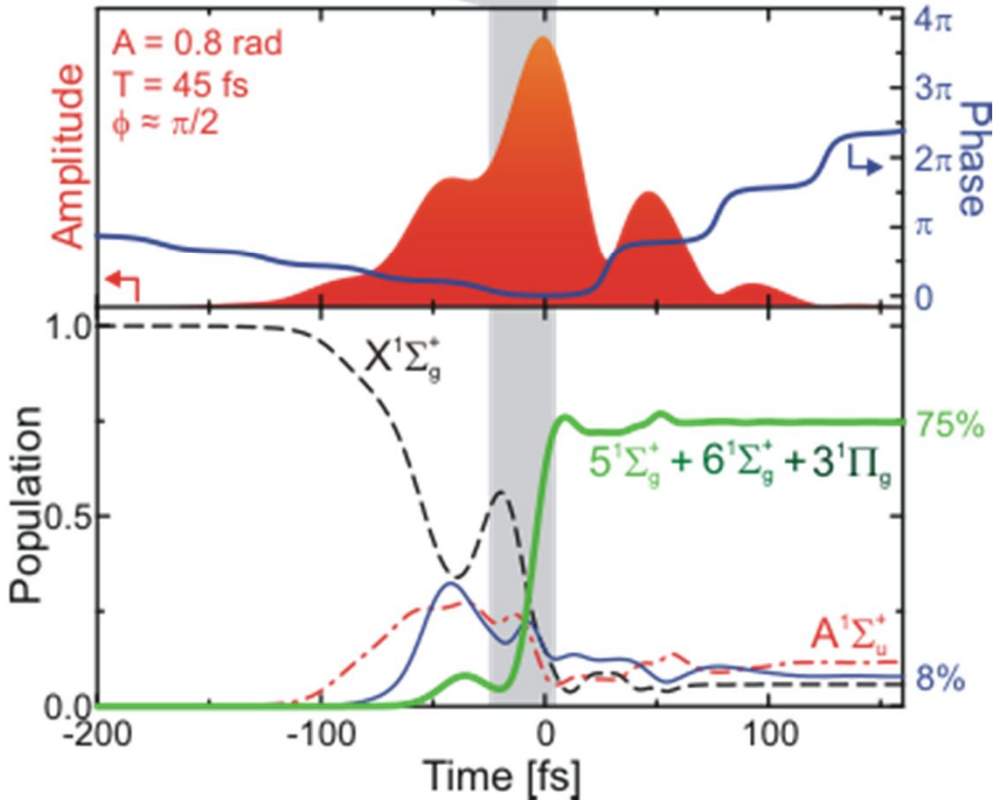




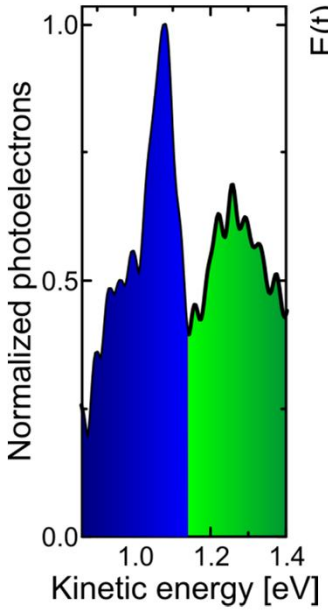
Discussion: Maximum

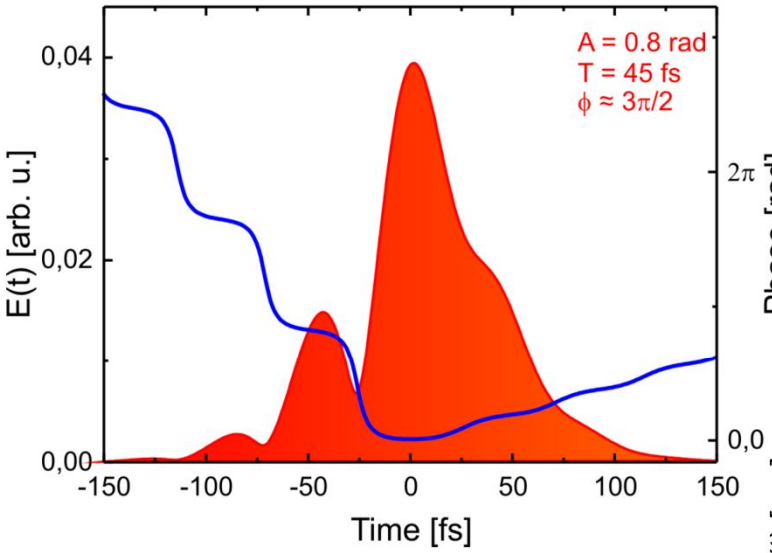


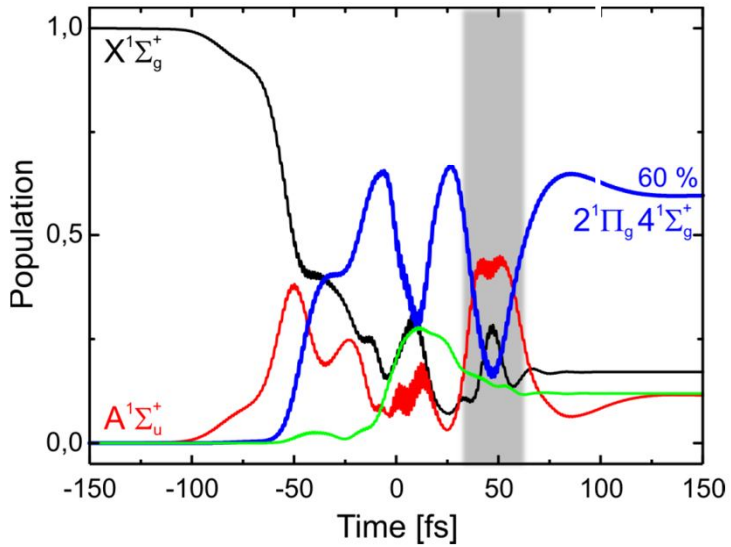
Increase in internuclear seperation during the whole interaction by 10 %



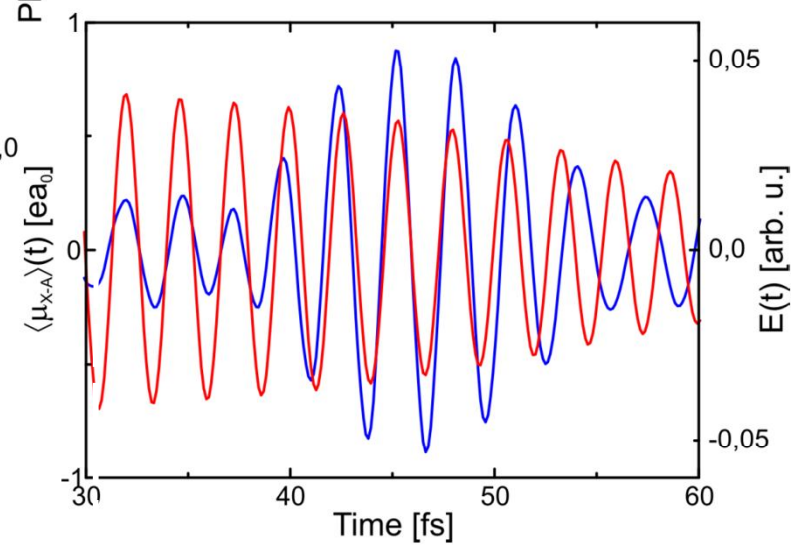
Discussion: Minimum

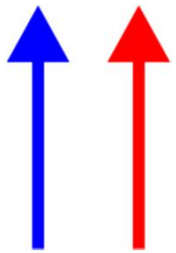




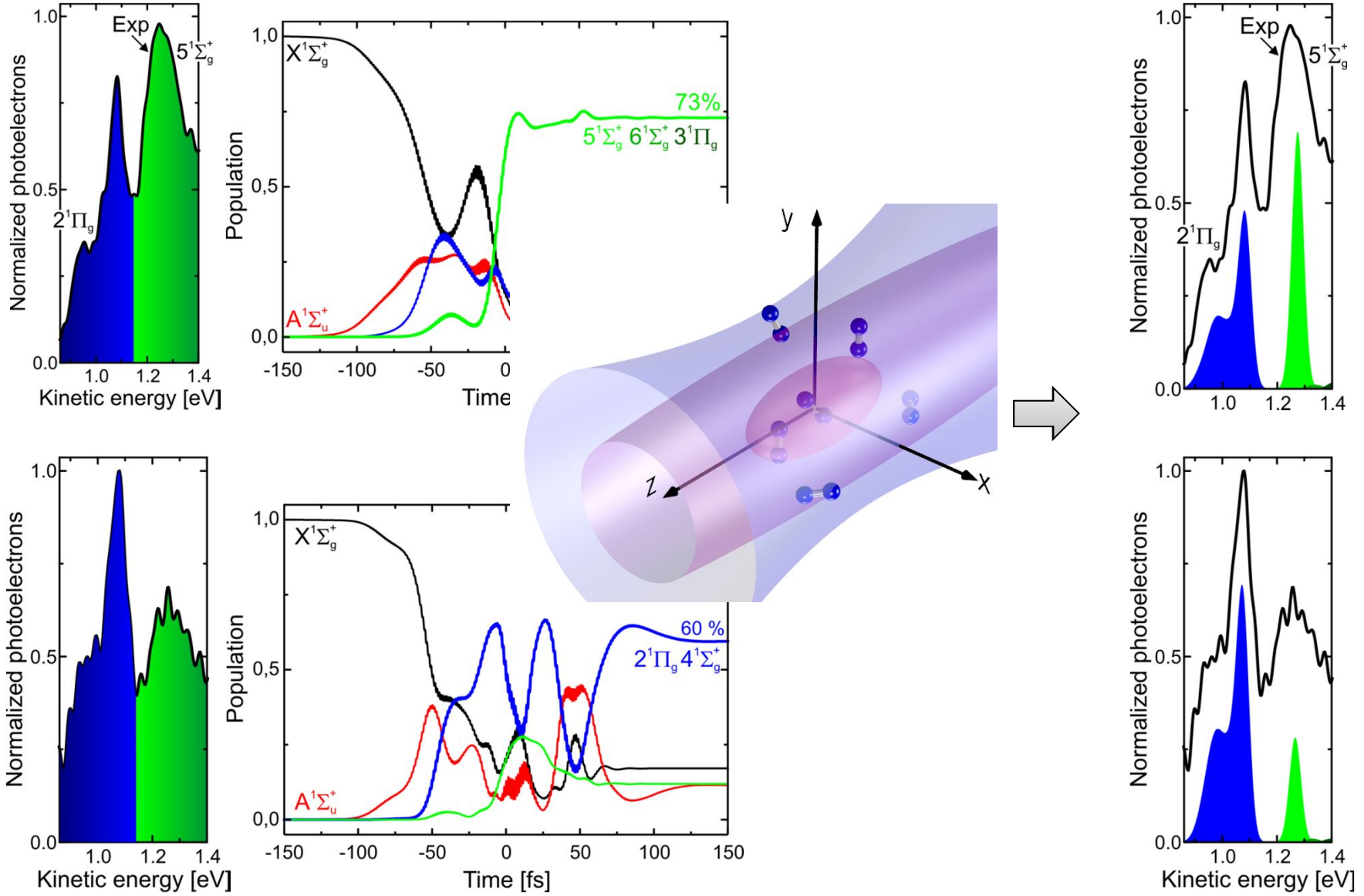


Dipole-Dynamics

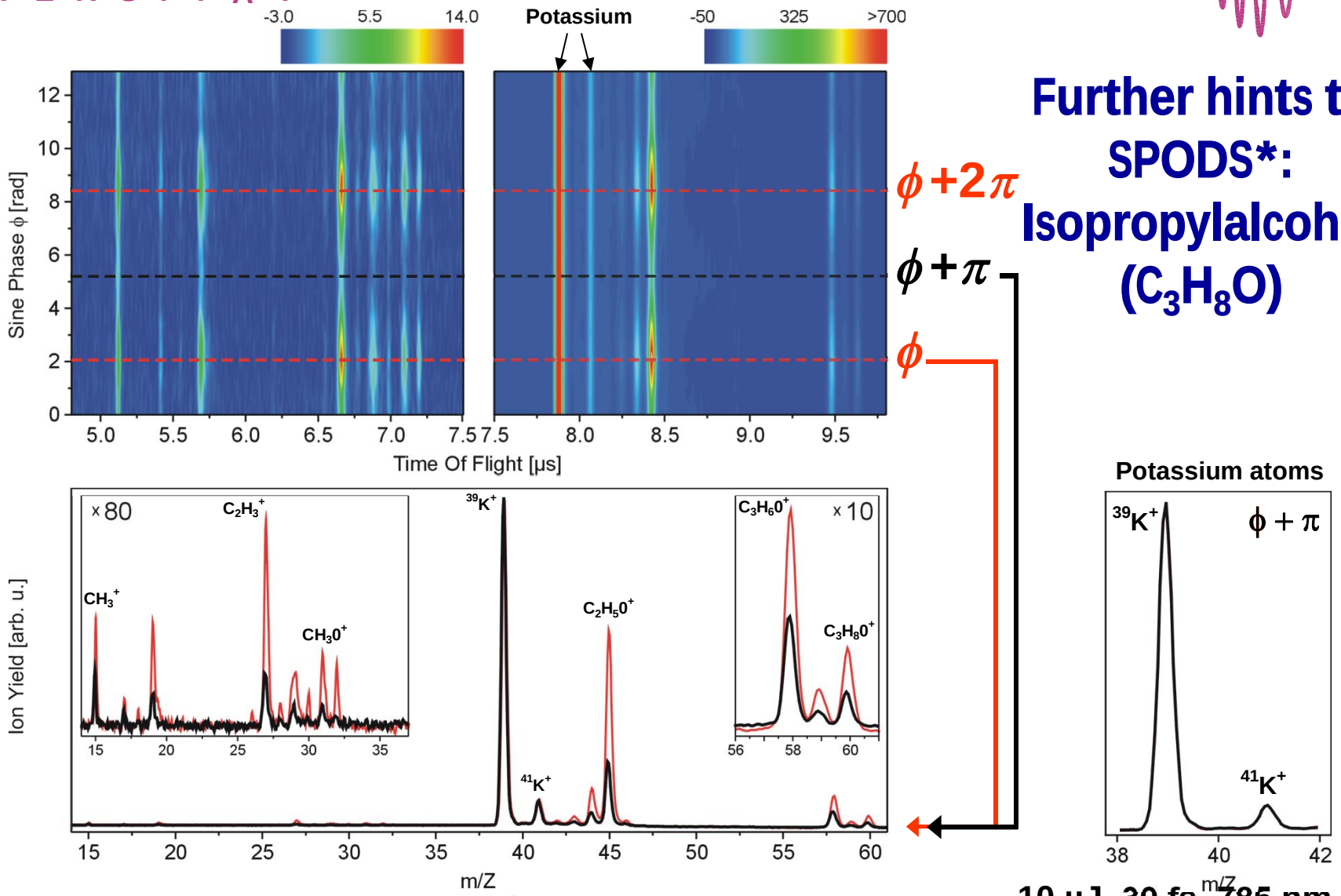




Comparison to Simulation (Intensity and Orientation Averaging)



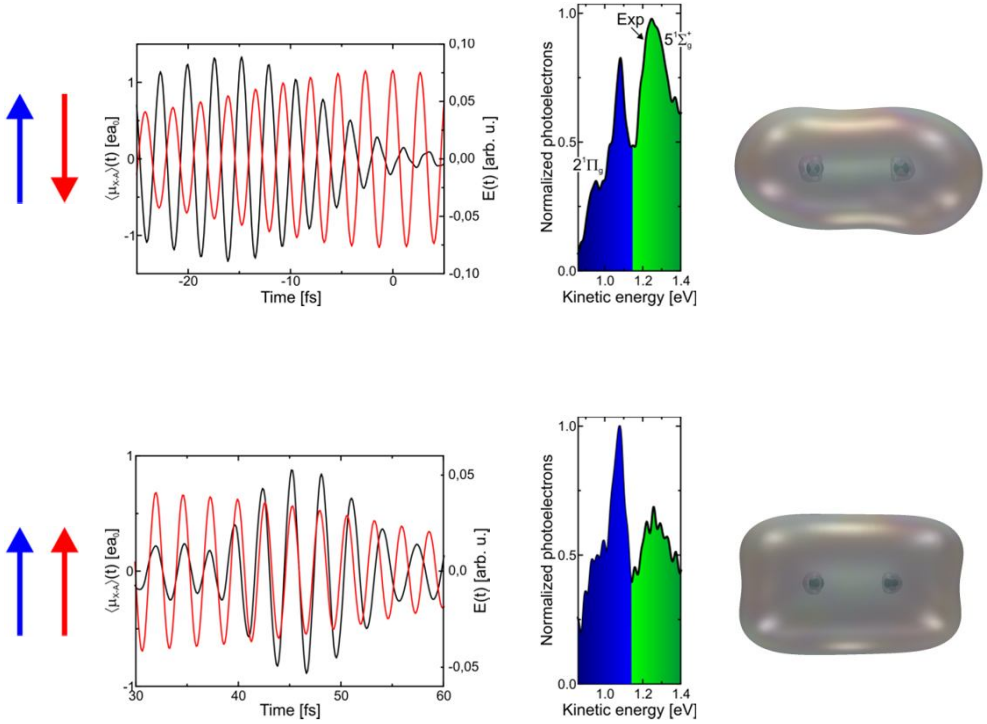
Further hints to SPODS*: Isopropylalcohol (C_3H_8O)



$$\varphi(\omega) = 0.5 \ \sin[50 \text{ fs } (\omega - 2.4 \text{ fs}^{-1}) + \phi]$$

10 μJ, 30 fs, 785 nm

Conclusions



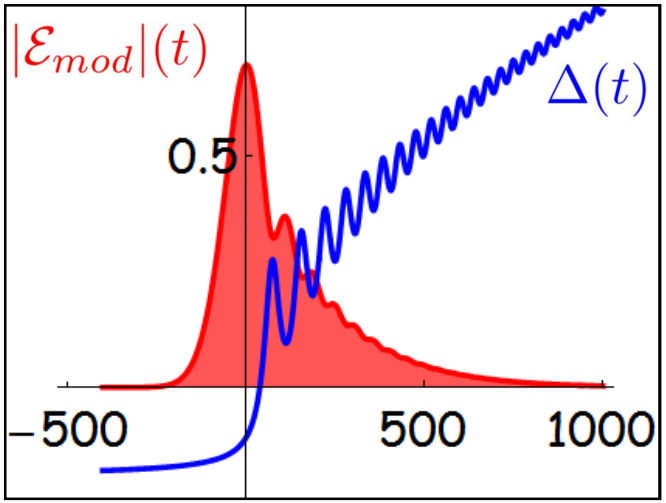
- **Tailoring the phase of the driving laser field to the oscillating dipole is the key to resonant strong field control.**
- **Femtosecond laserpulses with precisely shaped temporal phase can efficiently control the coupled electron and nuclear dynamics in molecules.**
- **This allows to steer the system into a preselected electronic target channel.**

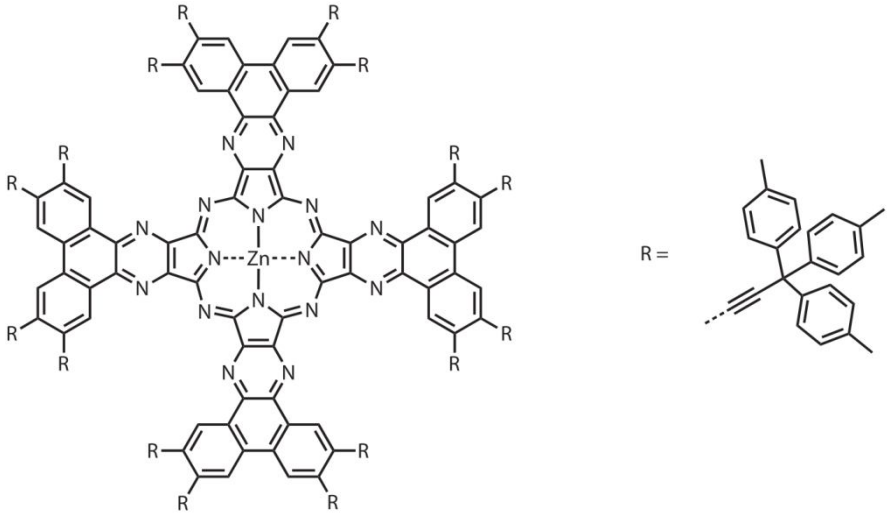
SPODS on K2 as benchmark for theory:

OCT: R. de Vivie-Riedle et al Faraday Disc. 153 (2011) 159

FISH: R. Mitric et al. PCCP 14 (2012) 8299

Strong Field Control on Molecules in the Liquid Phase





Joint Wave Packet Motion

and Adiabatic Population Transfer

Reminder 1: Chirped Rapid Adiabatic Passage (RAP)

See: Bruce Shore

COHERENT MANIPULATIONS OF ATOMS USING LASER LIGHT

acta physica slovaca 58 (2008) 243 –486

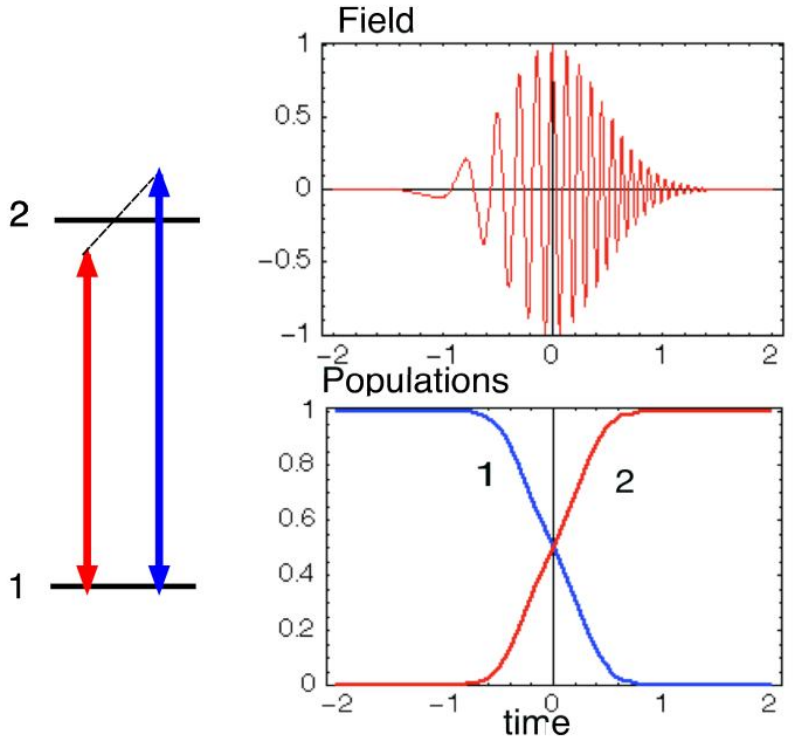


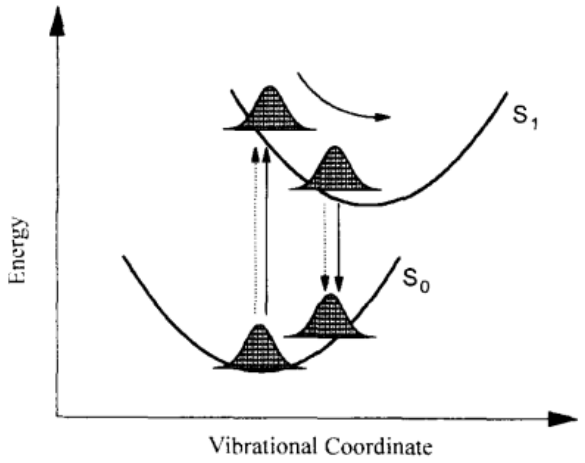
Fig. 17. Example of chirped rapid adiabatic passage. Above: the electric field. Below: the population histories. As the detuning sweeps through resonance, here at time $t = 0$, population transfer occurs from initial state 1 to final state 2.

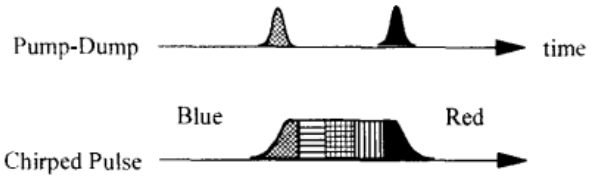
Coherent Strong Field Control of Multiple States in Na by a Single Chirped Femtosecond Laser Pulse
New Journal of Physics **11** (2009) 105051 (in coop. with N. Vitanov)

Reminder 2: Strong Field Control on Molecules in the Liquid Phase with Chirped Pulses

High-power femtosecond chirped pulse excitation of molecules in solution

G. Cerullo [a,1,b], C.J. Bardeen [a,2,b], Q. Wang [a,3,b], C.V. Shank [a,b]





Chemical Physics Letters 262 (1996) 362–368

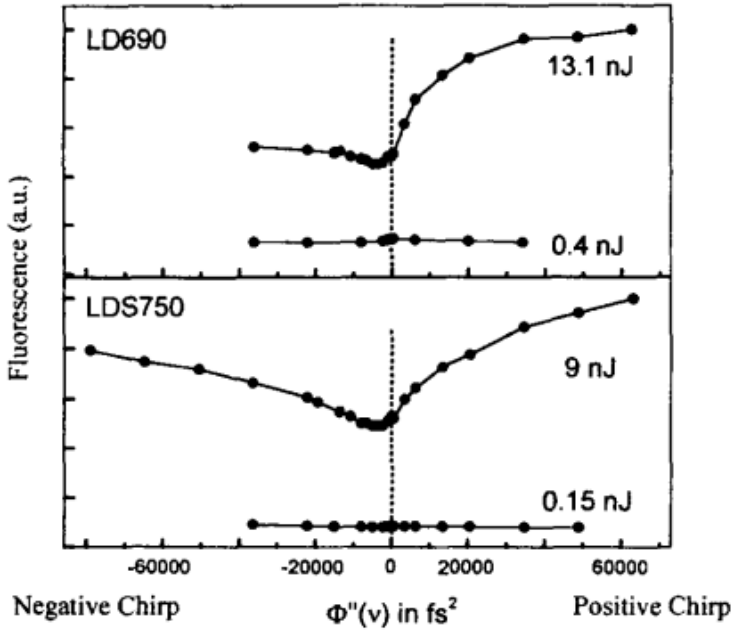


Fig. 2. Fluorescence yields for the laser dyes LD690 in methanol and LDS750 in acetonitrile, as a function of pulse chirp, for low- and high-power excitation.

Control by frequency ordering*

(in Gas Phase Na_2: CPL 259 (1996) 488)

*Ruhman and Kosloff JOSA B **7** (1990) 1748

Reminder 3: Theoretical Suggestions

VOLUME 80, NUMBER 7 PHYSICAL REVIEW LETTERS 16 FEBRUARY 1998

Molecular "π Pulse" for Total Inversion of Electronic State Population

Jianshu Cao, Christopher J. Bardeen, and Kent R. Wilson

take intense positively chirped broadband laser pulses and make use of vibrational coherence together with adiabatic inversion

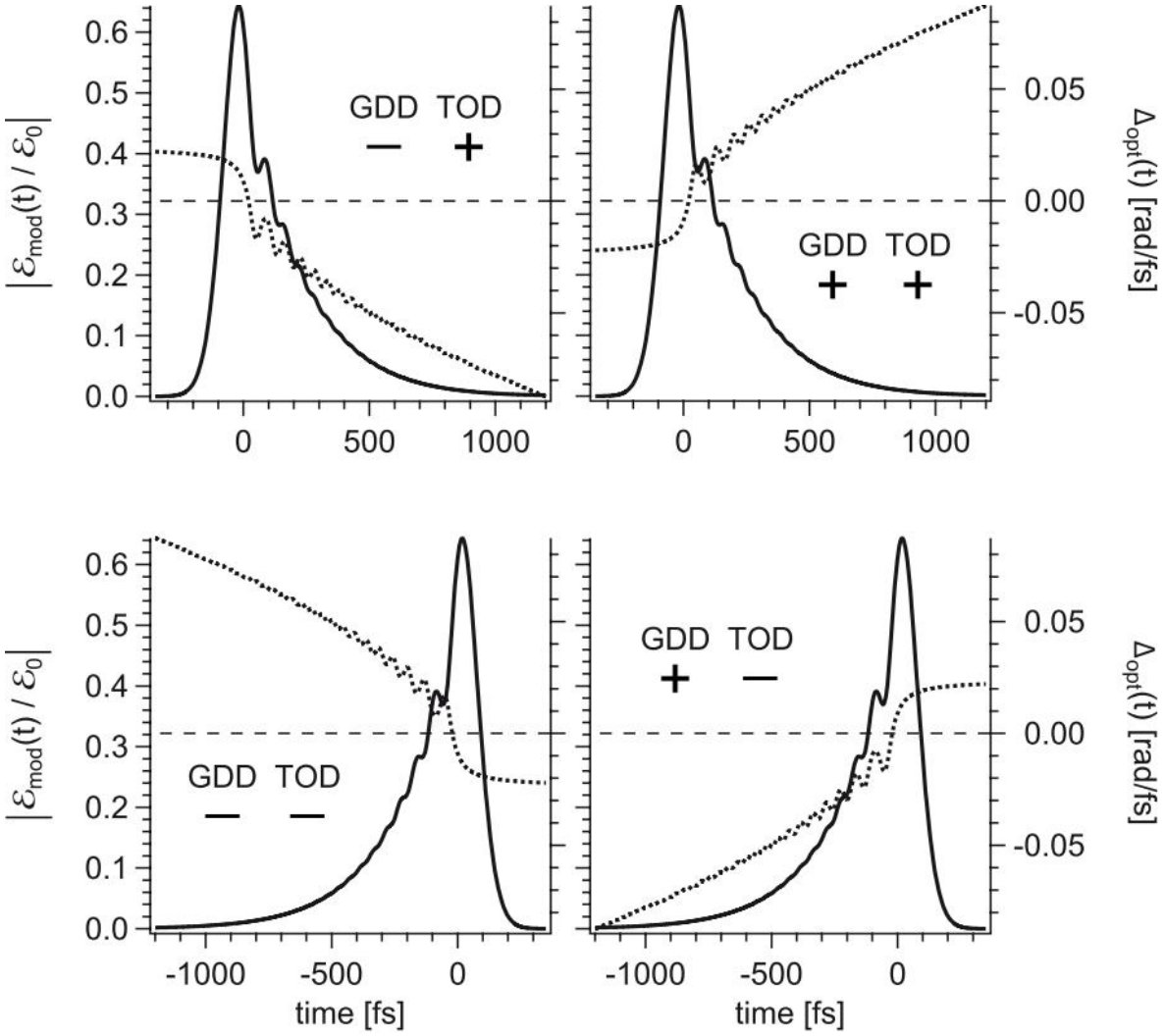
12 February 2001 / Vol. 8, No. 2 / OPTICS EXPRESS 238

Coherent Mechanism of Robust Population Inversion

J. Vala, and R. Kosloff

a phase angle between –pi and 0 of induced instantaneous phase of the transition dipole guarantees a monotonic and robust population transfer

Our Pulse Design : Combined GDD and TOD



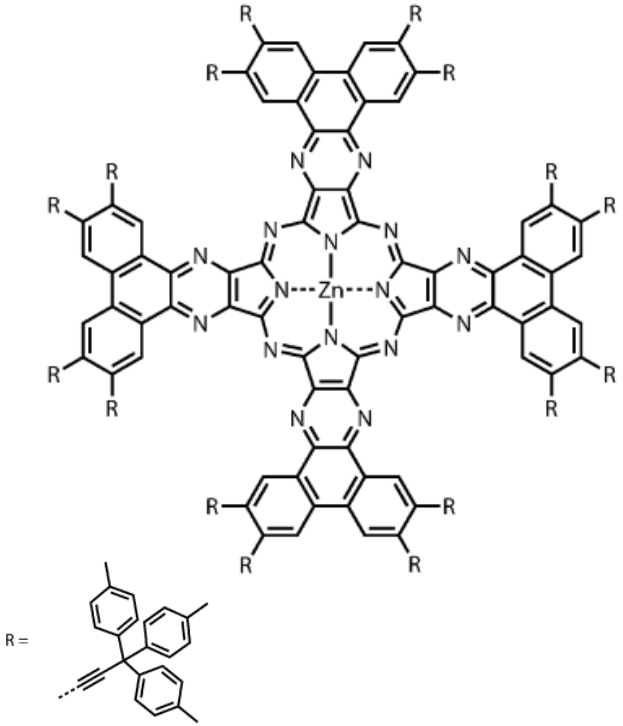
$$\tilde{M}(\omega) = e^{-i\left(\frac{1}{2}\phi_2\omega^2 + \frac{1}{6}\phi_3\omega^3\right)}$$

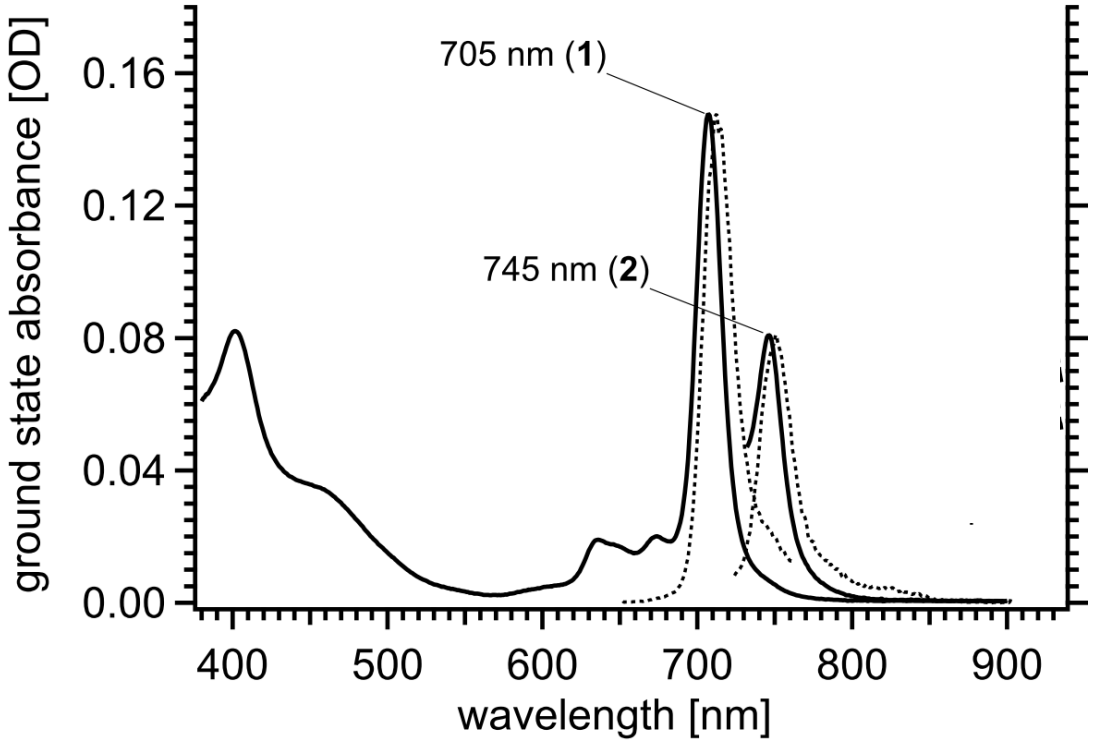
GDD (ϕ_2) controls frequency sweeps

TOD (ϕ_3) controls intensity asymmetries

GDD = +/- 5 kfs^2
TOD = +/- 200 kfs^3
Bwl: 60 fs @ 800 nm

Our Molecules: Sensitizer Dyes in the Liquid Phase



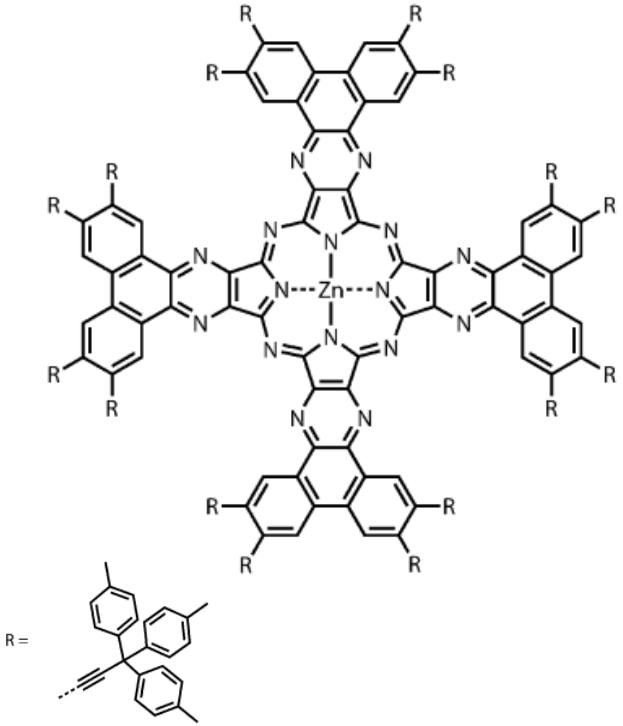


Porphyrazine dissolved in Chloroform

quinoxalinodibenzo[*f*,*h*]porphyrazines.

(2) is a monoprotonated analog of (1)

Our Molecules: Sensitizer Dyes in the Liquid Phase



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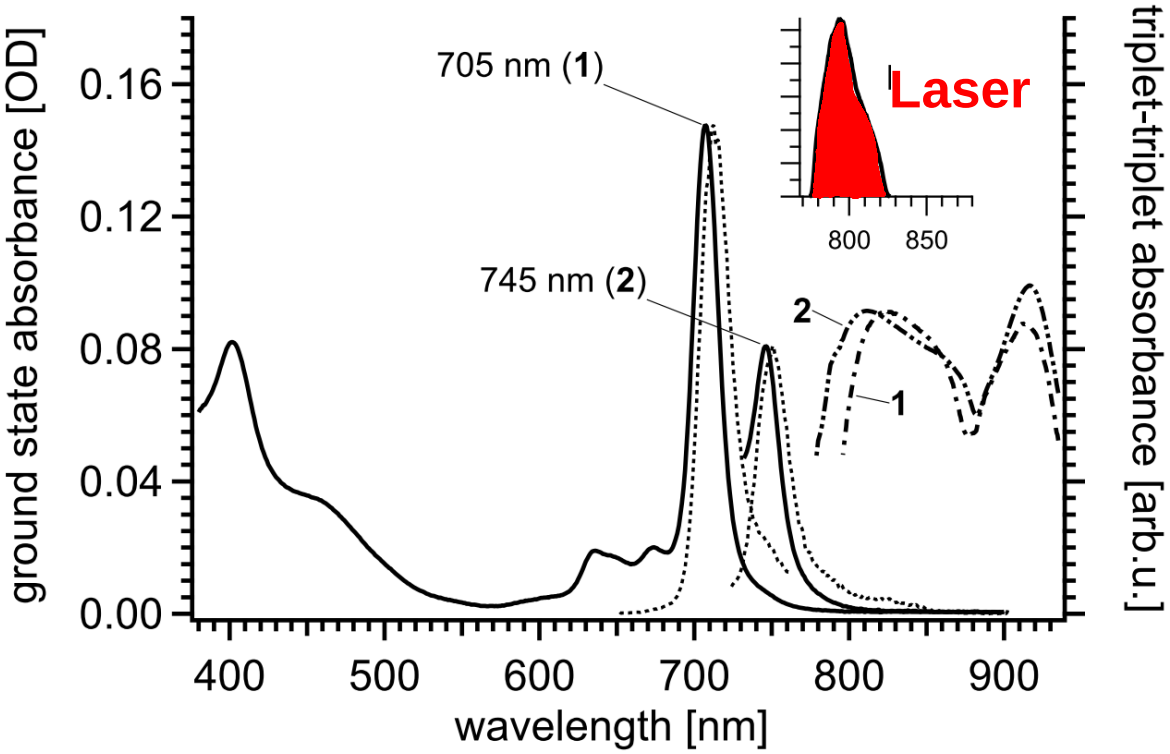
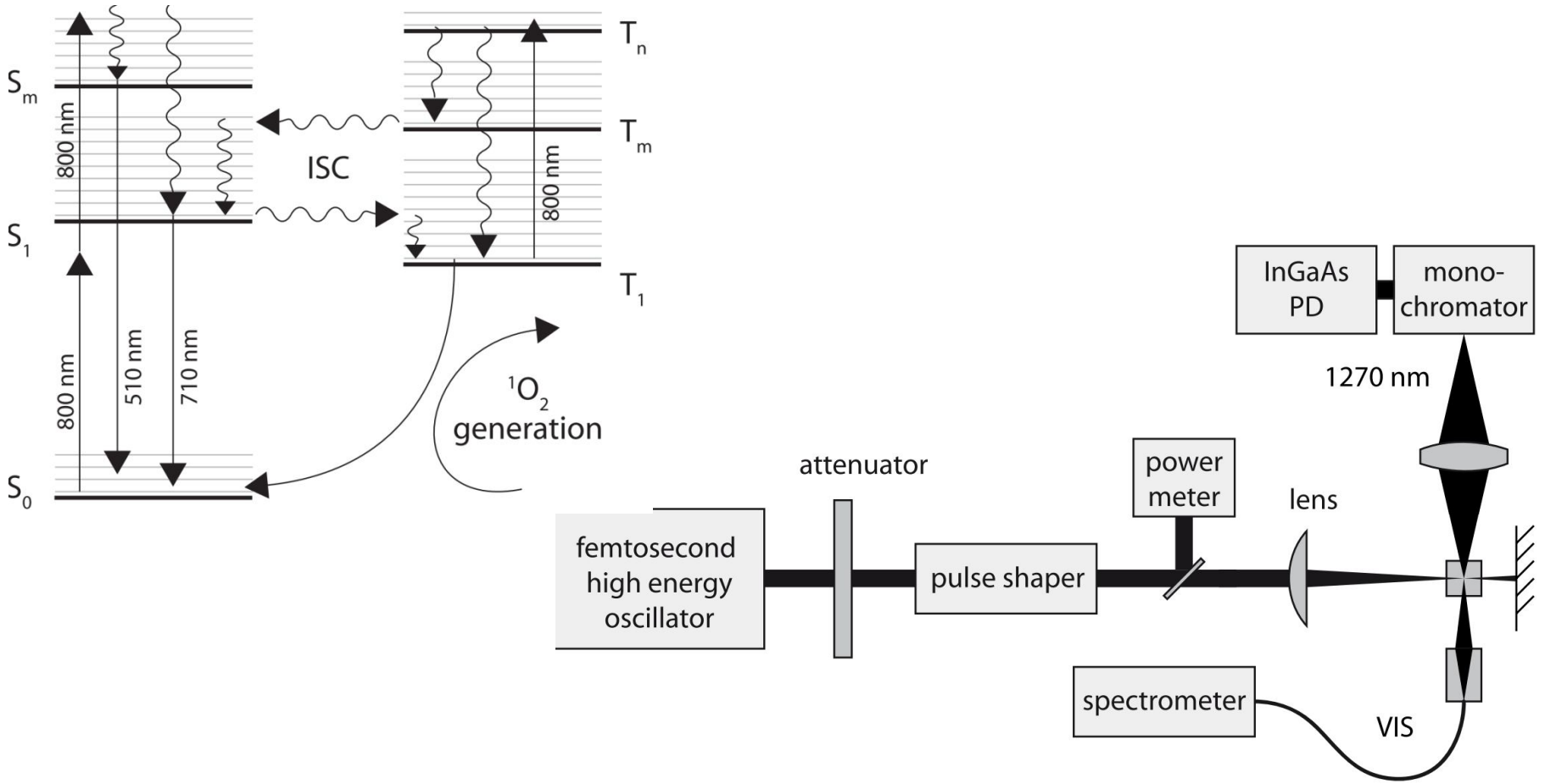


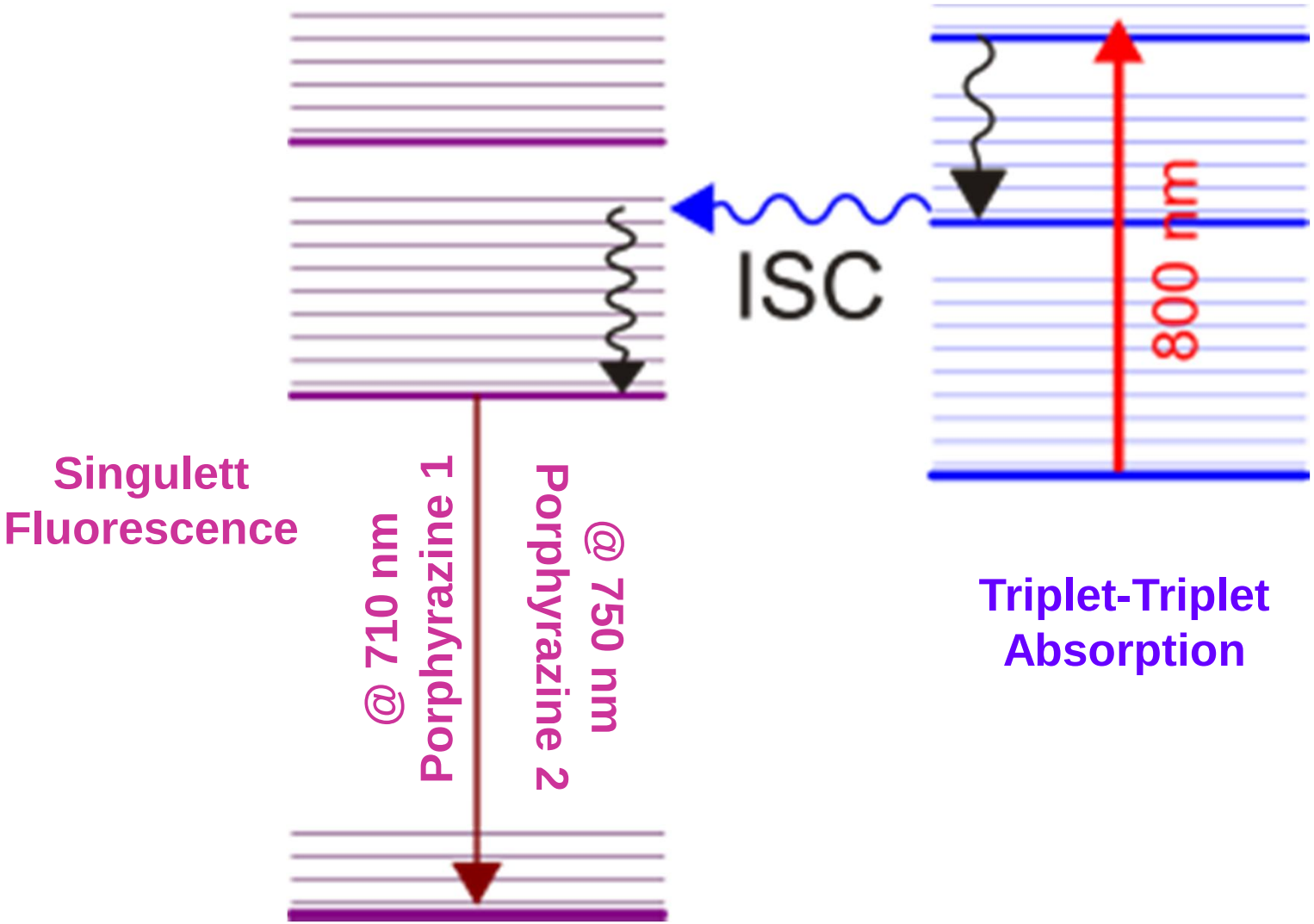
Triplet-Triplet Absorption

Excitation Scheme and Set-up

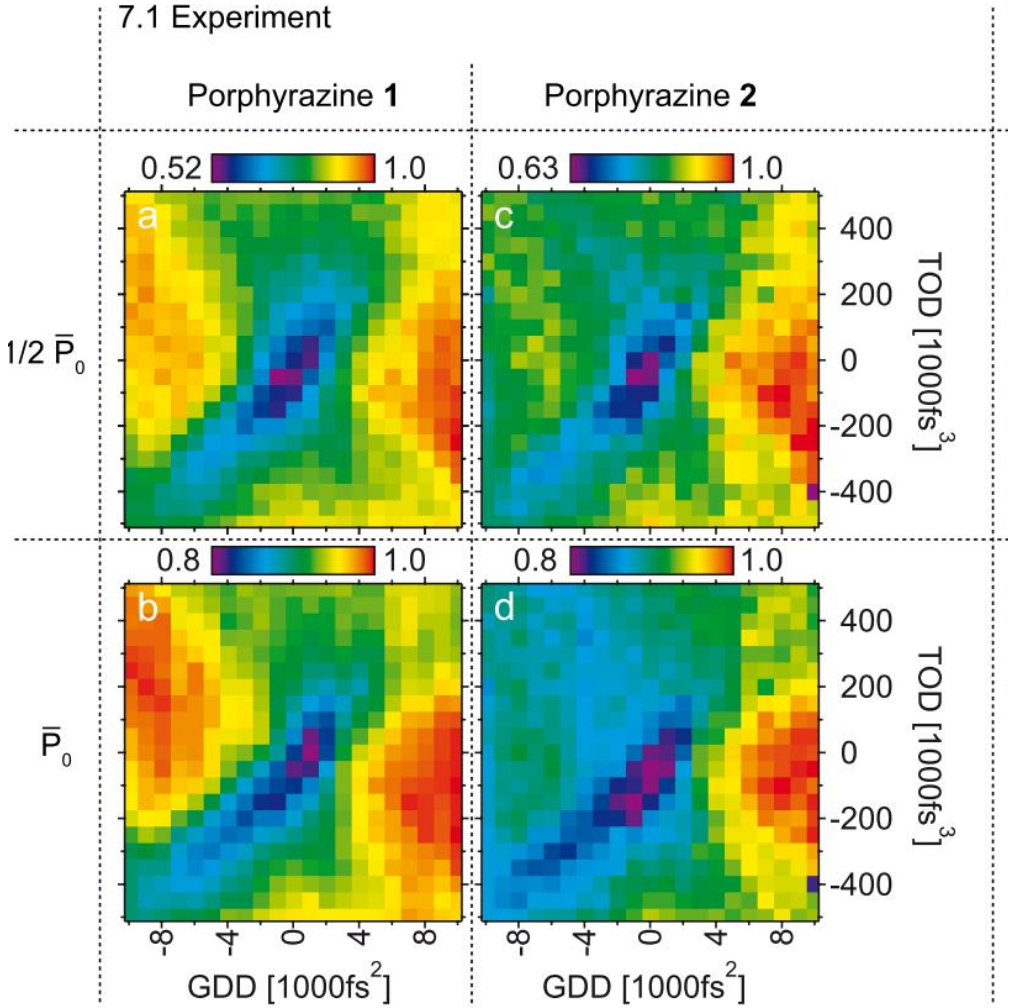


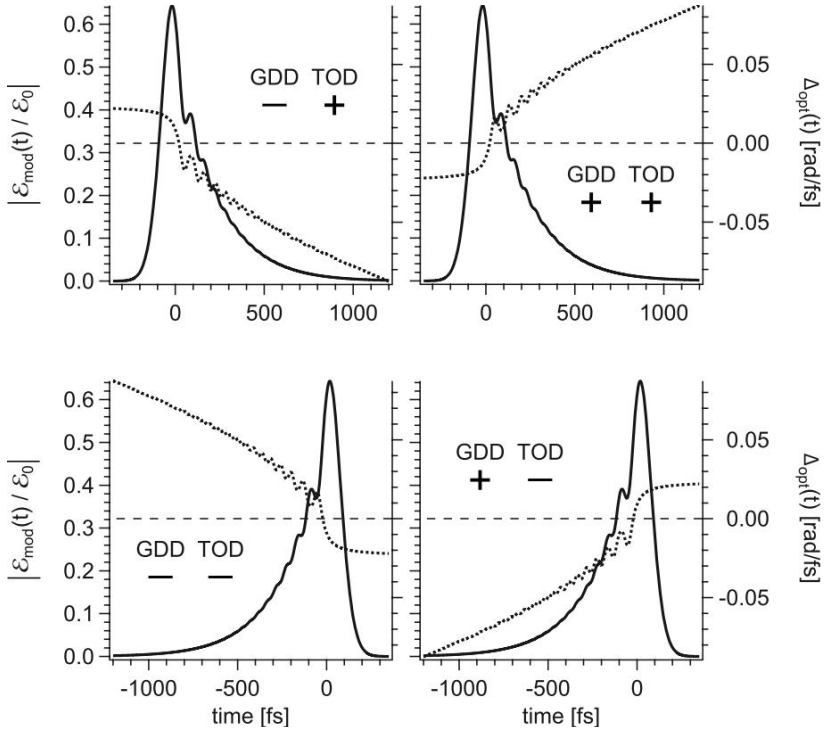
in Experiment: λ=800nm Δt=60fs 11 MHz P=60mW I_{max}=60GW/cm²
(biological damage threshold 200GW/cm²)

Quantum Control Landscapes



Quantum Control Landscapes



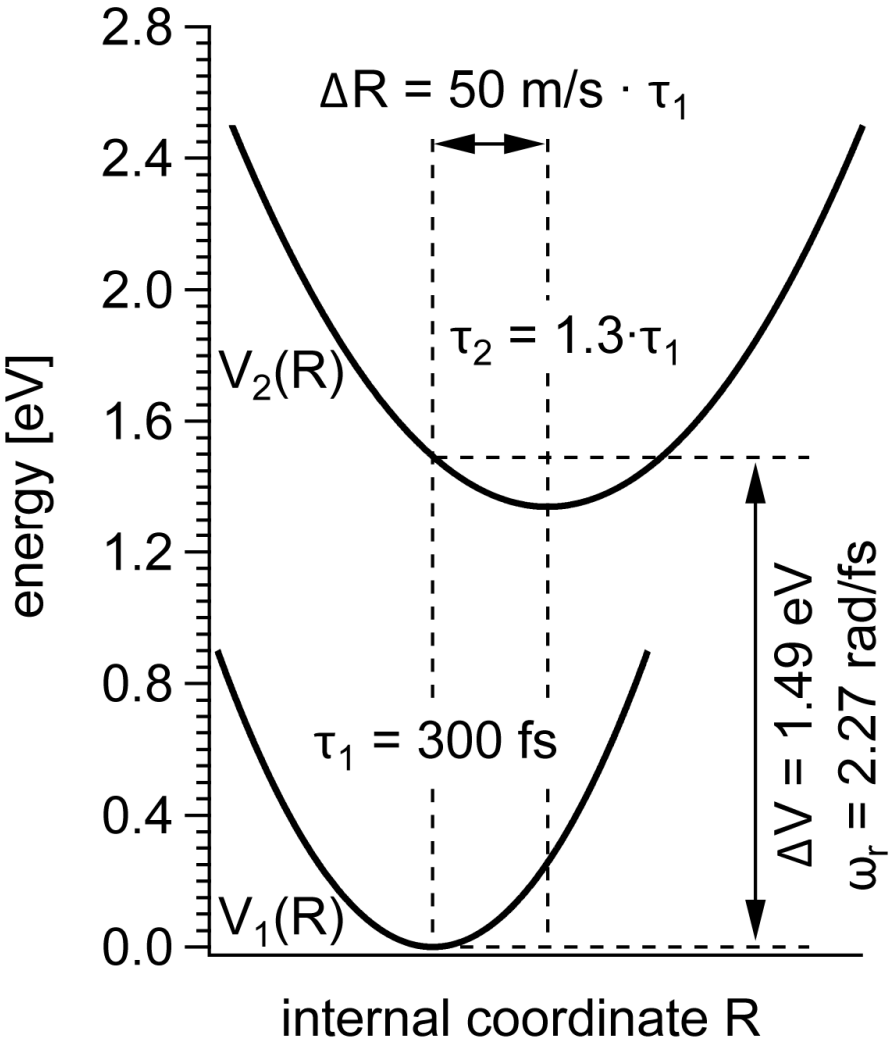


- **Large areas of maximum and minimum population transfer**
- **Comparison of porphyrazine 1 and 2: effect of detuning**

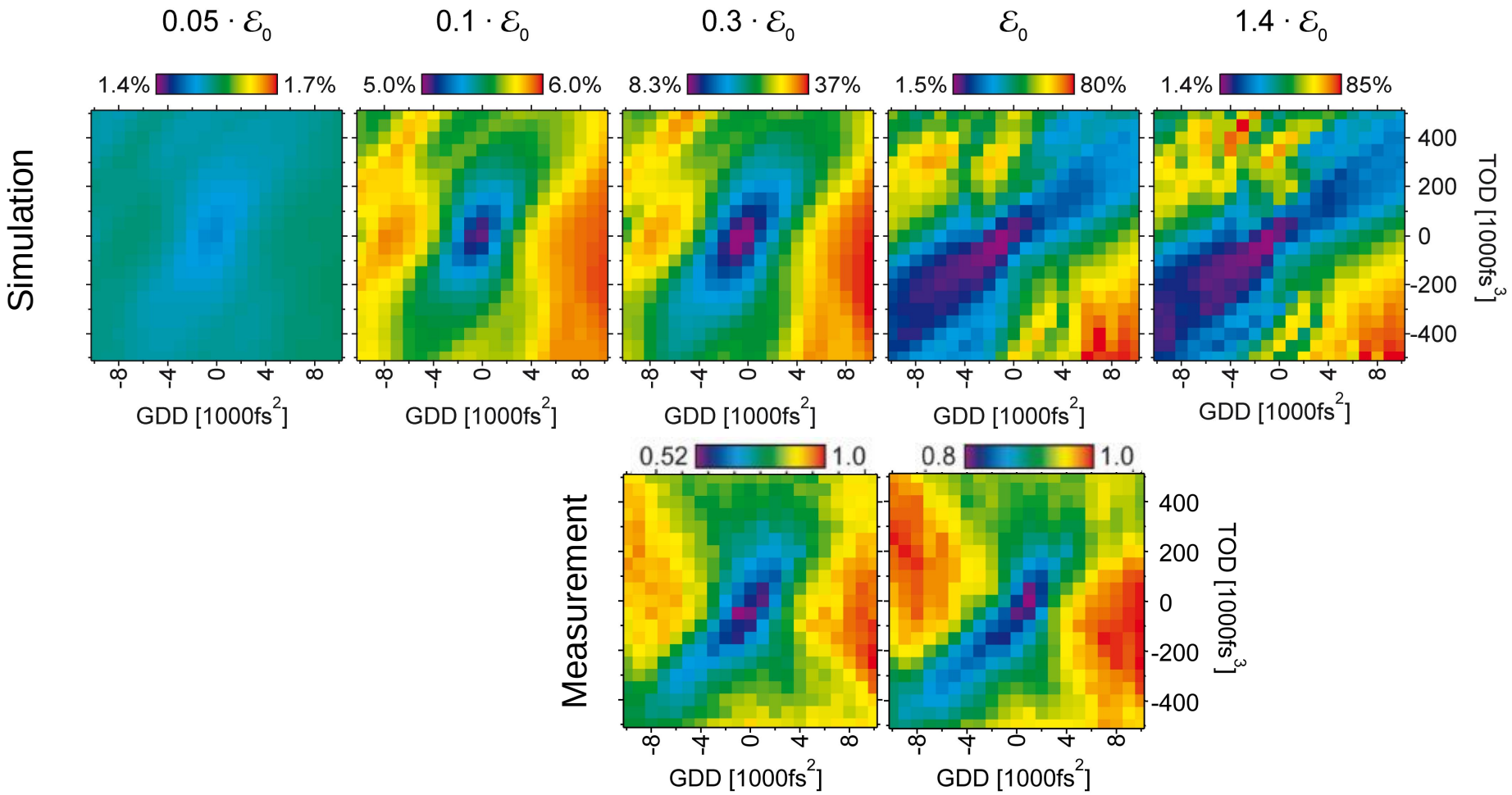
@ 710 nm **@ 750 nm**

PCCP **13** (2011) 8733

A Simple Harmonic Oscillator Model

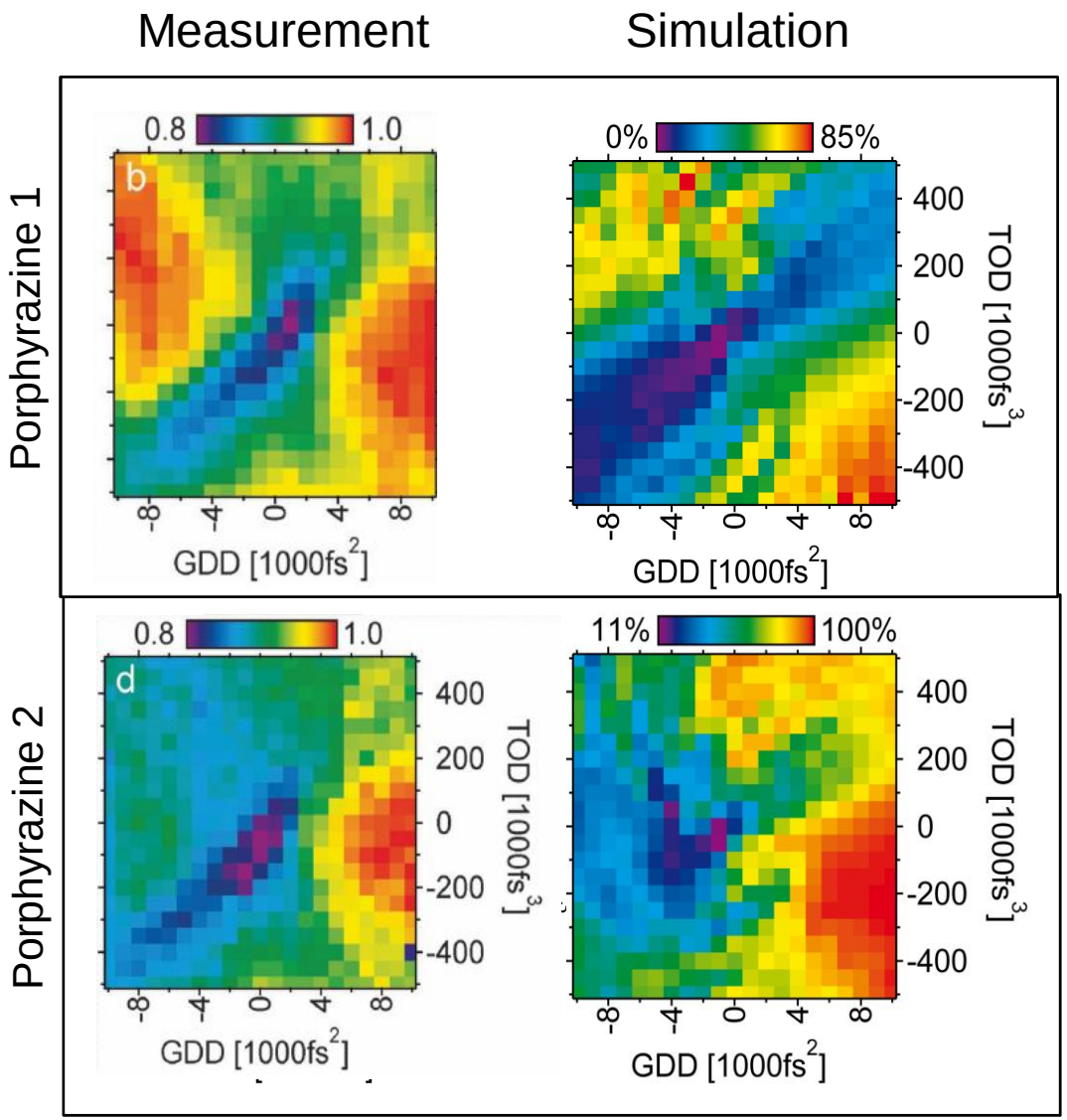


Intensity Dependence (Porphyrazine 1)

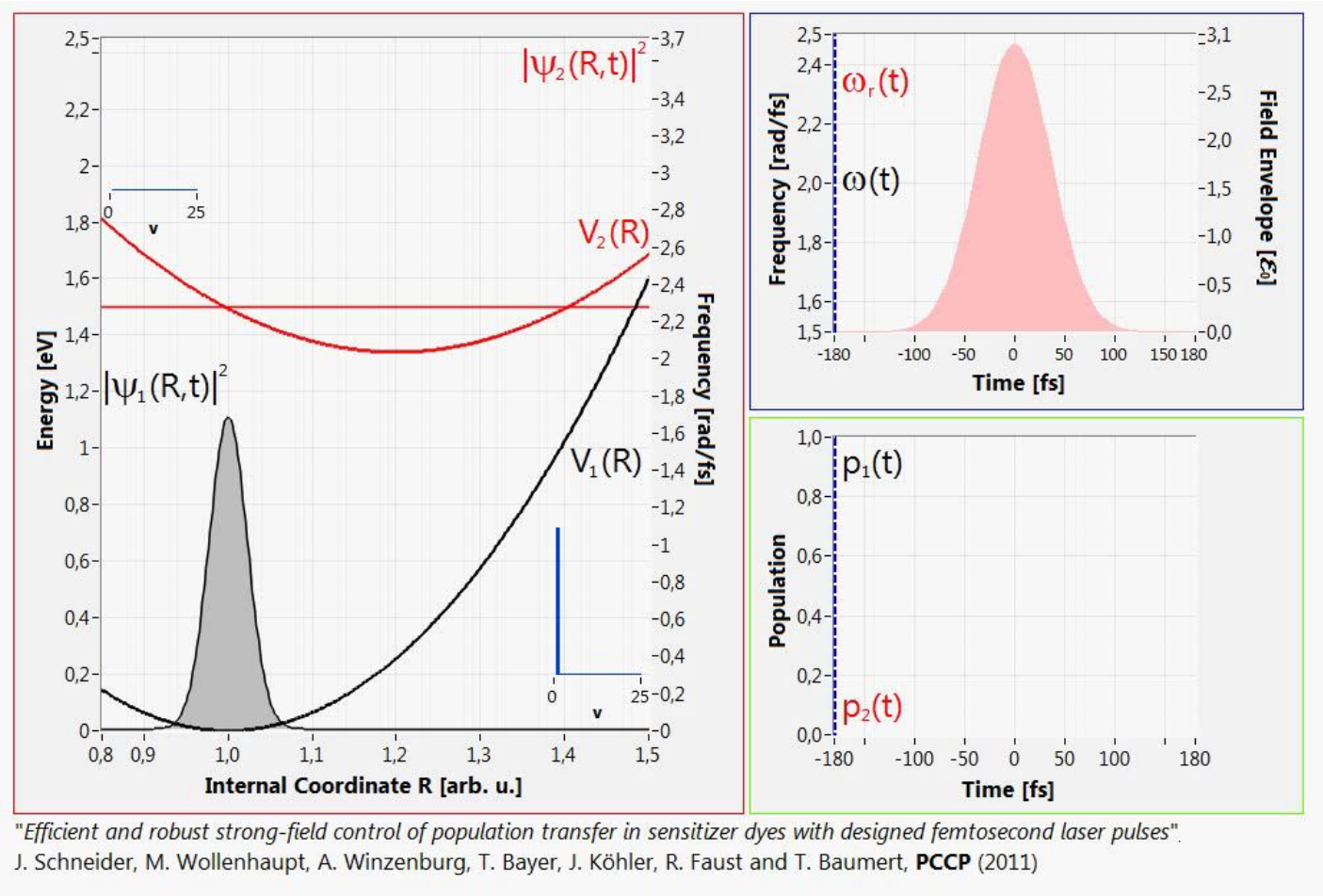


- **Transition from weak to strong field**
- **Robustness and efficient population transfer in several 10% regime**

Detuning Dependence



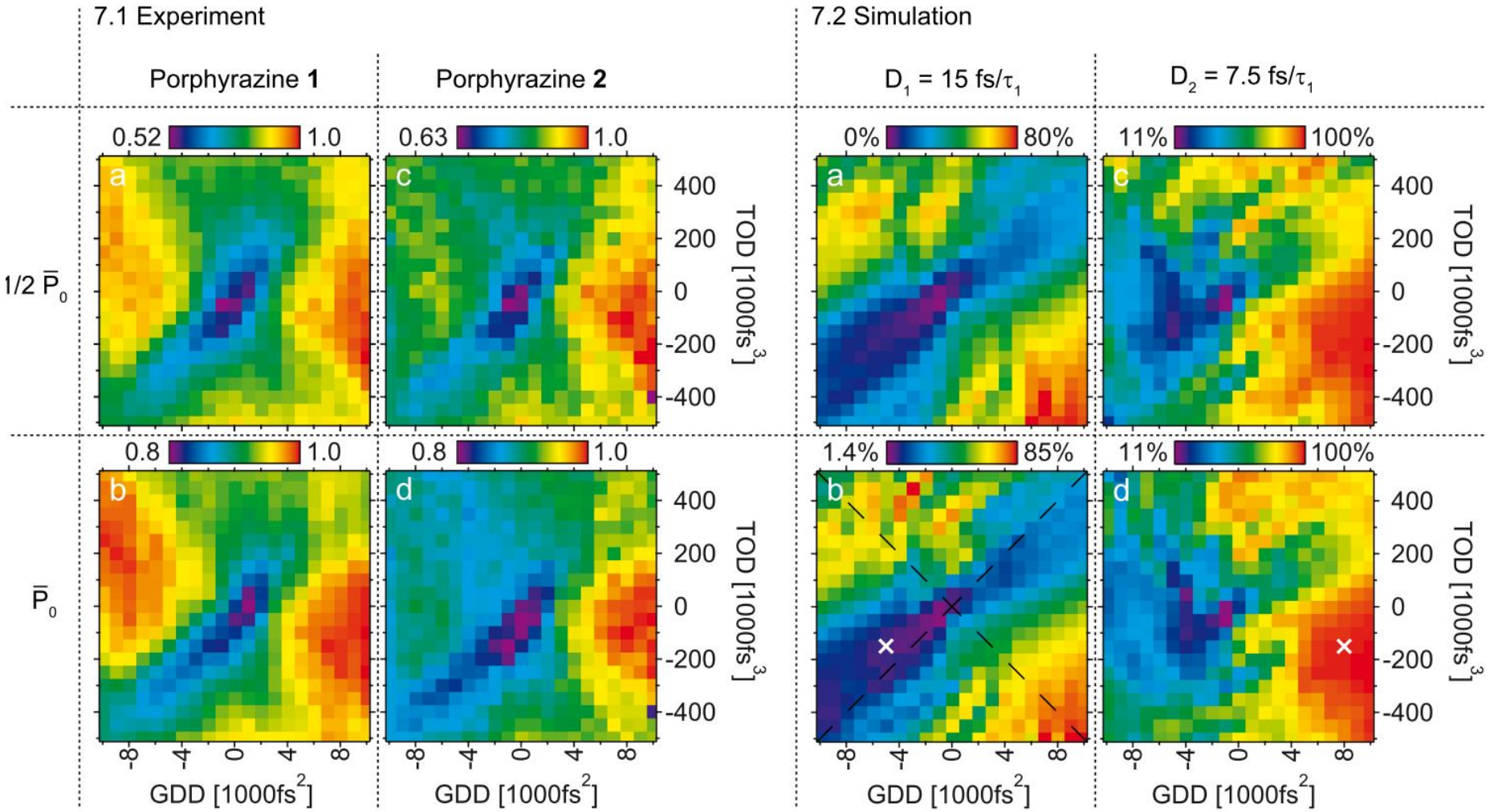
A Key Mechanism in Strong Field Control: Joint Wave Packet Motion (JOMO) and Adiabatic Population Transfer



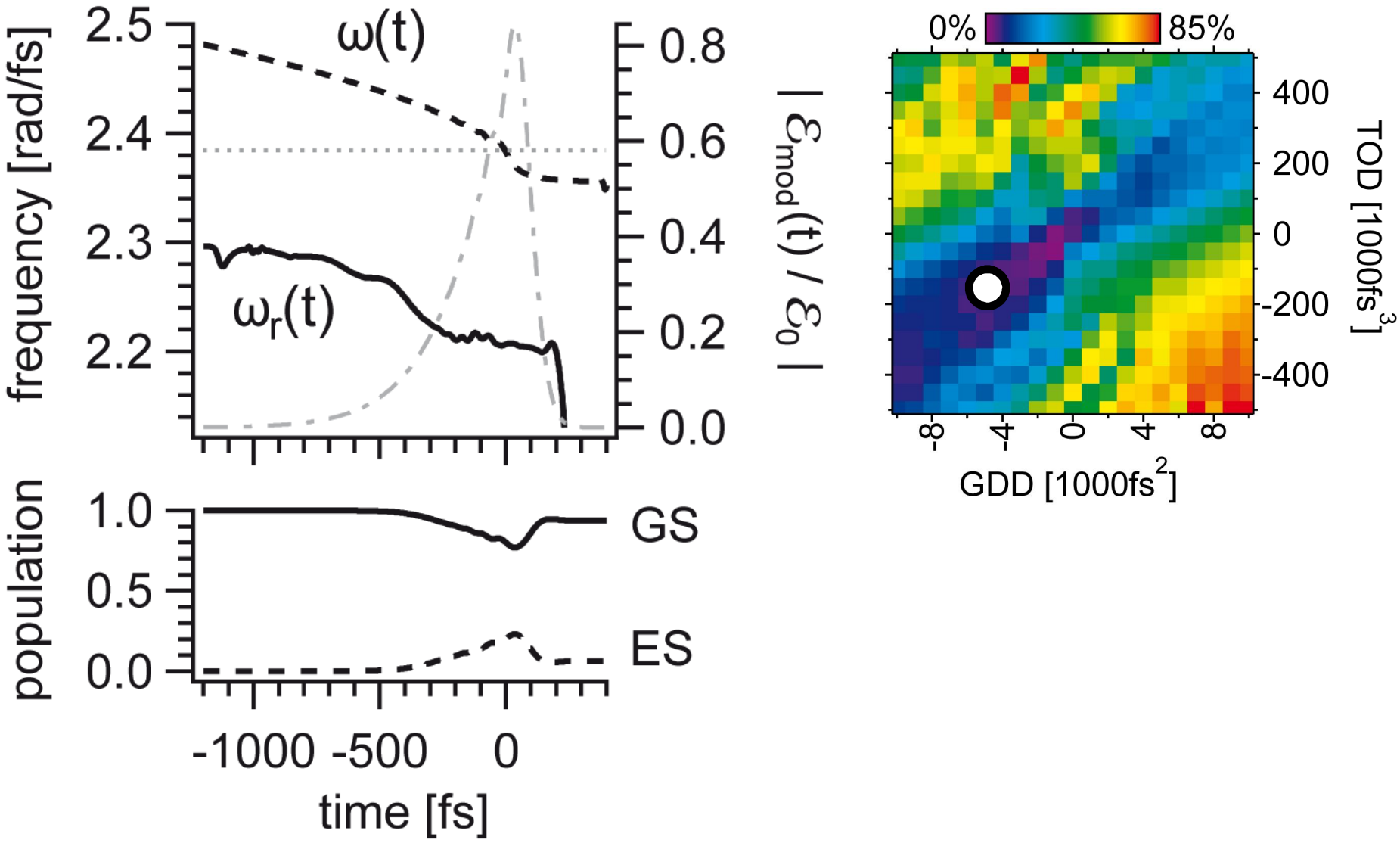
"*Efficient and robust strong-field control of population transfer in sensitizer dyes with designed femtosecond laser pulses*".
J. Schneider, M. Wollenhaupt, A. Winzenburg, T. Bayer, J. Köhler, R. Faust and T. Baumert, **PCCP** (2011)

$\omega_r(t)$ = time dependent MOLECULAR resonance $\omega(t)$ = instantaneous LASER frequency

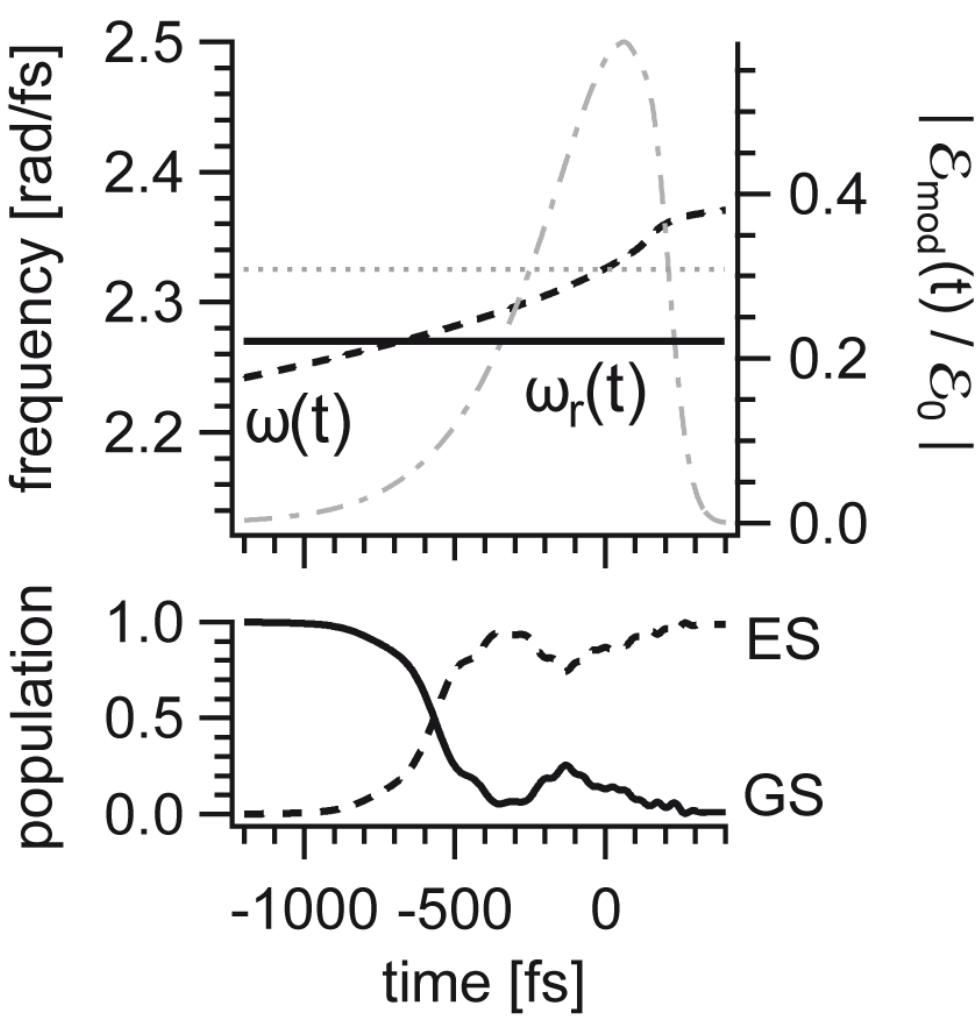
Quantum Control Landscapes

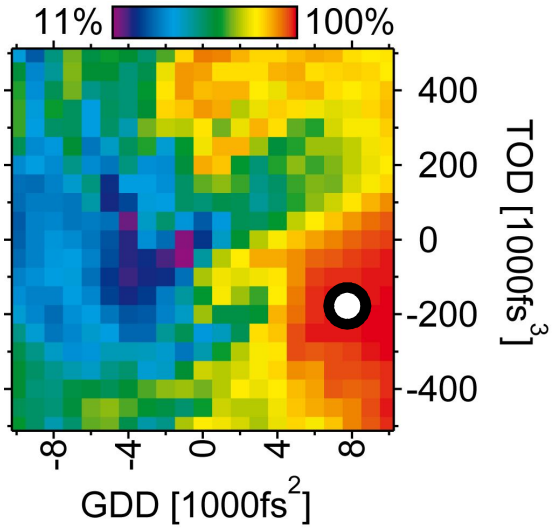


Joint Motion and Coherent Population Return



Eigenstate Preparation Followed by Rapid Adiabatic Passage





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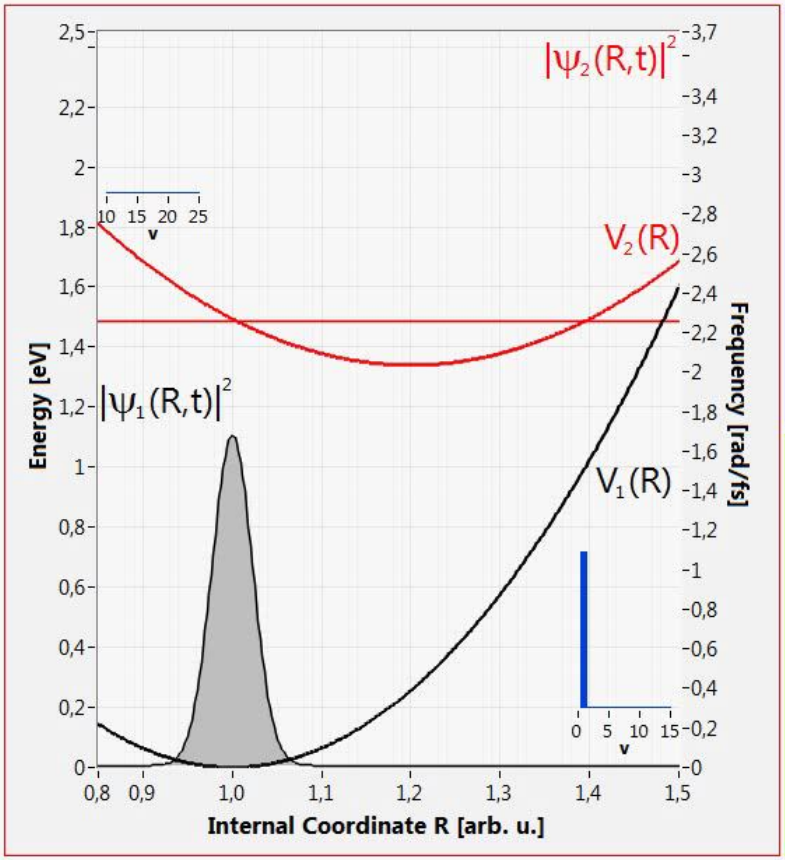
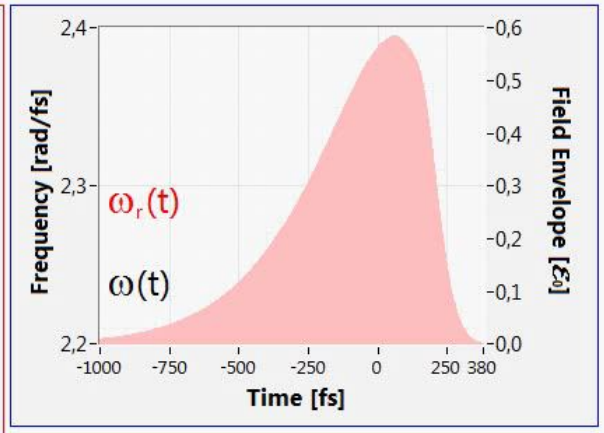
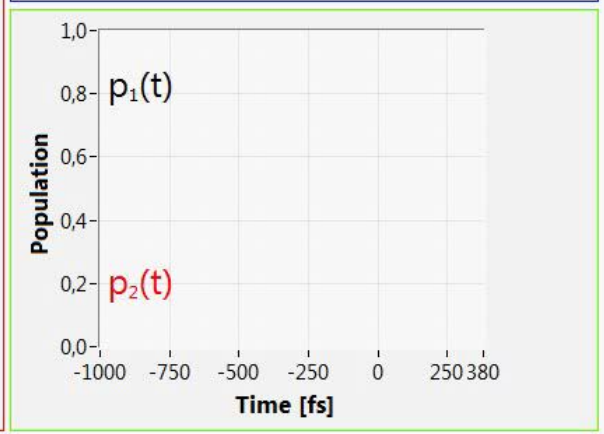
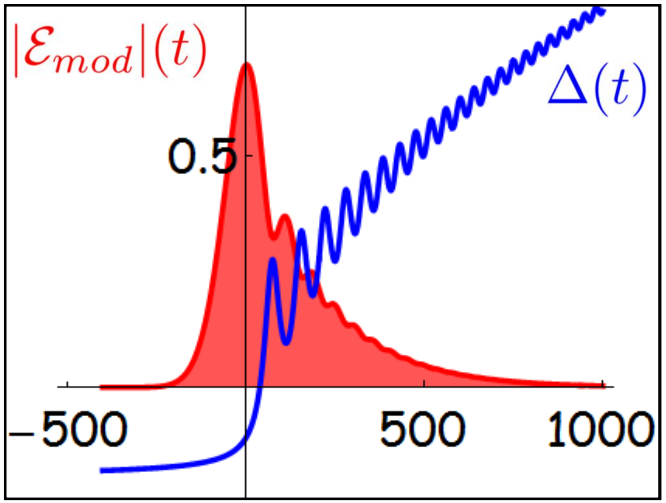


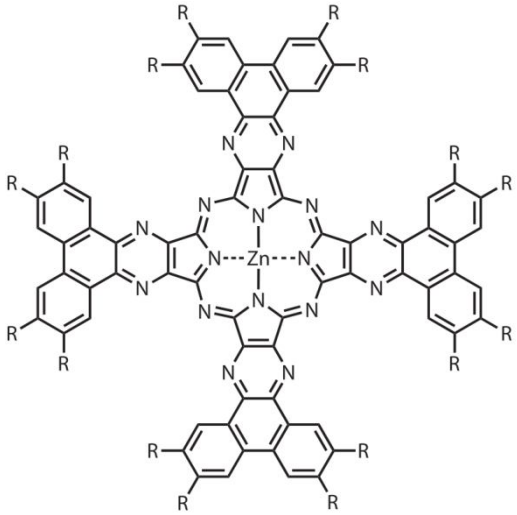




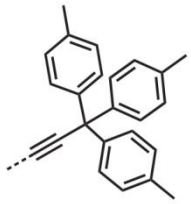
"Efficient and robust strong-field control of population transfer in sensitizer dyes with designed femtosecond laser pulses".
J. Schneider, M. Wollenhaupt, A. Winzenburg, T. Bayer, J. Köhler, R. Faust and T. Baumert, **PCCP** (2011)

SUMMARY: Strong Field Control on Molecules in the Liquid Phase





R =

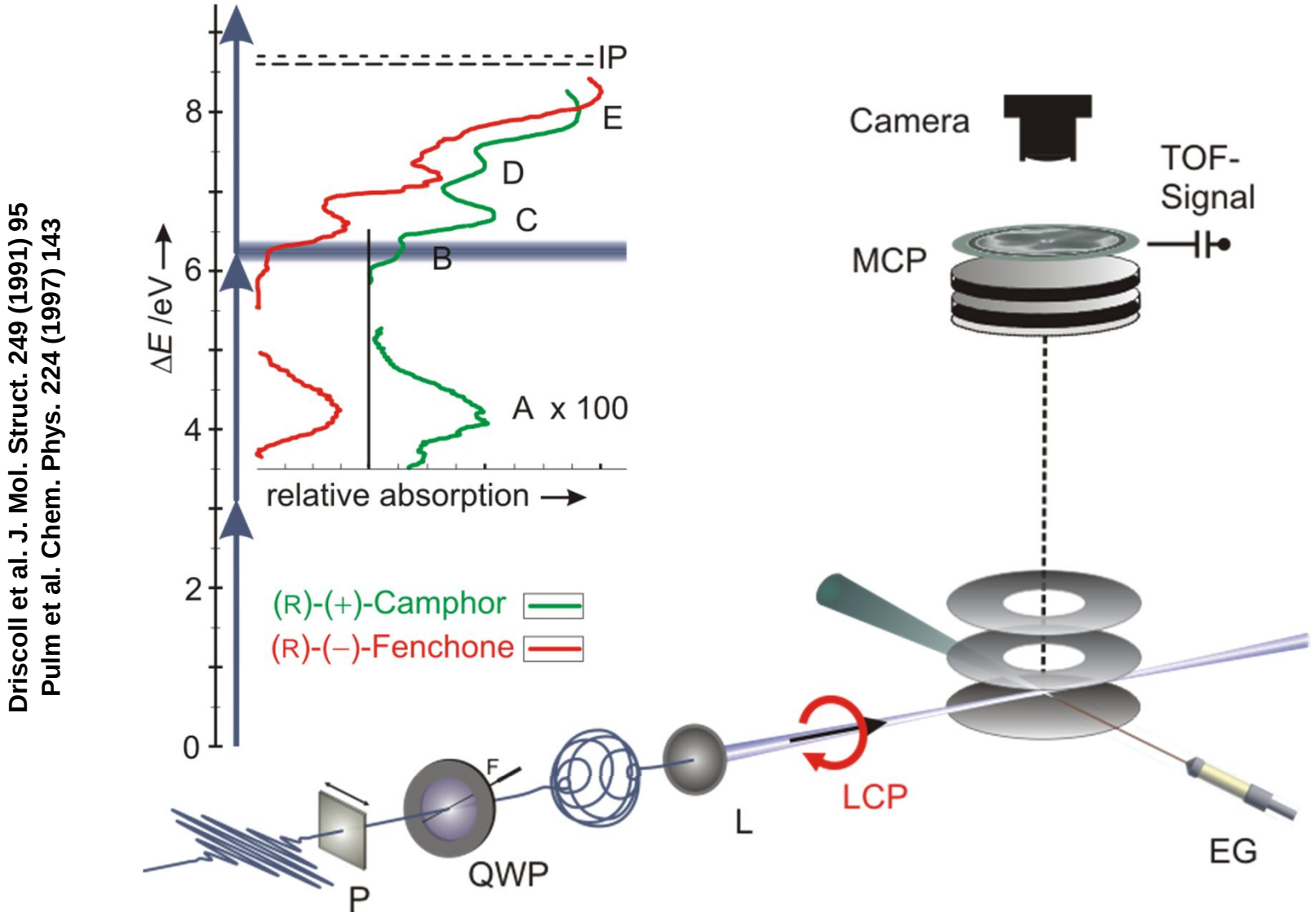


GDD-TOD pulses are a suitable parameterization to study strong field effects (quantum control spectroscopy)

Joint wave packet motion (JOMO) and Eigenstate preparation as strong field processes beyond frequency ordering and pump dump

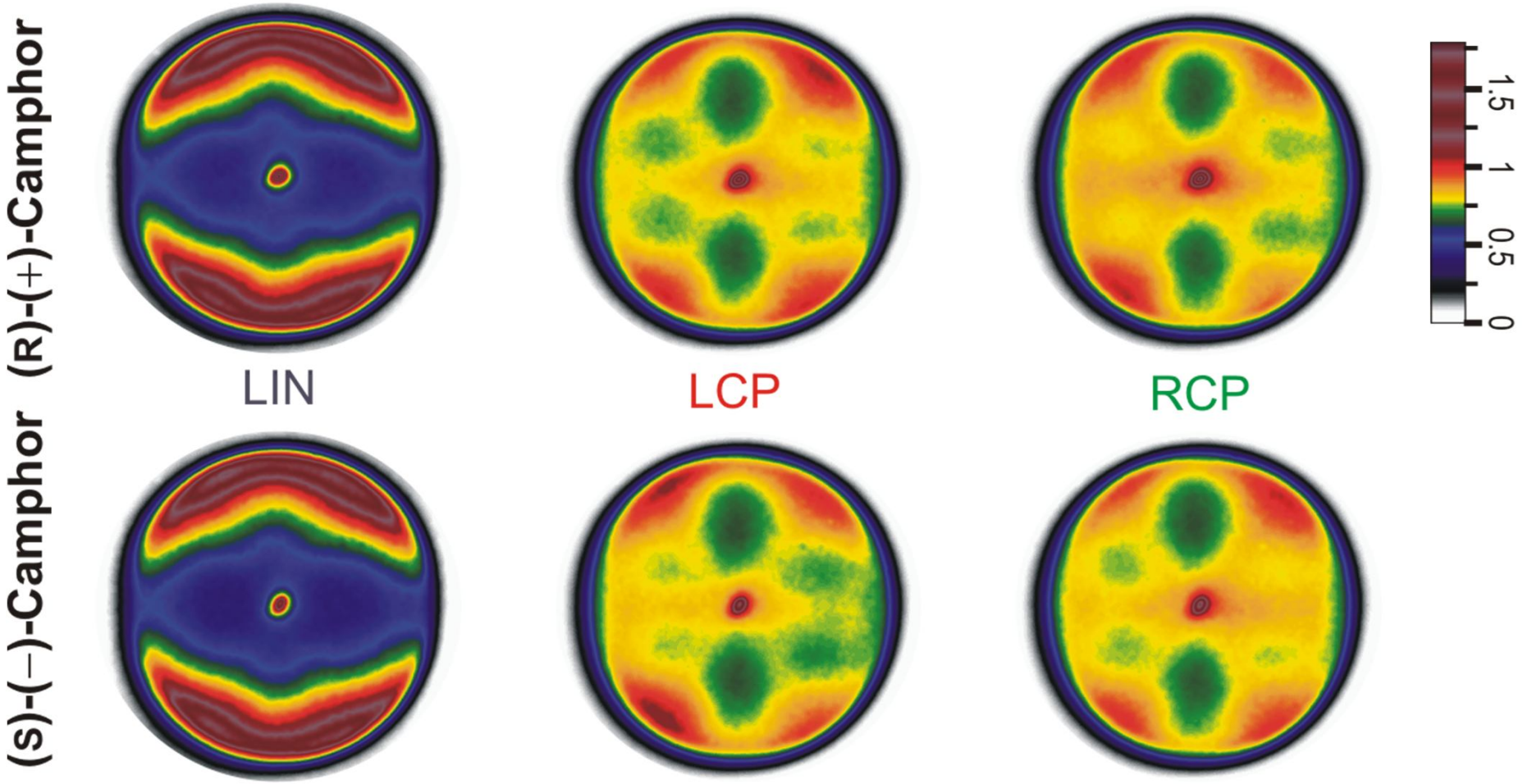
Adiabatic Population Transfer

Currently Chiral Recognition in Gas Phase
- PhotoElectronCircularDichroism with fs- Laser Pulses -

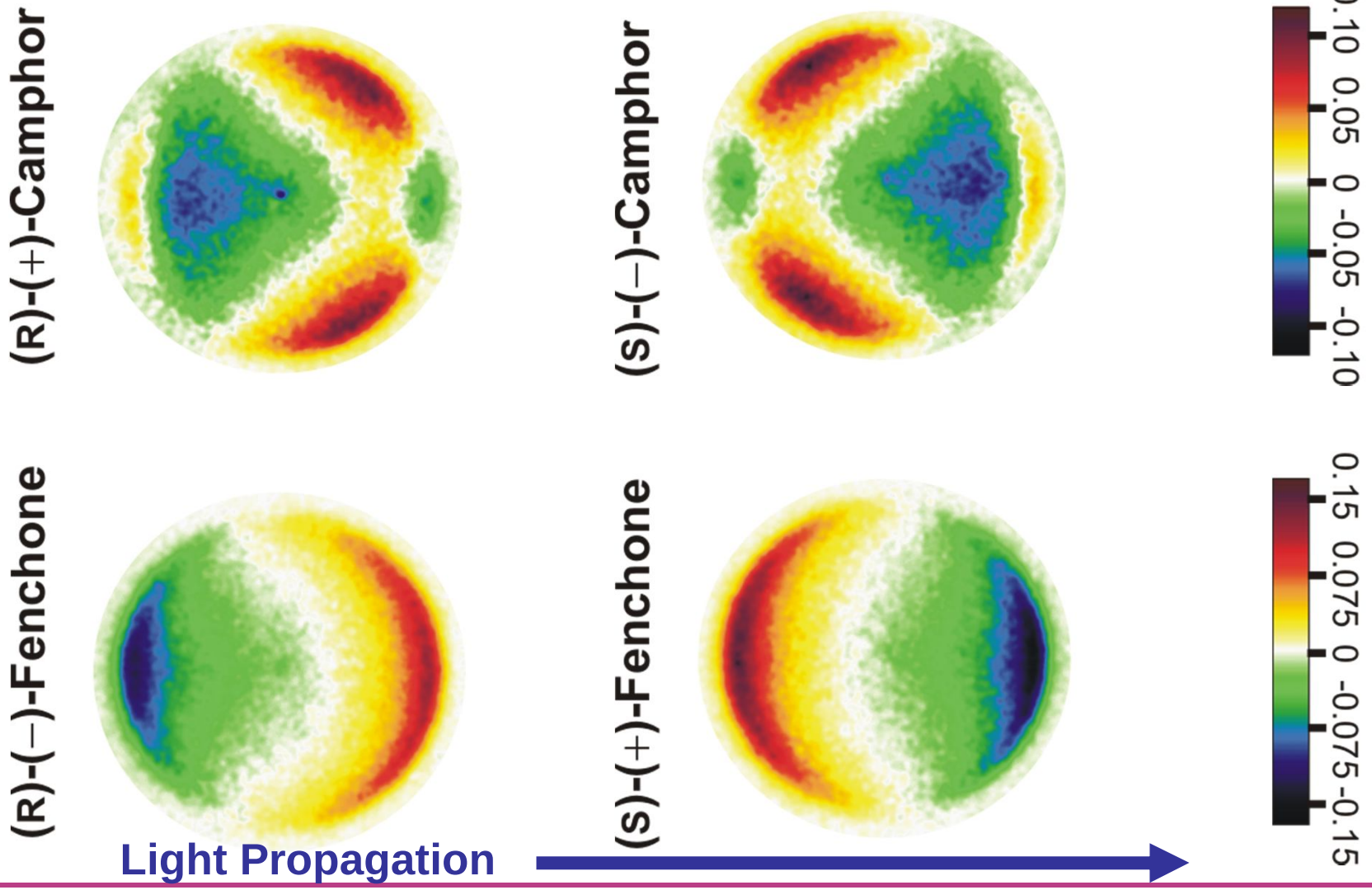


Driscoll et al. J. Mol. Struct. 249 (1991) 95
Pulm et al. Chem. Phys. 224 (1997) 143

Photoelectron Angular Distributions



PhotoElectronCircularDichroism (PECD): Image (LCP) – Image (RCP)



SUMMARY Chiral Recognition

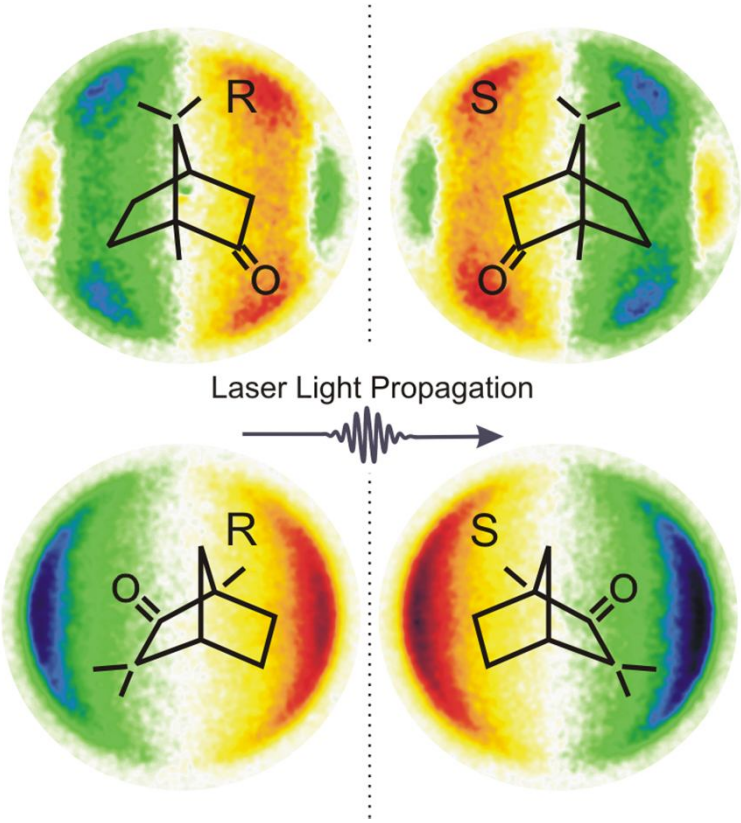
PECD effect in +/- ten % regime

Complete asymmetry in odd Legendere polynomials

Future:

Exploit nuclear and electron dynamics on intermediate resonance with coherent control techniques

Dynamics on resonant intermediates together with highly differential detection scheme may contribute to determination of absolute configuration by comparison to ab initio quantum dynamic calculations



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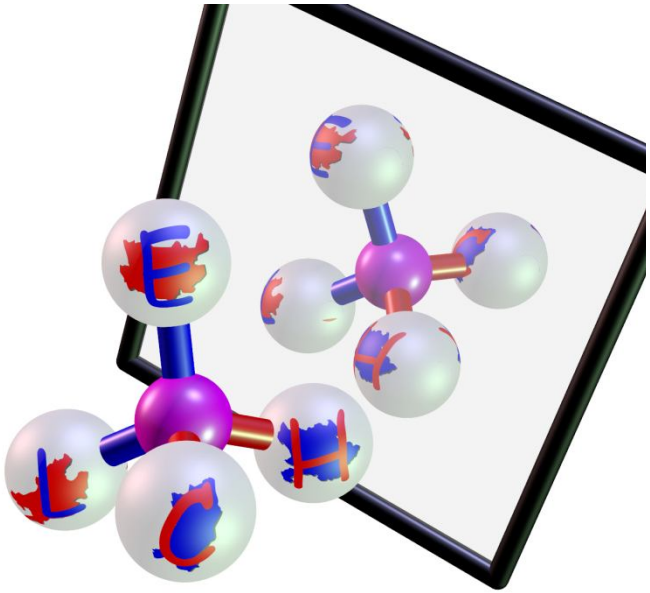
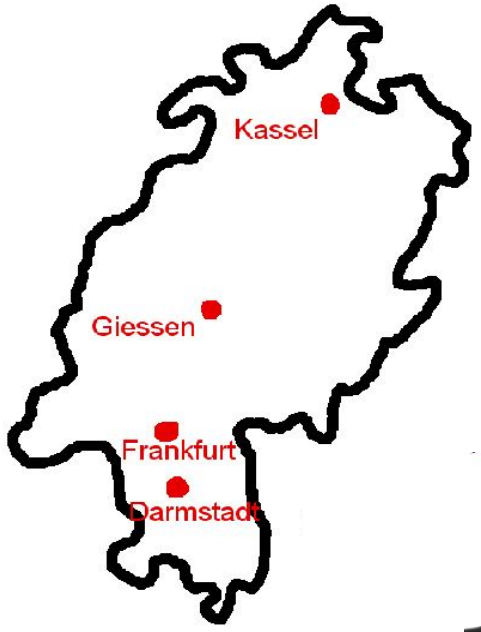
Electron Dynamics of Chiral Systems (ELCH)






Baumert


Wollenhaupt


Ehresmann


Koch


Müller


Schippers


Dörner


Berger


Stöhlker

Junior professor (W1, 6 Years) “Theoretical atomic and molecular physics”
focussed on developments for the description of photo-electron and fluorescence angular distributions
+ PhD Positions (three years)

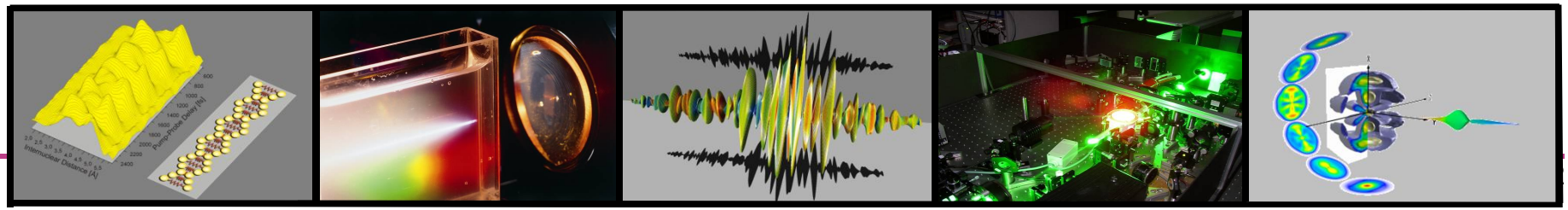
Summary

- Introduction to Ultrafast Laser Control and Current Status of our Pulse Shaping Device **Polarization Shaping and Zeptosecond Temporal Resolution**

- **Efficient Sub-cycle Control** of the Coupled Electron and Nuclear Dynamics in **Molecules (K_2)***

- Strong Field Control on Molecules in the Liquid Phase: **Joint Wave Packet Motion and Adiabatic Population Transfer**

* In coop. with Regina de Vivie-Riedle



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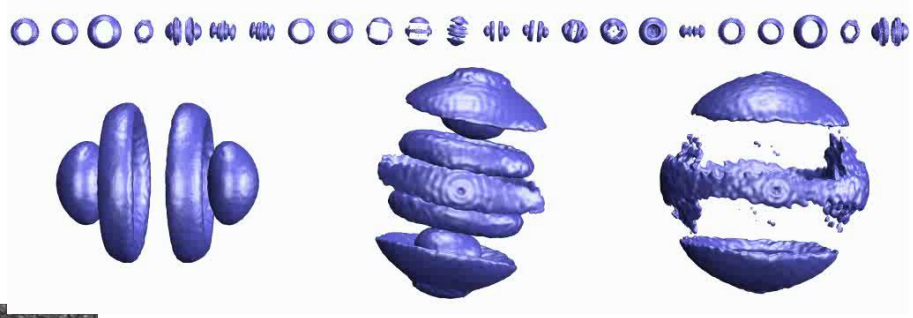
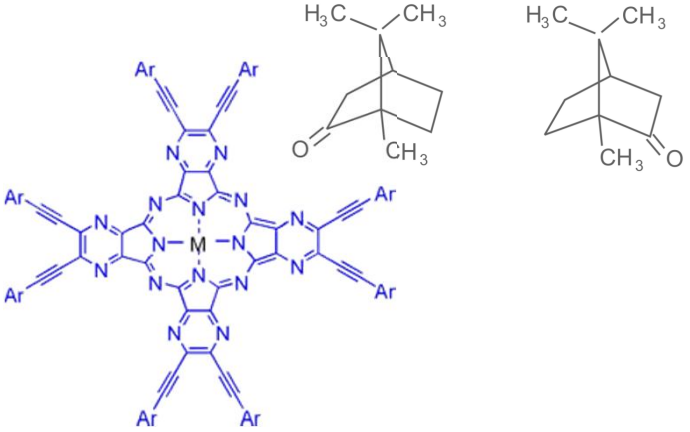
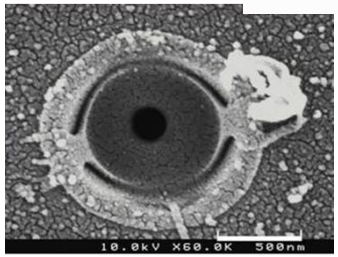
Our Current Research Topics Based on Pulse Shaping

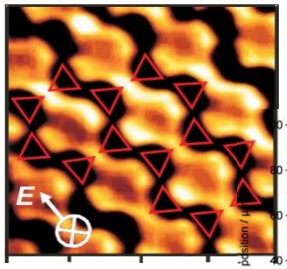
Coherent Control of Quantum Systems (Electrons, Atoms, Molecules)



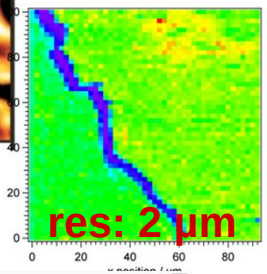




< 100 nm

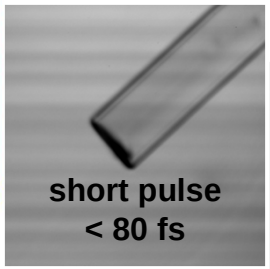


6 µm x 4 nm x 100 nm

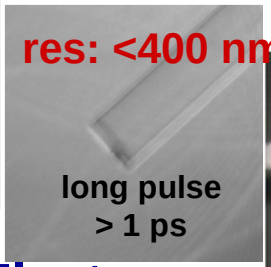


res: 2 µm

Material Processing on nm Scale, Plasma Dynamics, SPM-Microscopy, LIBS

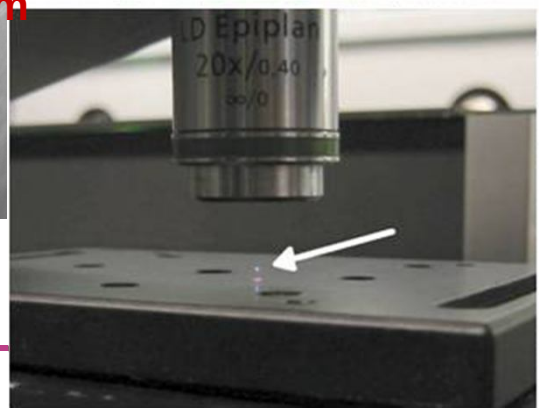


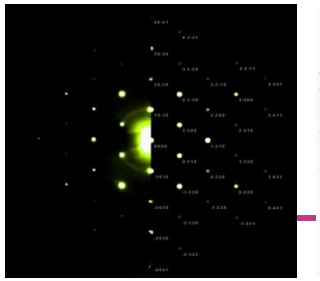
short pulse
< 80 fs

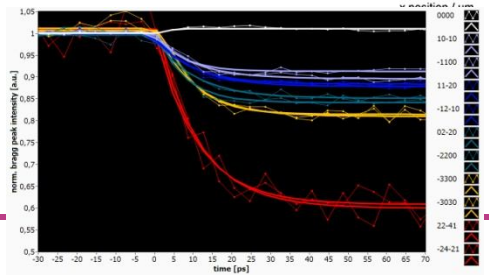


res: <400 nm

long pulse
> 1 ps







Ultrafast Electron Diffraction - Control of Structural Dynamics