

Gas Phase Dynamics in Small Molecules and Clusters: From Analysis to Control

Stefan Vajda

*APS Workshop on Time Domain Science
Using X-ray Techniques*

The Abbey, Fontana, Lake Geneva Area, Wisconsin

August 31, 2004

Argonne National Laboratory

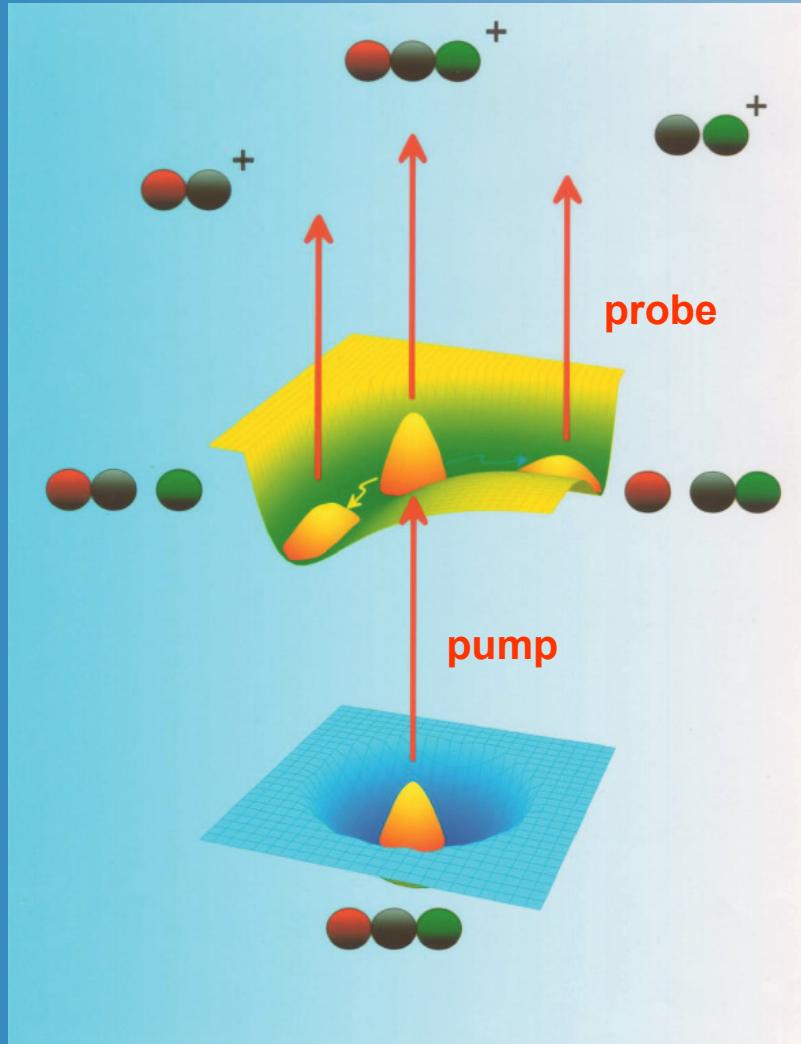


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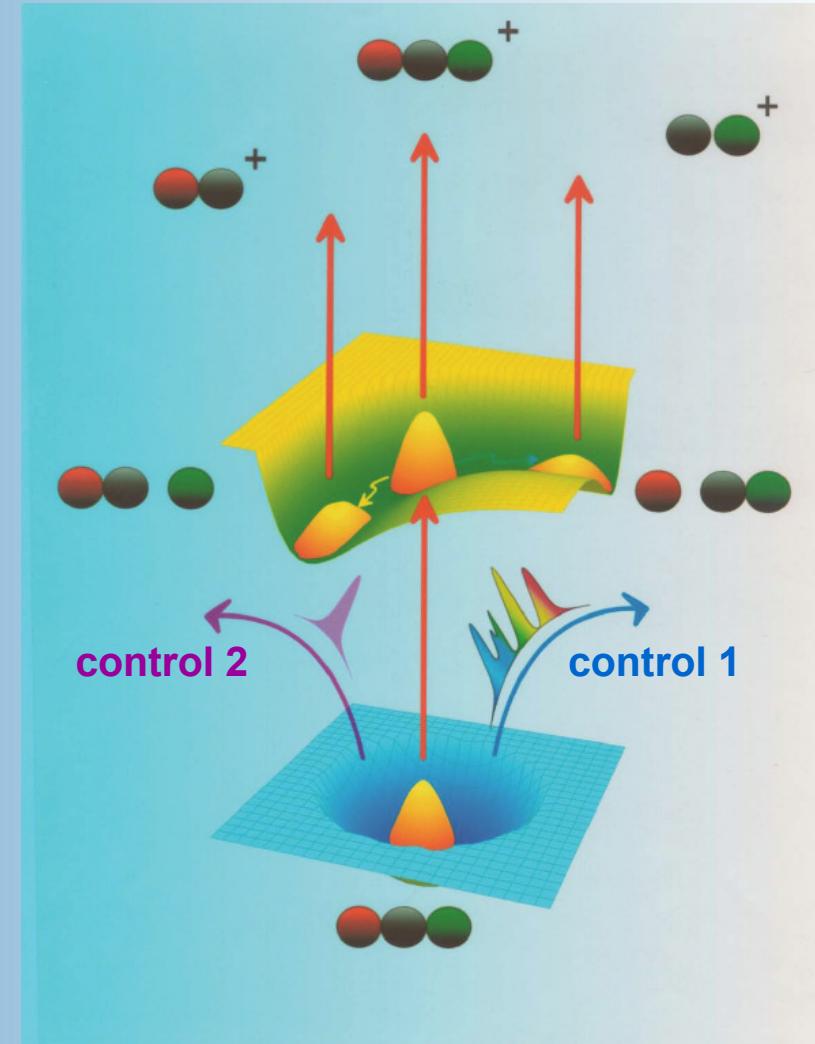


Introduction: Analysis & control of molecular dynamics with ultrafast lasers

Analysis



Control



Outline

Motivation

- to study elementary photochemical processes (analysis)
- to influence these processes (control)

Choice of molecular systems of increasing complexity

- small clusters and molecules
- larger molecules

Analysis

- time-resolved spectroscopy combined with mass spectrometry

Control

- control knobs (manual turn on the knobs – „trial & error“)
- pulse shaping technique (computerized)
- computerized automatic control of multiphotonic processes

Processes / molecular systems addressed

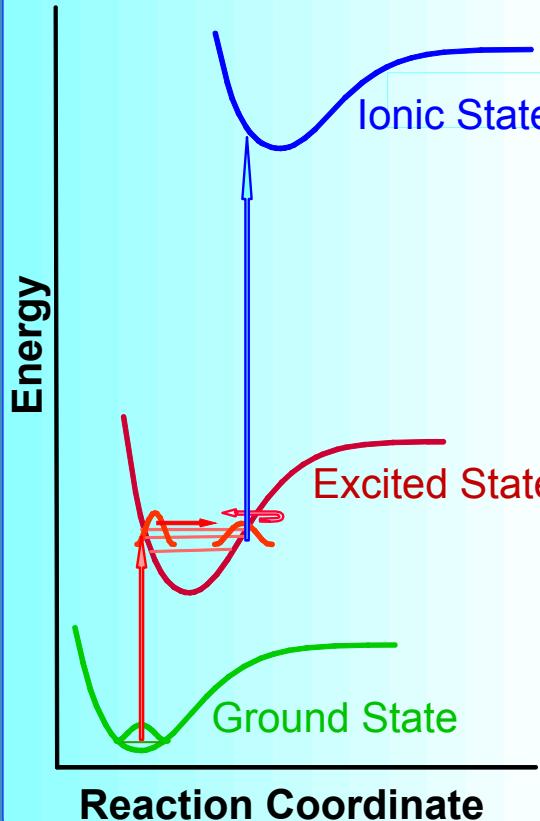
- **bound-bound transitions**
control of population of selected states in Na₃
- **dissociation**
control of the ion yield in the highly dissociative MnCp(CO)₃ molecule
- **predisociation**
control of the ion yield in the Na₂K/NaK system

Summary & Outlook

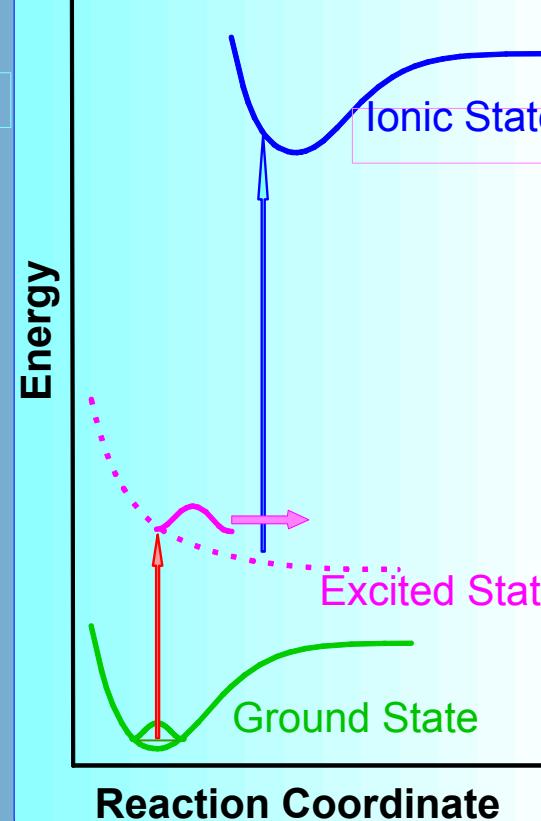


Processes addressed

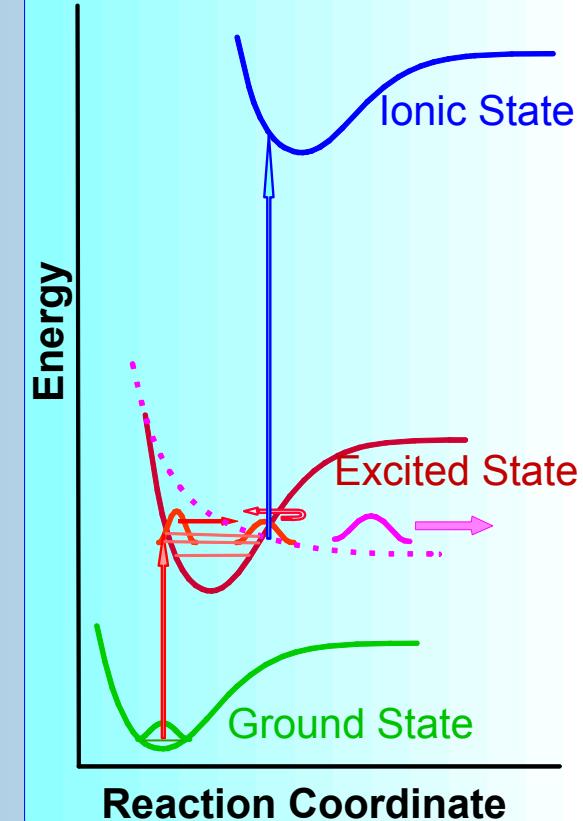
Bound-Bound Transition



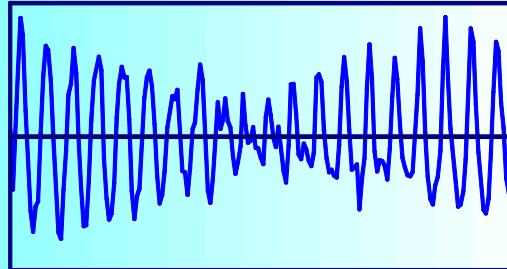
Bound-Free Transition



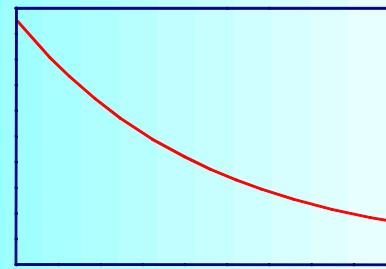
Predissociation



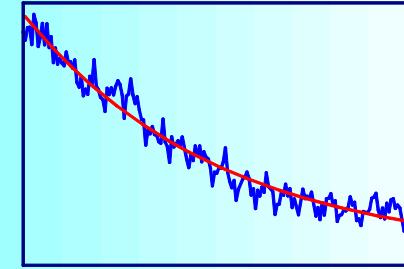
Pump & Probe Signal



Pump & Probe Signal



Pump & Probe Signal



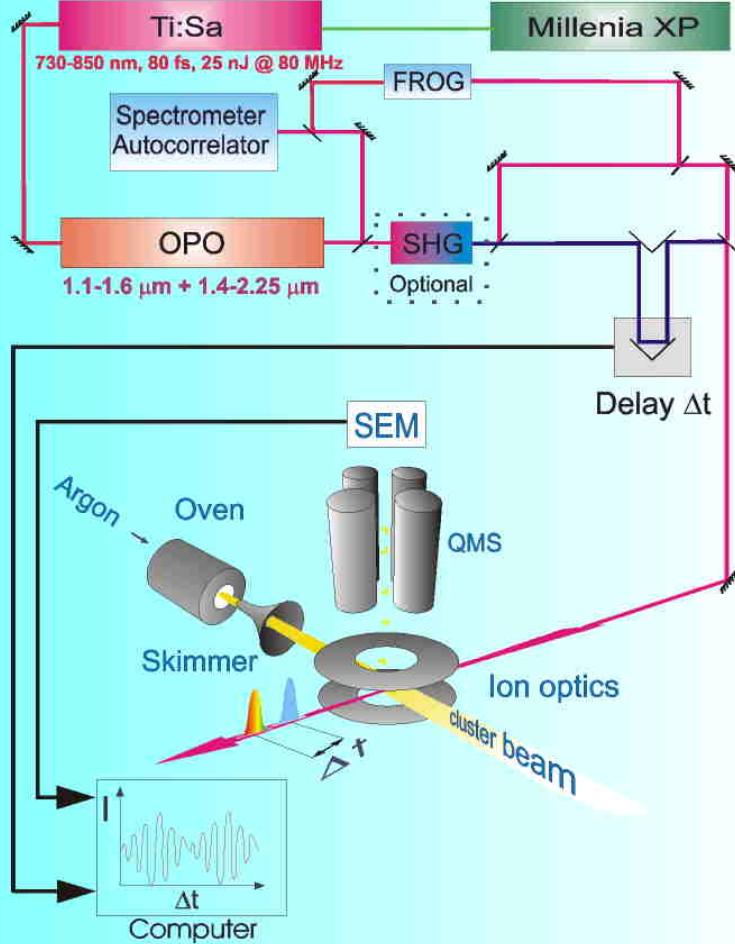
Stefan:pump_probe_schemes_signal_boxes_20.dsfc



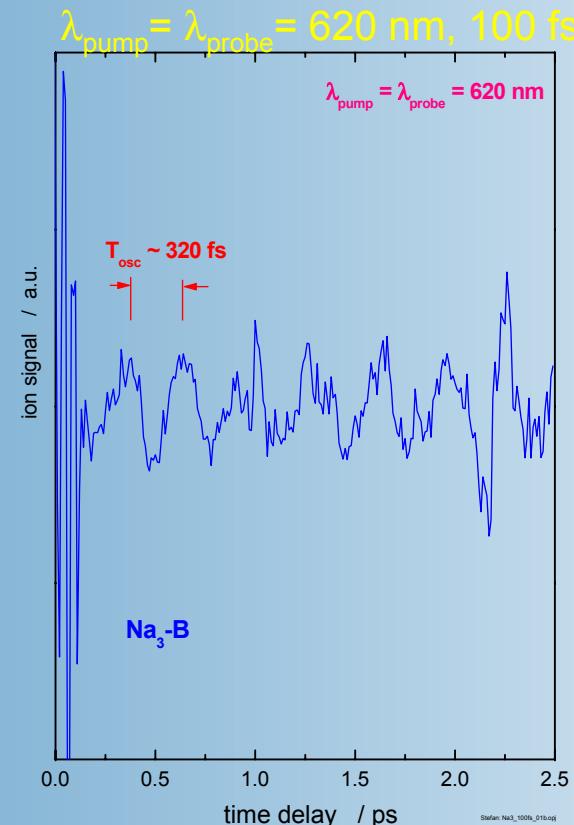
Bound-bound transitions in Na_3

Analysis of the vibration dynamics in the B state of Na_3

Experimental Setup

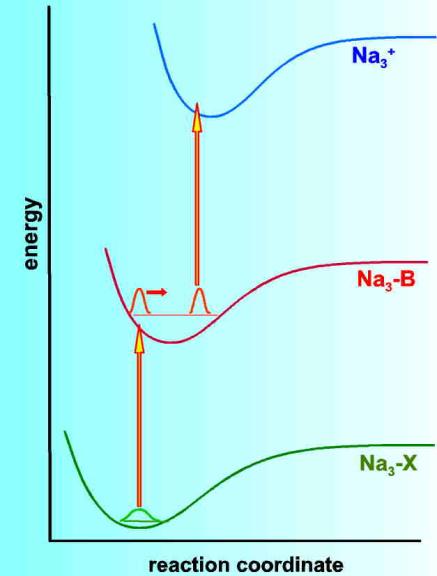


Pump & probe spectrum of
 Na_3 B-state



Pump & probe scheme

Schematic of the 2-photonic pump & probe process in Na_3



$T_{\text{osc}} \sim 320 \text{ fs}$, symmetric stretch mode of the B-state of Na_3

S. Vajda, and L. Wöste, in „*Femtochemistry*“, Eds.: F.C. De Schryver, S. De Feyter and G. Schweitzer, John Wiley-VCH, 2001, ISBNs: 3-527-30259-X, Chapter 10, pp. 199-216

A. Lindinger, C. Lupulescu, A. Bartelt, S. Vajda, and L. Wöste, *Spectrochim. Acta B* **58**, 1109, (2003)



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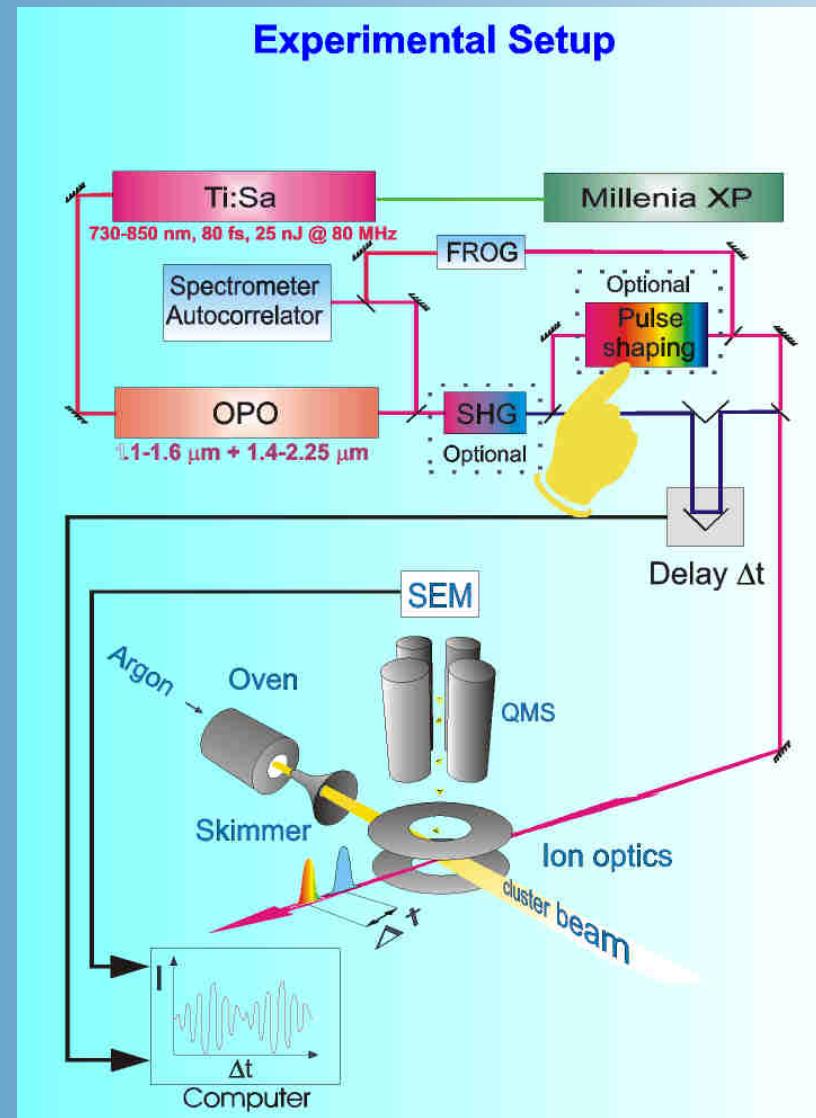
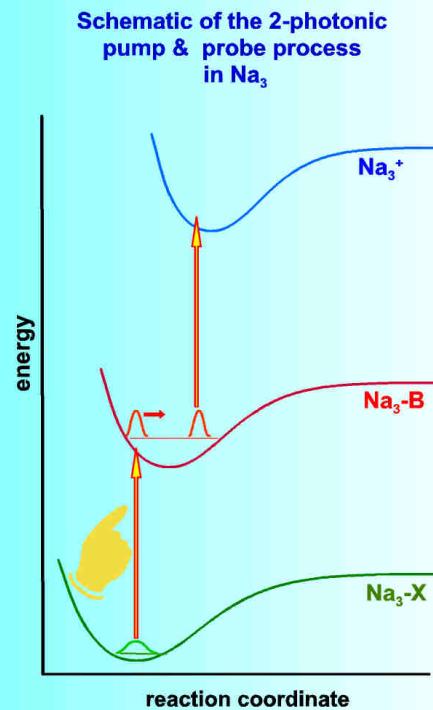
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Bound-bound transitions in Na_3

Control of the population of bound states in Na_3 by applying manually chirped pulses

Pump & probe scheme
with chirped pump pulse

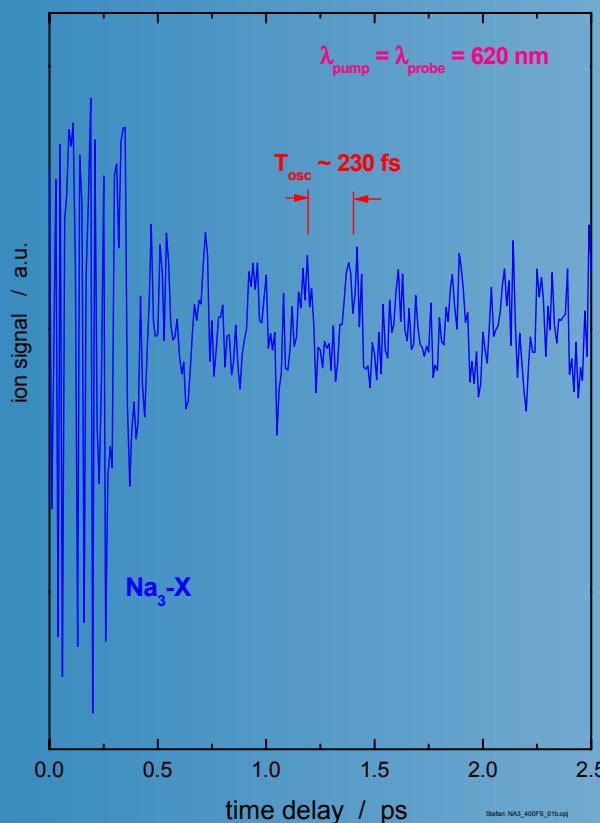


Bound-bound transitions in Na_3

Control of the population of states in Na_3 by applying manually chirped pulses

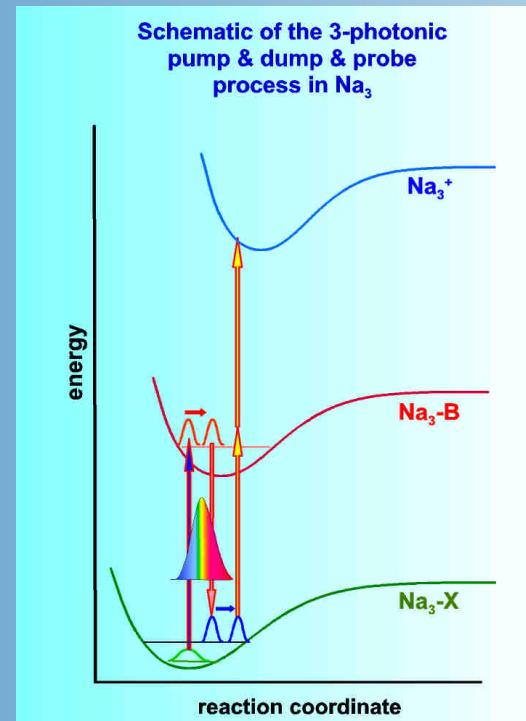
Pump & probe spectrum

$$\lambda_{\text{pump}} = 620 \text{ nm, } 400 \text{ fs down-chirped}$$
$$\lambda_{\text{probe}} = 620 \text{ nm, } 100 \text{ fs unchirped}$$

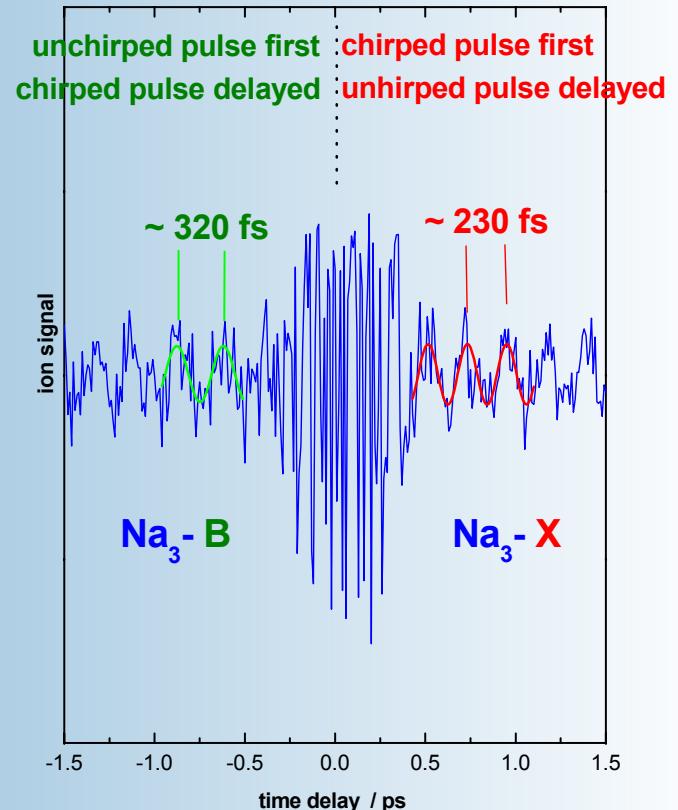


$T_{\text{osc}} \sim 230 \text{ fs}$
symmetric stretch mode
of the **ground** state of Na_3

Pump & dump & probe scheme



Proof of the control scheme



- The **ground** state dynamics is controlled with the chirped pulse arriving first and acting as a pump&dump pulse.

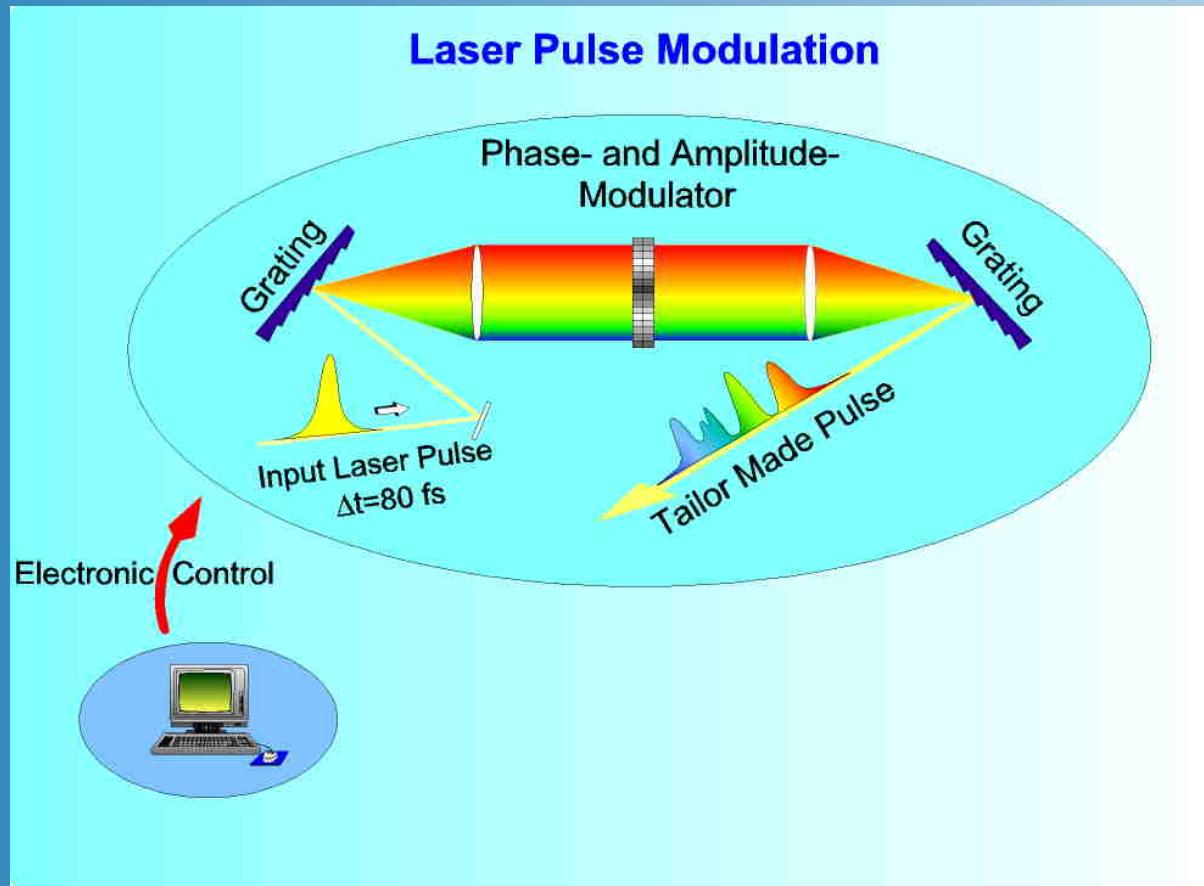
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A. Lindinger, C. Lupulescu, A. Bartelt, S. Vajda, and L. Wöste, *Spectrochim. Acta B* **58**, 1109, (2003)

Tailor-made pulses

Generation of shaped pulses using a liquid crystal modulator

Scheme of the experimental setup

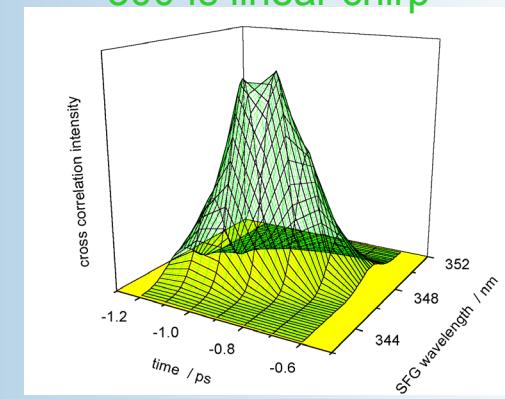


- Pulse shaper design as of Weiner et. al. (*IEEE, J Quant. Electron.*, **28**, 908, (1992))
- Two spatial liquid modulators each with 128 pixels used.
- Simultaneous phase and amplitude modulation possible.

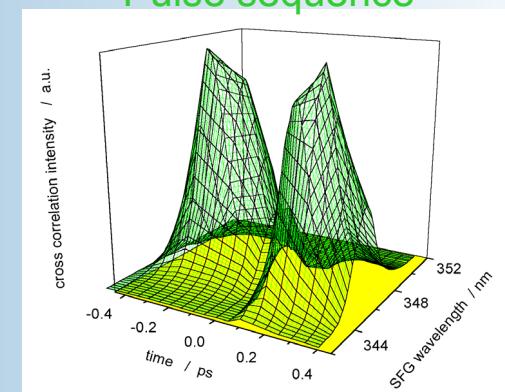
Examples of shaped VIS pulses generated in the setup

Input pulse: 120 fs @ 620 nm (OPO)
Reference pulse used for cross-correlation:
80 fs @ 775 nm (Ti:Sa)

300 fs linear chirp



Pulse sequence



S. Vajda, Habilitation Thesis, Freie Universität Berlin, 2002



VOLUME 68, NUMBER 10

PHYSICAL REVIEW LETTERS

9 MARCH 1992

Teaching Lasers to Control Molecules

Richard S. Judson^(a)

Center for Computational Engineering, Sandia National Laboratories, Livermore, California 94551-0969

Herschel Rabitz

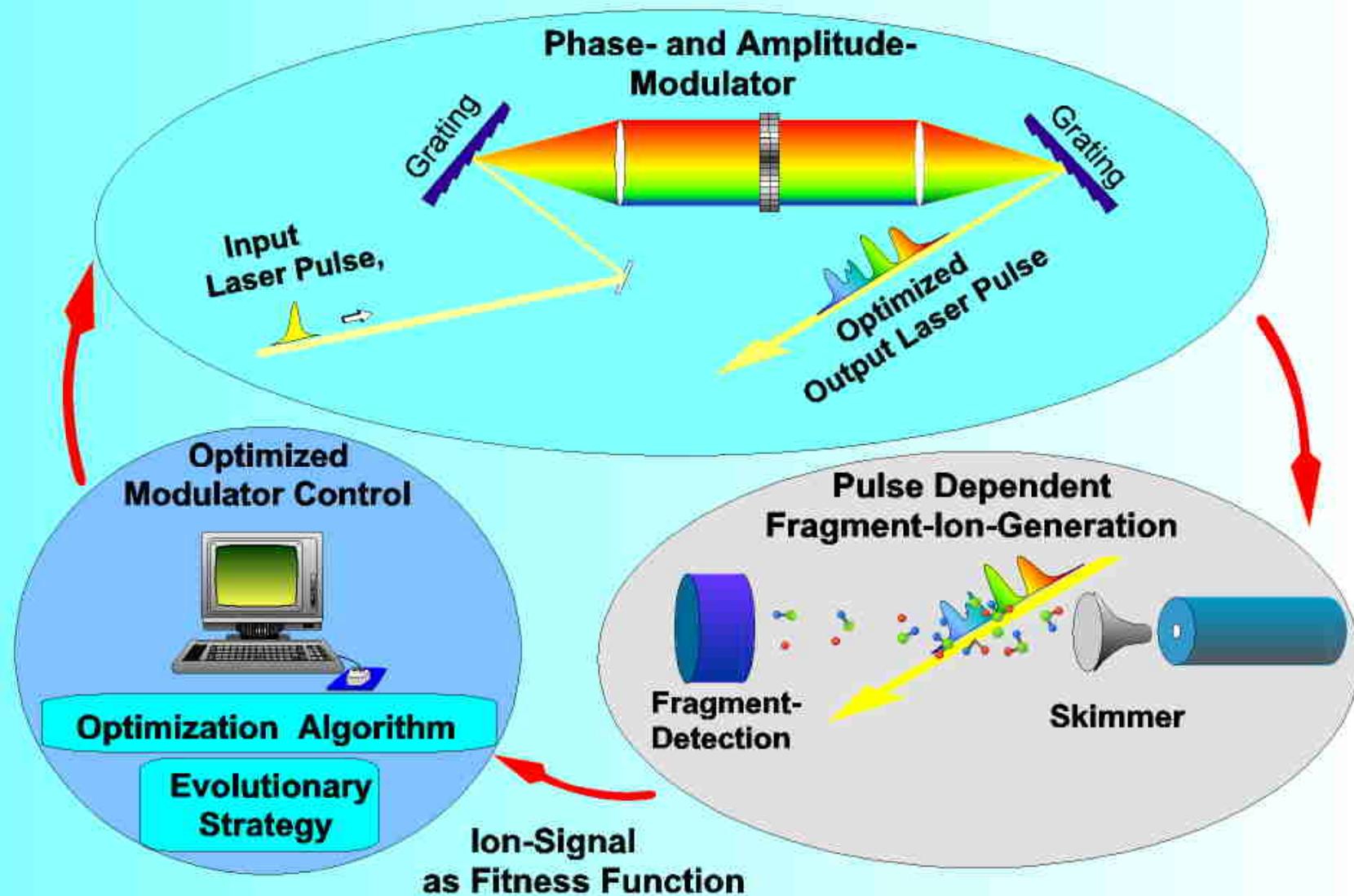
Department of Chemistry, Princeton University, Princeton, New Jersey 08544

(Received 26 August 1991)

We simulate a method to teach a laser pulse sequences to excite specified molecular states. We use a learning procedure to direct the production of pulses based on “fitness” information provided by a laboratory measurement device. Over a series of pulses the algorithm learns an optimal sequence. The experimental apparatus, which consists of a laser, a sample of molecules, and a measurement device, acts as an analog computer that solves Schrödinger’s equation exactly, in real time. We simulate an apparatus that learns to excite specified rotational states in a diatomic molecule.

Optimal control - experiment

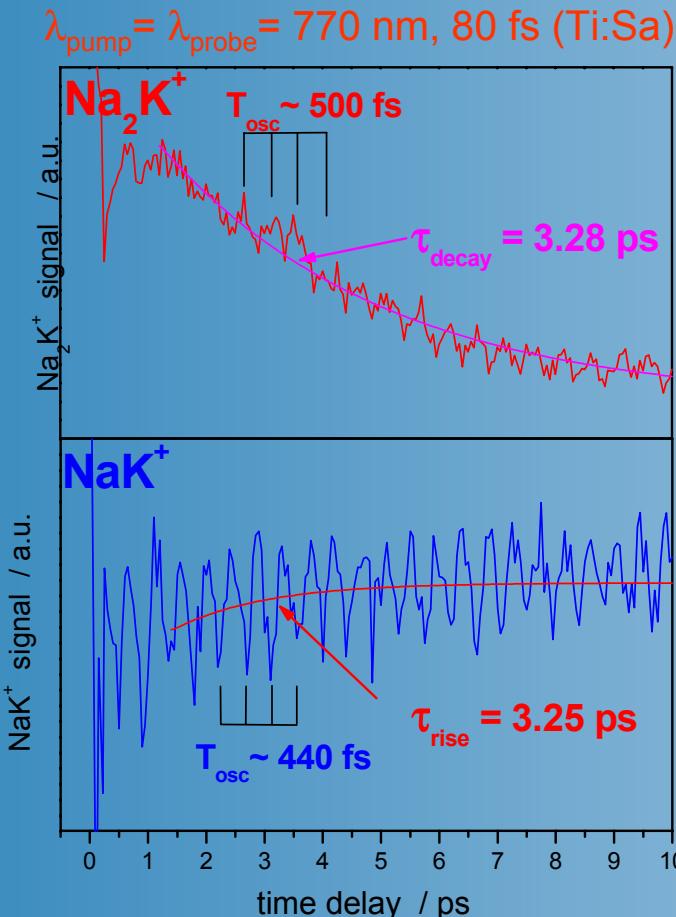
Control of the Fragmentation of Small Clusters & Molecules



Photodissociating system $\text{Na}_2\text{K} \longrightarrow \text{NaK}$

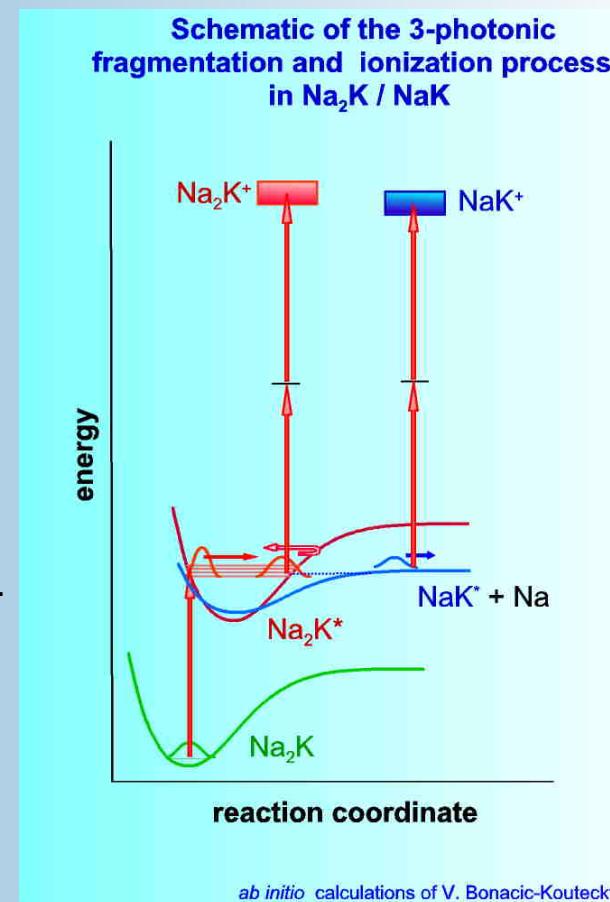
Analysis of the fragmentation dynamics

Pump & probe spectra of Na_2K and its fragment NaK



- Dominantly trimers and dimers in the molecular beam, ~30% of the NaK^+ signal comes from the fragments.
- The rise-time of the NaK fragment signal matches the decay time of the parent Na_2K trimer signal.
- Wavepacket dynamics in NaK and Na_2K clearly resolved.

Pump & probe scheme



S. Vajda, A. Bartelt, C. Kaposta, T. Leisner, C. Lupulescu, S. Minemoto, P. Rosendo-Francisco, and L. Wöste
Chem. Phys. **267**, 231 (2001), Special Issue on „Laser Control of Molecular Dynamics“, Guest Editors : R. de Vivie-Riedle, H. Rabitz, and K. Kompa



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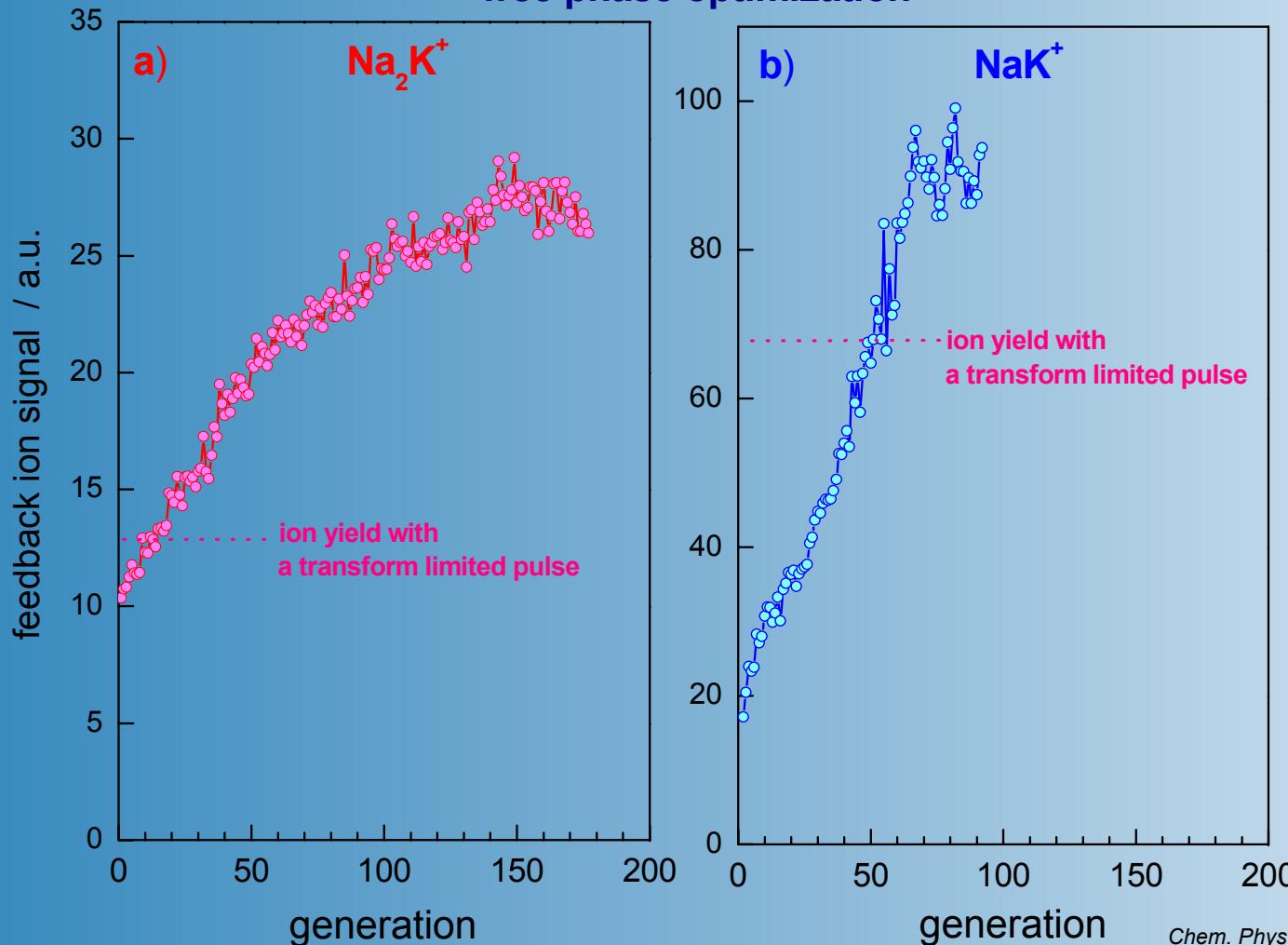


Photodissociating system $\text{Na}_2\text{K} \longrightarrow \text{NaK}$

Control of the ion yield

Input laser pulse: 80 fs, $\lambda = 770 \text{ nm}$ (Ti:Sa)

Evolution of the ion yield during optimization
free phase optimization



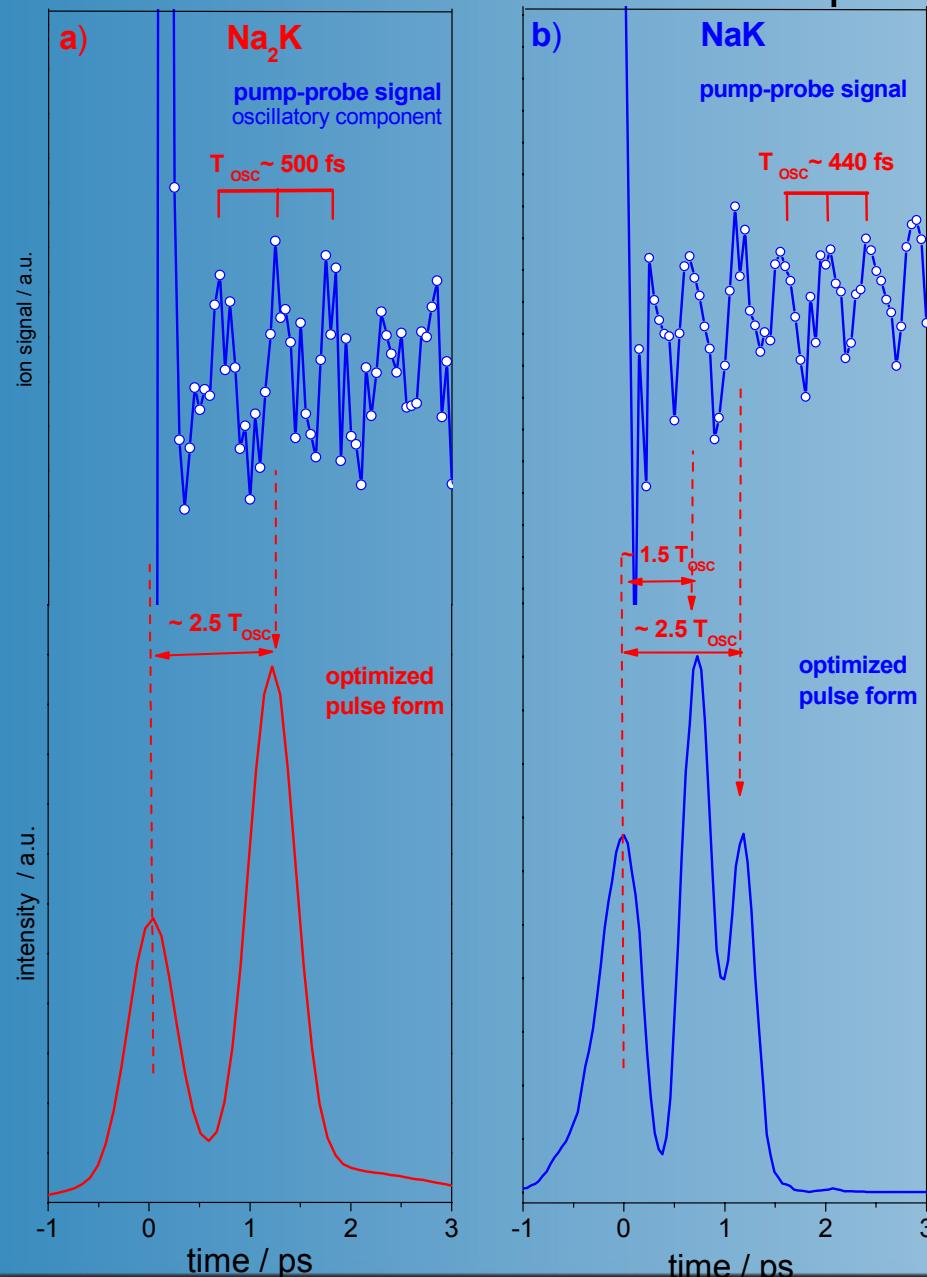
- Significant increase of the ion yield with optimal pulse in comparison with the ion yield achieved with a single pulse of same energy.
- Increase of the ion yield of one product is accompanied by a decrease of the ion yield of the second product

S. Vajda, A. Bartelt, C. Kaposta, T. Leisner, C. Lupulescu, S. Minemoto, P. Rosendo-Francisco, and L. Wöste

Chem. Phys. **267**, 231 (2001), Special Issue on „Laser Control of Molecular Dynamics“, Guest Editors : R. de Vivie-Riedle, H. Rabitz, and K. Kompa

Photodissociating system $\text{Na}_2\text{K} \longrightarrow \text{NaK}$

Information content of the obtained optimal pulse forms



Comparison of the transient spectra with the optimal pulse form: What can we learn from the optimal pulse forms?

Na_2K

- The algorithm „counts“ the right number of photons needed in the excitation and ionization step, 1 and 2 respectively.
- The algorithm identifies the frequency of the vibration clock of the system.

NaK

- Same information found as for Na_2K .
- The triple-pulse structure is indicative of a complex underlying mechanism.

?

Why a triple pulse for NaK ?
Only the time plays a role?
Role of wavelength/chirp?

S. Vajda, A. Bartelt, C. Kaposta, T. Leisner, C. Lupulescu, S. Minemoto, P. Rosendo-Francisco, and L. Wöste

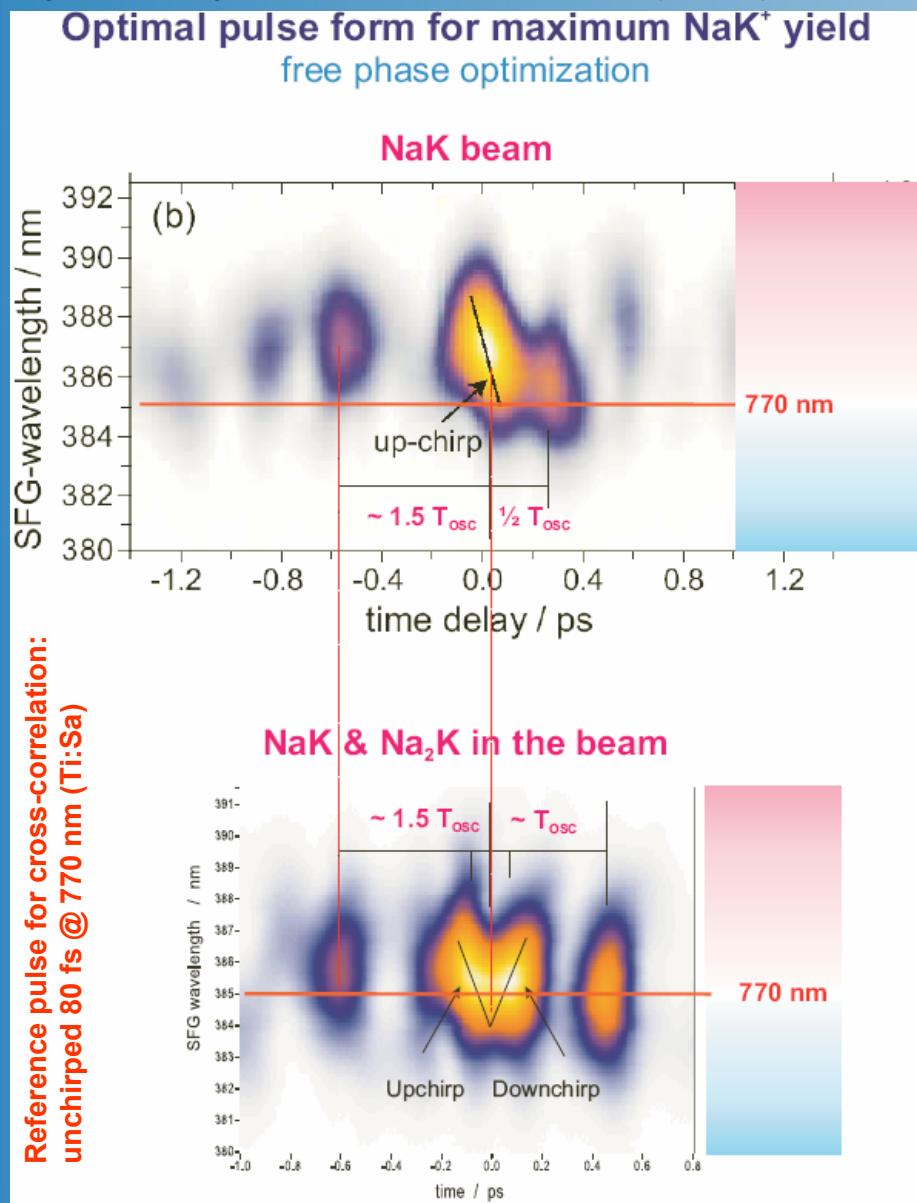
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Photodissociating system $\text{Na}_2\text{K} \longrightarrow \text{NaK}$

Role of the color and chirp

Input laser pulse: 80 fs, $\lambda = 770$ nm (Ti:Sa)



Color

The first (excitation) pulse for NaK is red-shifted with respect to that for Na_2K .

NaK beam only

- The timing of the pulses reflects the vibration period of NaK^* .

Chirp

- The up-chirp superimposed on the second sub-pulse compensates for defocussing of the propagating wavepacket.

NaK/ Na_2K beam

- The timing of the pulses reflects the vibration period of NaK^* .

Chirp

- The sub-pulse structure of the second pulse reflects the optimization of the NaK ionization and Na_2K fragmentation.

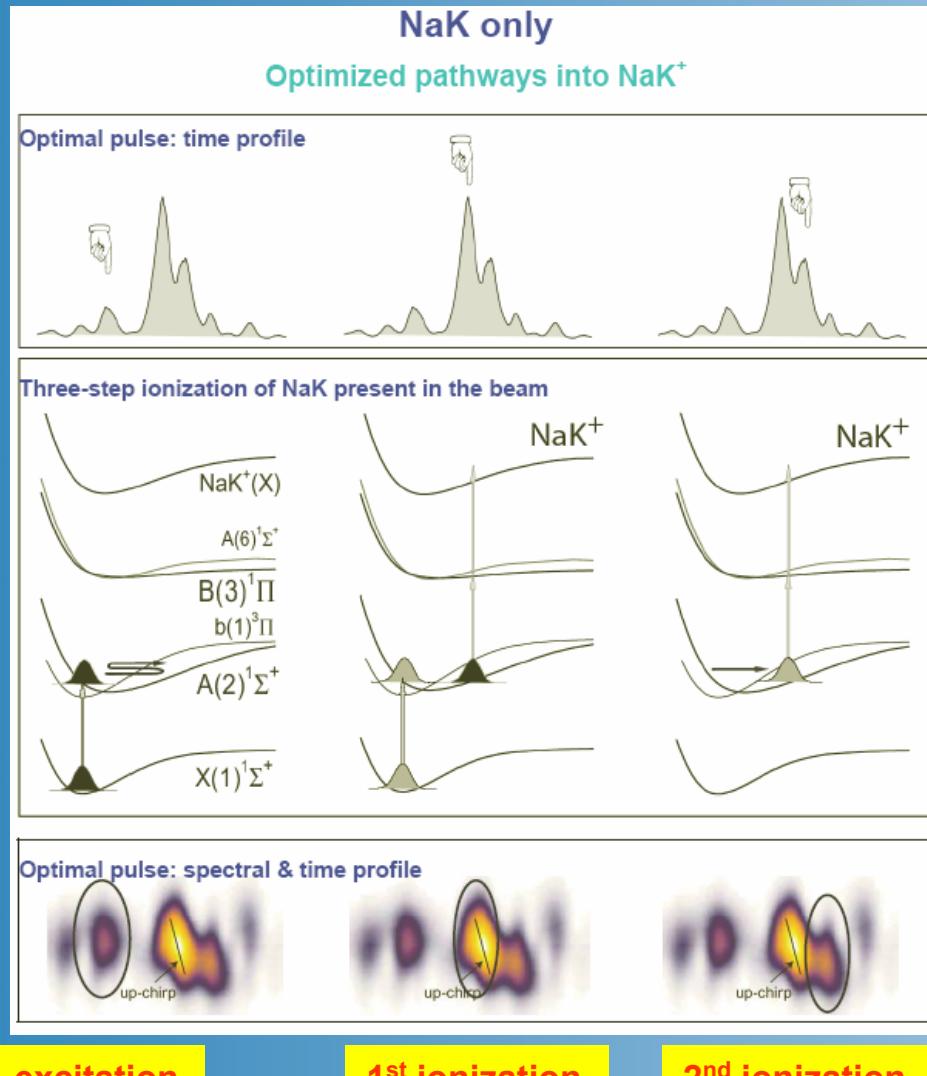
A. Bartelt, A. Lindinger, C. Lupulescu, S. Vajda, and L. Wöste,
Phys. Chem. Chem. Phys. **6**, 1679 (2004)

B. Schäfer-Bung, R. Mitric, and V. Bonacic-Koutecky, A. Bartelt, C. Lupulescu, A. Lindinger, S. Vajda, S. M. Weber, and L. Wöste,
J. Phys. Chem. A, **108**, 4175 (2004)



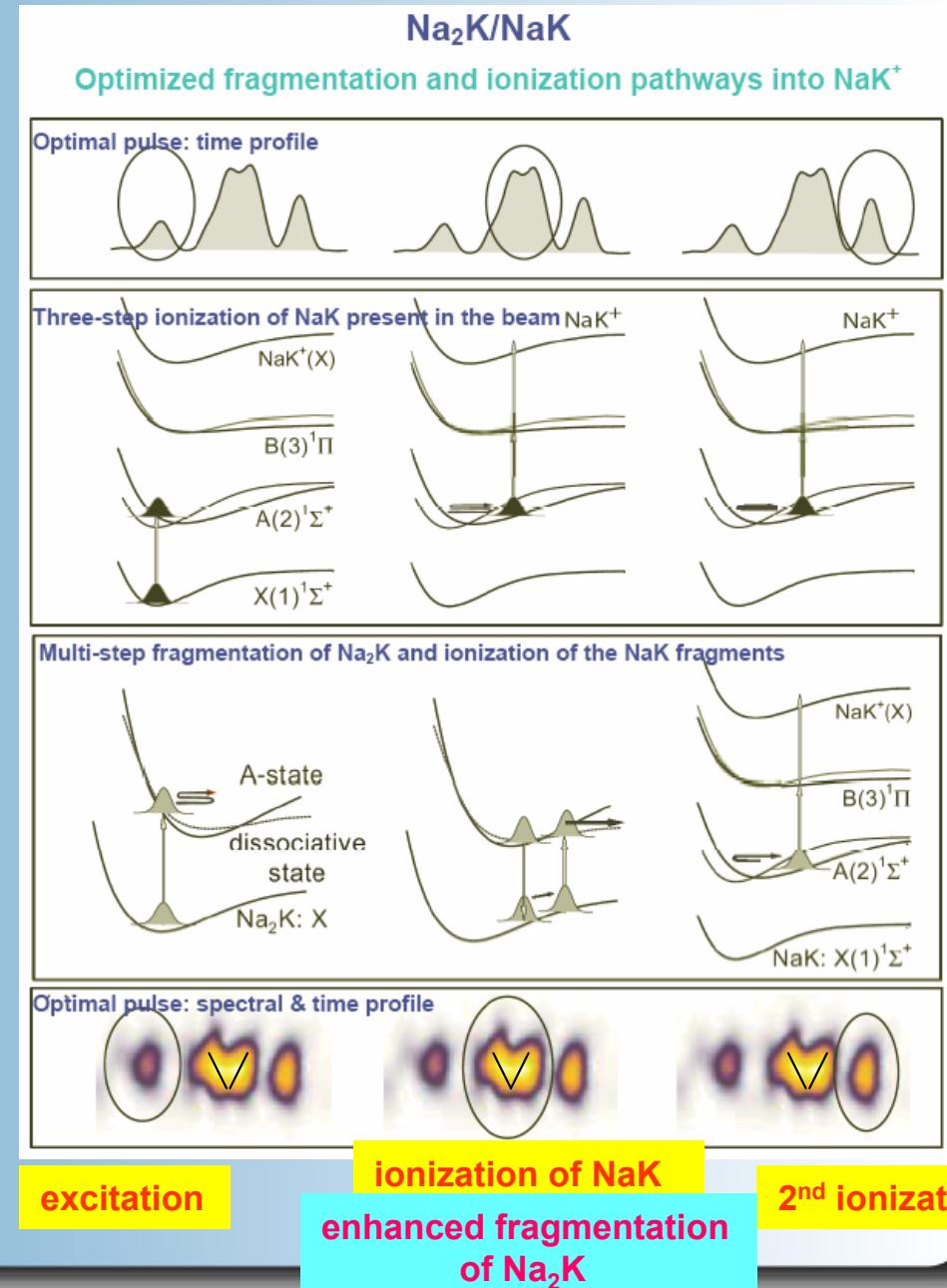
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A. Bartelt, A. Lindinger, C. Lupulescu, S. Vajda, and L. Wöste,
Phys. Chem. Chem. Phys. **6**, 1679 (2004)

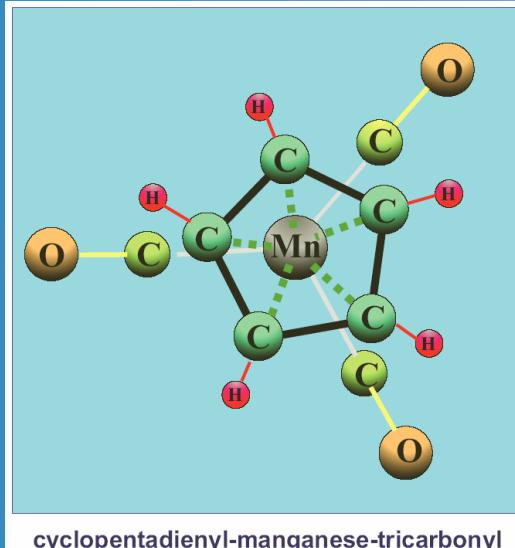
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J. Phys. Chem. A, **108**, 4175 (2004)



Photodissociating molecule $\text{MnCp}(\text{CO})_3$

Analysis of the fragmentation dynamics

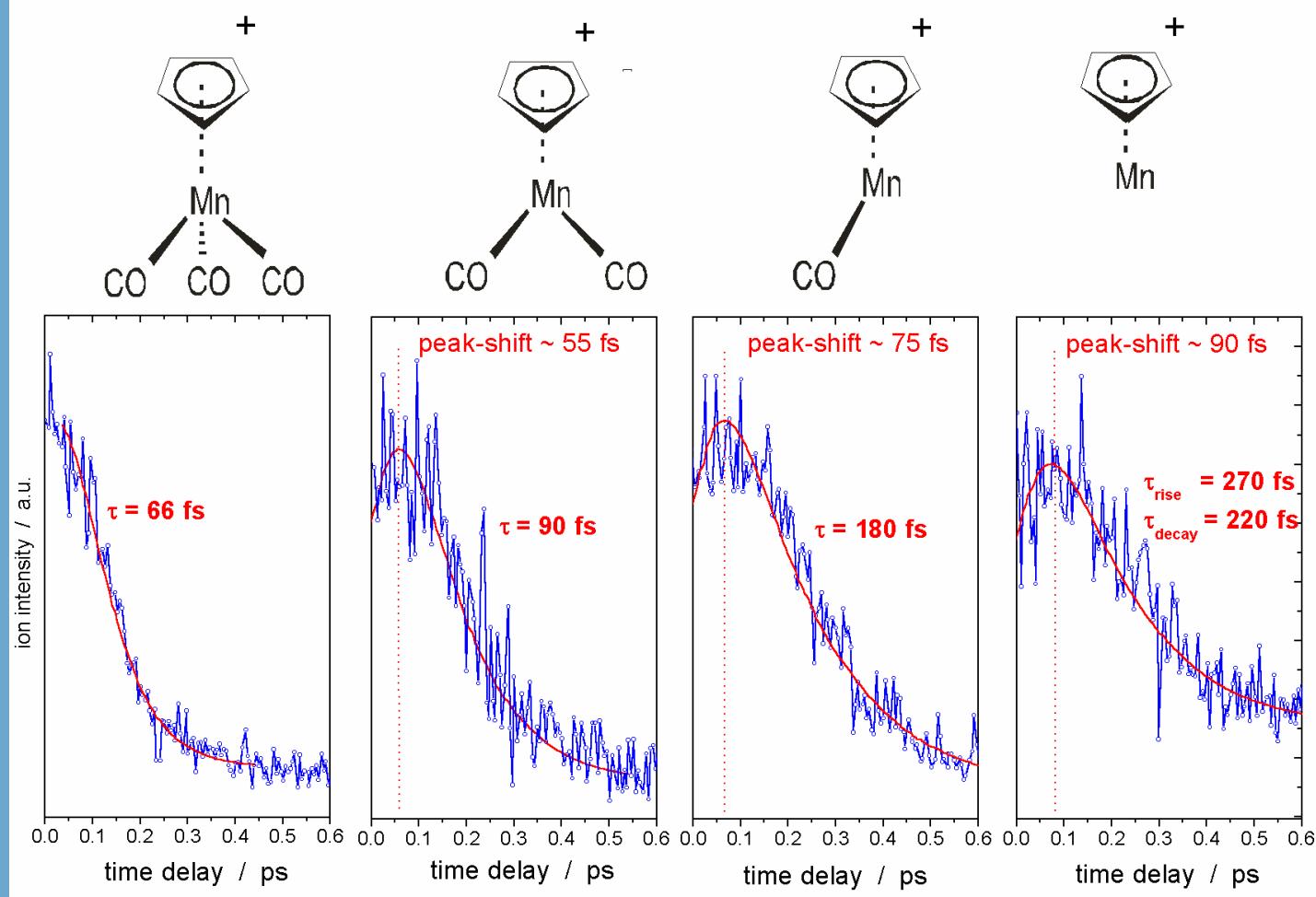
Crystal structure of
 $\text{MnCp}(\text{CO})_3$



A.F. Berndt and R.E. Marsh,
Acta Cryst. **16**, 118 (1963)

Transients of $\text{MnCp}(\text{CO})_3^+$ and its fragment ions

Pump pulse: ~100 fs @ 400 nm, Probe pulse: ~90 fs @ 800 nm (Ti:Sa RegA)



S. Vajda, P. Rosendo-Francisco, C. Kaposta, M. Krenz, C. Lupulescu, and L. Wöste,
Eur. Phys. J. D **16**, 161 (2001)

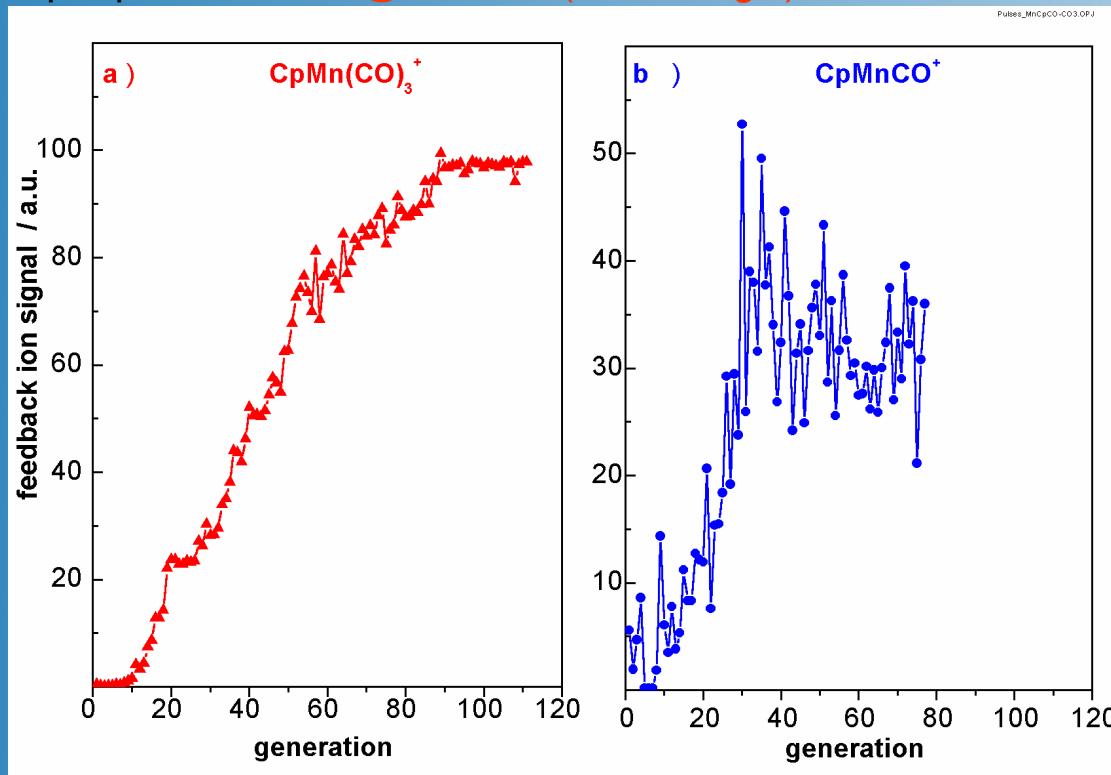
C. Daniel, Jürgen Full, L. González*, C. Kaposta, M. Krenz, C. Lupulescu, J. Manz, Sh. Minemoto, M. Oppel, P. Rosendo-Francisco, S. Vajda* and L. Wöste
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Photodissociating molecule $\text{MnCp}(\text{CO})_3$

Control of the ion yield of the reaction products

Evolution of the ion yield during optimization

Input pulse: ~90 fs @ 800 nm (Ti:Sa RegA)



Pulse form	$\text{CpMnCO}^+ : \text{CpMn}(\text{CO})_3^+$ mass peak ratio
optimized for $\text{CpMn}(\text{CO})_3^+$	1:16
reference puls (no chirp)	1:13
optimized for CpMnCO^+	1:6

S. Vajda, P. Rosendo-Francisco, C. Kaposta, M. Krenz, C. Lupulescu, and L. Wöste, *Eur. Phys. J. D* **16**, 161 (2001)

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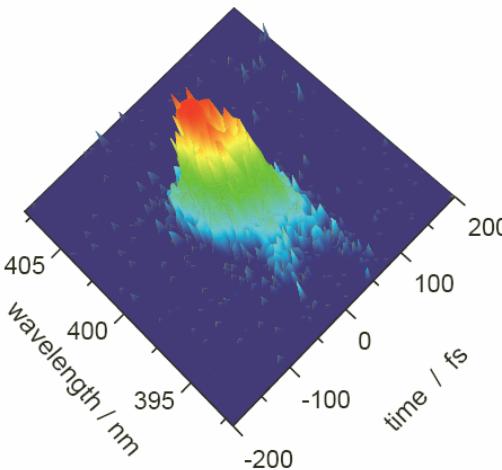
Photodissociating molecule $\text{MnCp}(\text{CO})_3$

Control of the ion yield of the reaction products

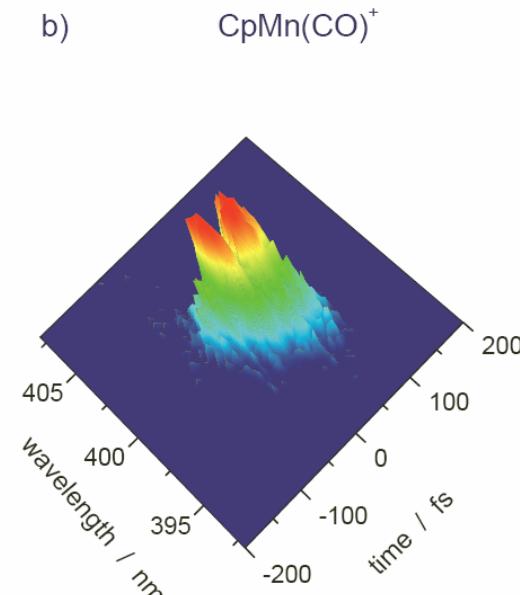
Optimal pulse shapes

SHG FROG traces of the optimized pulses

a)



b)



a) $\text{CpMn}(\text{CO})_3^+$

pulse 1: 38 fs
pulse 2: 40 fs
pulse 3: 36 fs

pulse-sequence
time shift 1-2: 70 fs
time shift 2-3: 100 fs

intensity / a.u.

-300 -200 -100 0 100 200 300

time / ps

b) $\text{CpMn}(\text{CO})^+$

pulse 1: 61 fs
pulse 2: 70 fs

pulse-sequence
time shift 1-2: 80 fs

-300 -200 -100 0 100 200 300

time / ps

S. Vajda, P. Rosendo-Francisco, C. Kaposta, M. Krenz, C. Lupulescu, and L. Wöste, *Eur. Phys. J. D* **16**, 161 (2001)

C. Daniel, Jürgen Full, L. González*, C. Kaposta, M. Krenz, C. Lupulescu, J. Manz, Sh. Minemoto, M. Oppel, P. Rosendo-Francisco, S. Vajda* and L. Wöste *Chem. Phys.* **267**, 247 (2001), Special Issue on „Laser Control of Molecular Dynamics“, Guest Editors : R. de Vivie-Riedle, H. Rabitz, and K. Kompa

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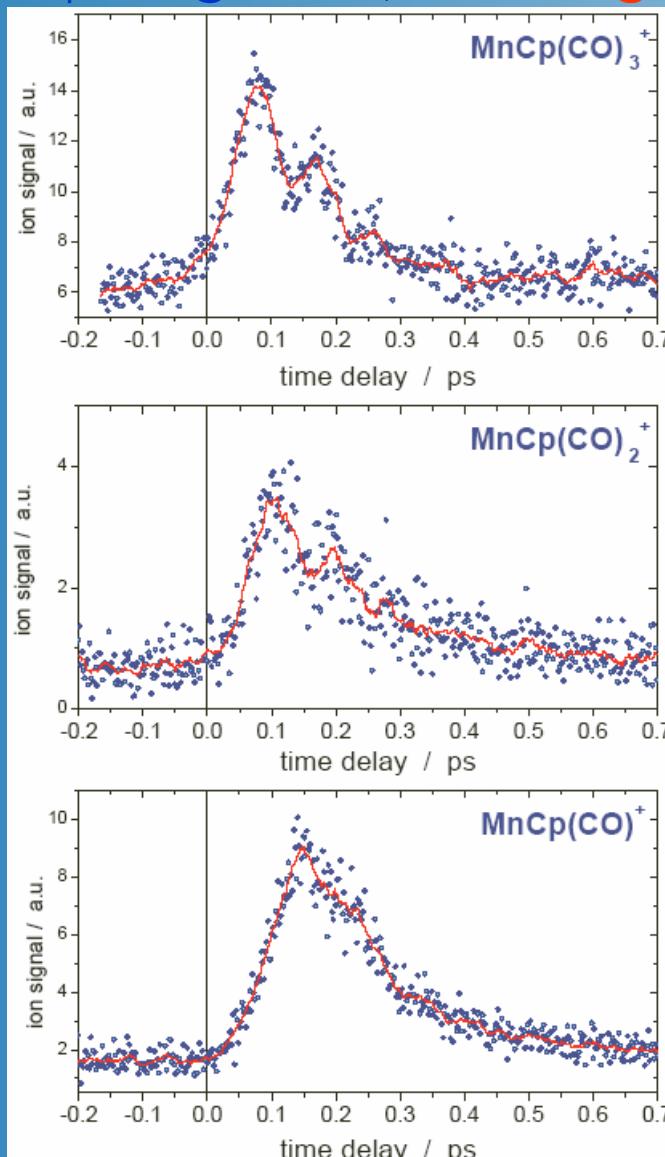


Photodissociating molecule $\text{MnCp}(\text{CO})_3$

Information content of the obtained optimal pulse forms

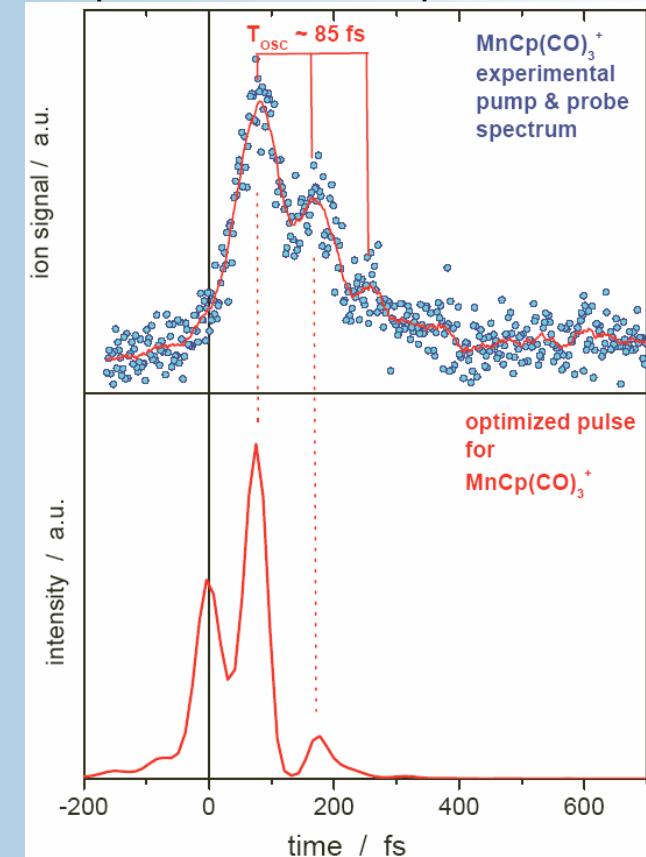
Transients of $\text{MnCp}(\text{CO})_3^+$ and its fragment ions

Pump: 45 fs @ 402.5 nm, Probe : 35 fs @ 805 nm (Ti:Sa Odin)



- Wavepacket dynamics resolved in the $\text{MnCp}(\text{CO})_3^+$ signal.
- Fingerprints of the oscillating wavepacket observed in the transients of the fragment ions as well.

$\text{MnCp}(\text{CO})_3^+$ - Optimal pulse shape and transient spectrum



- Pulse structure reflects:
 - 2 photon excitation
 - 3 photon ionization
 - wavepacket motion

C. Daniel, J. Full, L. González*, C. Lupulescu, J. Manz, A. Merli, S. Vajda*, and L. Wöste, *Science* **299**, 536 (2003)

C. Lupulescu, S. Vajda, A. Lindinger, A. Merli, and L. Wöste, *Phys. Chem. Chem. Phys.*, **6**, 3420 (2004)

Photodissociating molecule MnCp(CO)₃

Theoretical calculations and interpretation of the pump & probe data

• Calculation of PES

ab initio multireference contracted configuration interaction/complete active space selfconsistent field (MRCCI/CASSCF) adiabatic PES of the involved electronic states

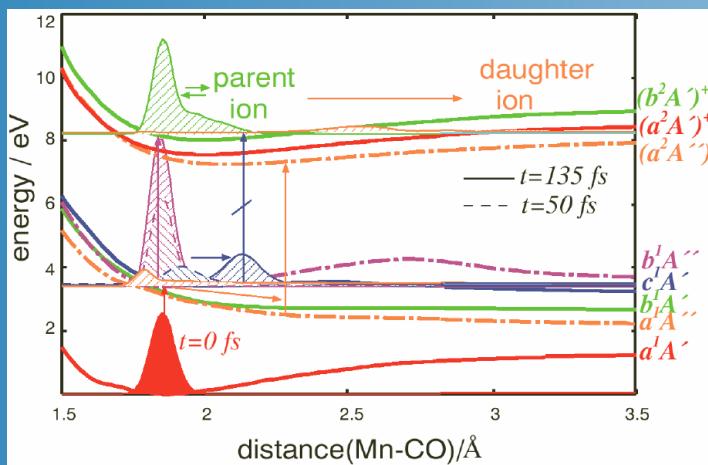
• Calculation of couplings

Numerical nonadiabatic couplings for the neutral CpMn(CO)₃ and for its ion along the one-dimensional dissociative Mn-CO reaction coordinate.

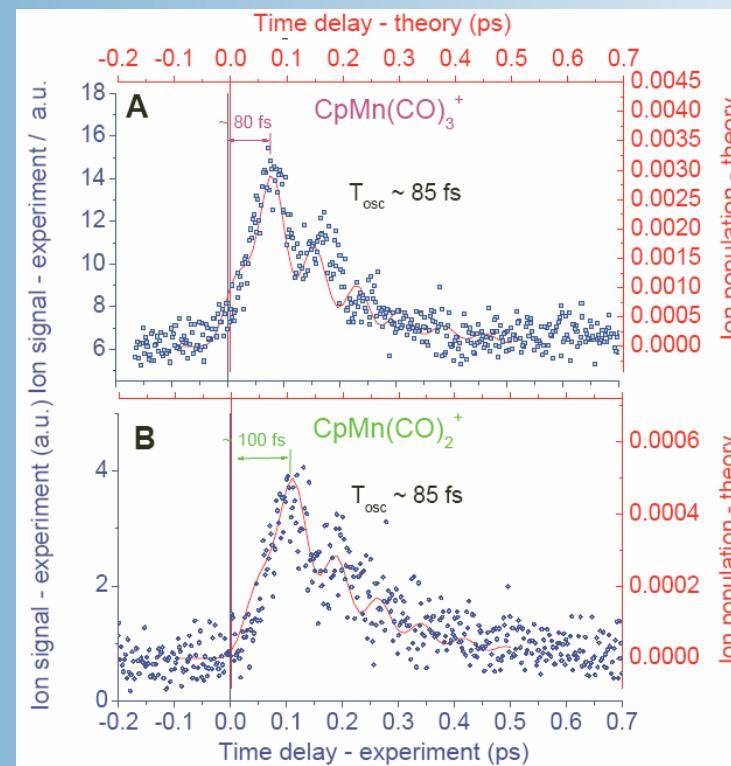
• Quantum simulations of the pump&probe signals

The time evolution of the laser induced process was simulated by representative wave packets calculated as solutions of the time-dependent Schrödinger equation. The laser pulses were introduced in the semiclassical dipole approximation as linear polarized pulses. Interactions with the x, y, and z components of the molecular transition dipole operators were all considered.

The total parent/daughter ion signals were calculated as a superposition of the (classically) rotationally averaged signals of the individual contributions. The resulting pump-probe spectra were calculated as the corresponding yields of populations in the ionic states.



- states ***b*¹*A*''** and ***c*¹*A*'** populated by the pump
- ***b*¹*A*''** oscillates with $T_{osc} = 80$ fs and decays simultaneously to the dissociative ***a*¹*A*''** state
- the ion signal reflects the vibrations and dissociation of the excited molecule
- the wavepacket in ***c*¹*A*'** does not contribute to the signal because of off-resonant probe

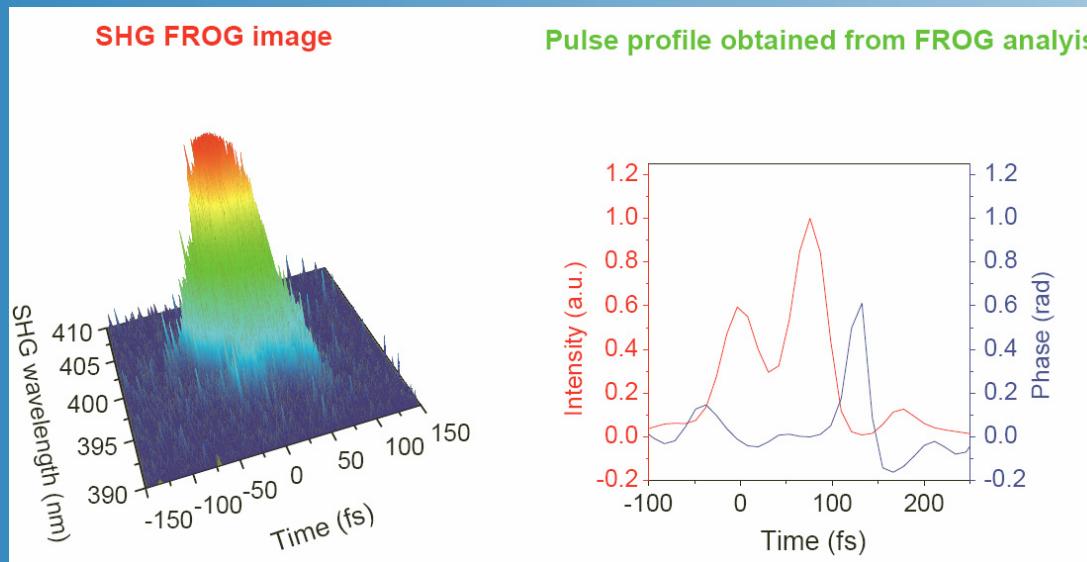


C. Daniel, J. Full, L. González*, C. Lupulescu, J. Manz, A. Merli, S. Vajda*, and L. Wöste,
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Photodissociating molecule MnCp(CO)₃

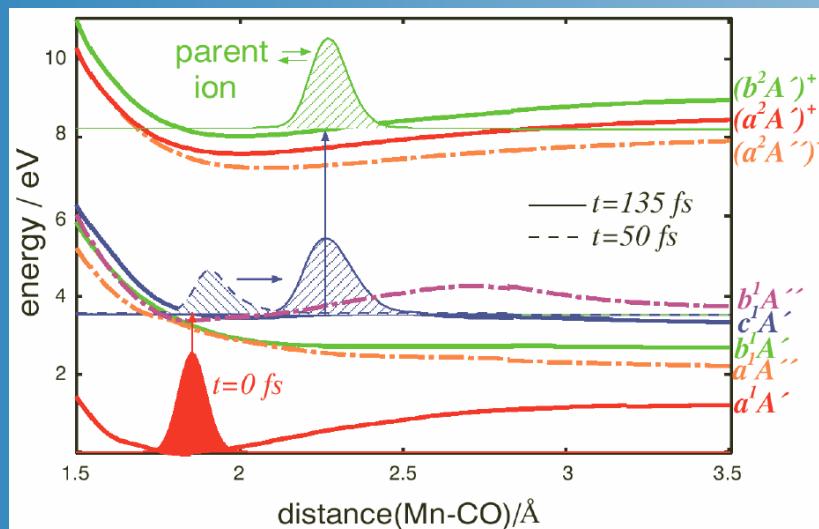
Interpretation of the optimal pulse shape for MnCp(CO)₃⁺ – role of the chirp

Experiment



- First sub-pulse blue-shifted (798.7 nm)
- Second sub-pulse centered @ 800.1 nm
- Third sub-pulse centered @ 801.1 nm
- First sub-pulse: pump
- Second sub-pulse:
 - ionization of the excited molecules
 - excitation of an additional fraction of molecules from their ground state
- Third sub-pulse: ionization of molecules excited by the second sub-pulse.

Theory



- The first sub-pulse of the tailored pulse preferentially populates the non-dissociative **c¹A'** state.
- After 85 fs, the wavepacket reaches the outer turning point where ionization mostly into the **b²A'** state takes place.

C. Daniel, J. Full, L. González*, C. Lupulescu, J. Manz, A. Merli, S. Vajda*, and L. Wöste, *Science* **299**, 536 (2003)

Summary

Analysis & choice of molecular systems

- time-resolved spectroscopy: powerful tool

Active control of multiphotonic processes by means of shaped femtosecond laser pulses

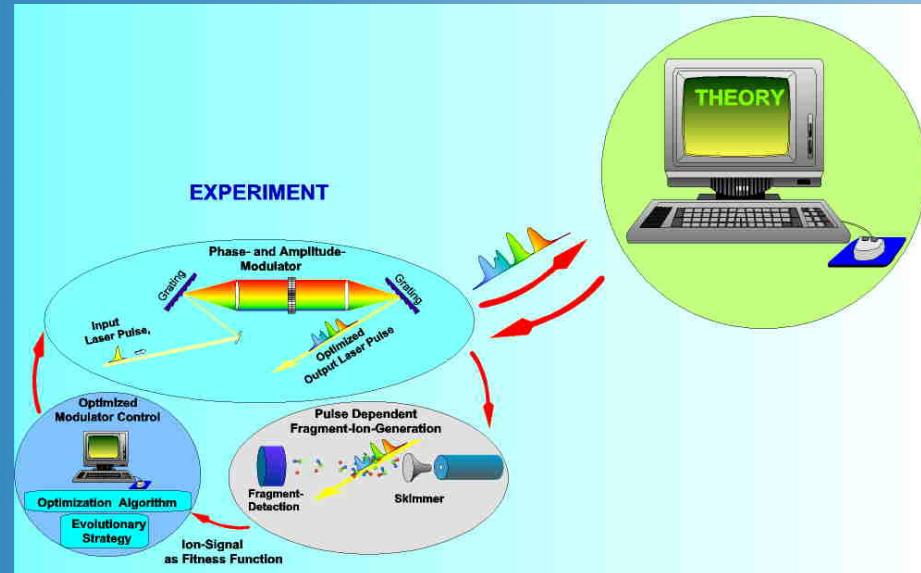
- Na_3 :
control of population of selected coherently coupled bound states
- $\text{MnCp}(\text{CO})_3$:
control of the yield of selected intermediate ions during the ultrafast photofragmentation process
- Na_2K / NaK :
control of the ion yield of Na_2K^+ and NaK^+ during the predissociation of Na_2K

Outlook



Outlook : I. Coherent control

Control pulse shapes delivered by theory



Example: pulse for the control of isomerization in Na_3F_2

J. Phys. Chem. 106 (44) 2002
cover page

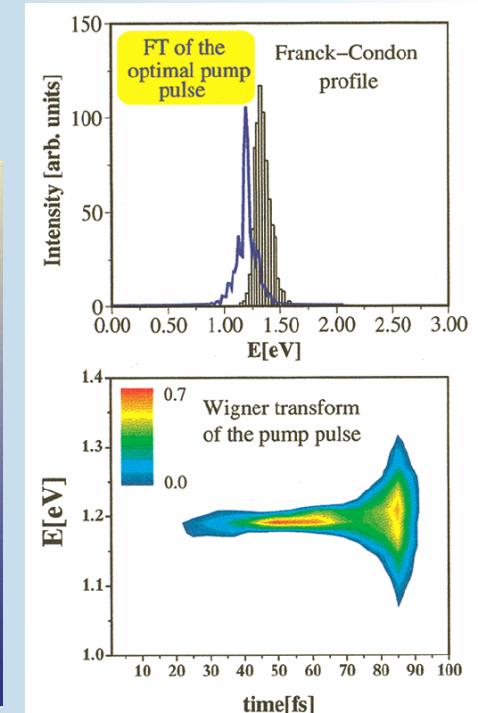
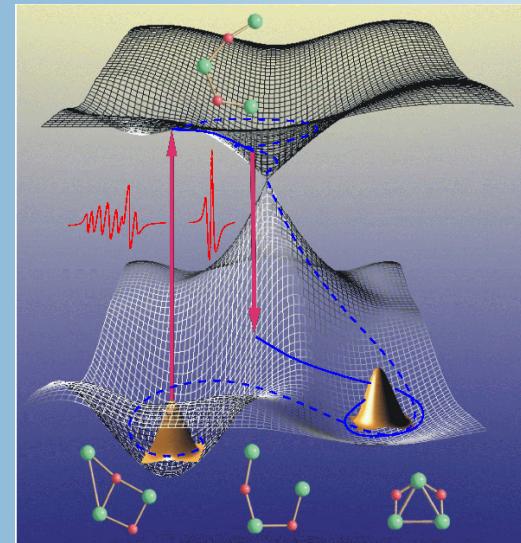


Figure 2. Fourier transform of the optimal pump pulse and the Franck-Condon profile for the first excited state corresponding to the excitation energy $T_e = 1.33$ eV (upper panel (a)) and Wigner transform of the optimal pump pulse (lower panel (b)).

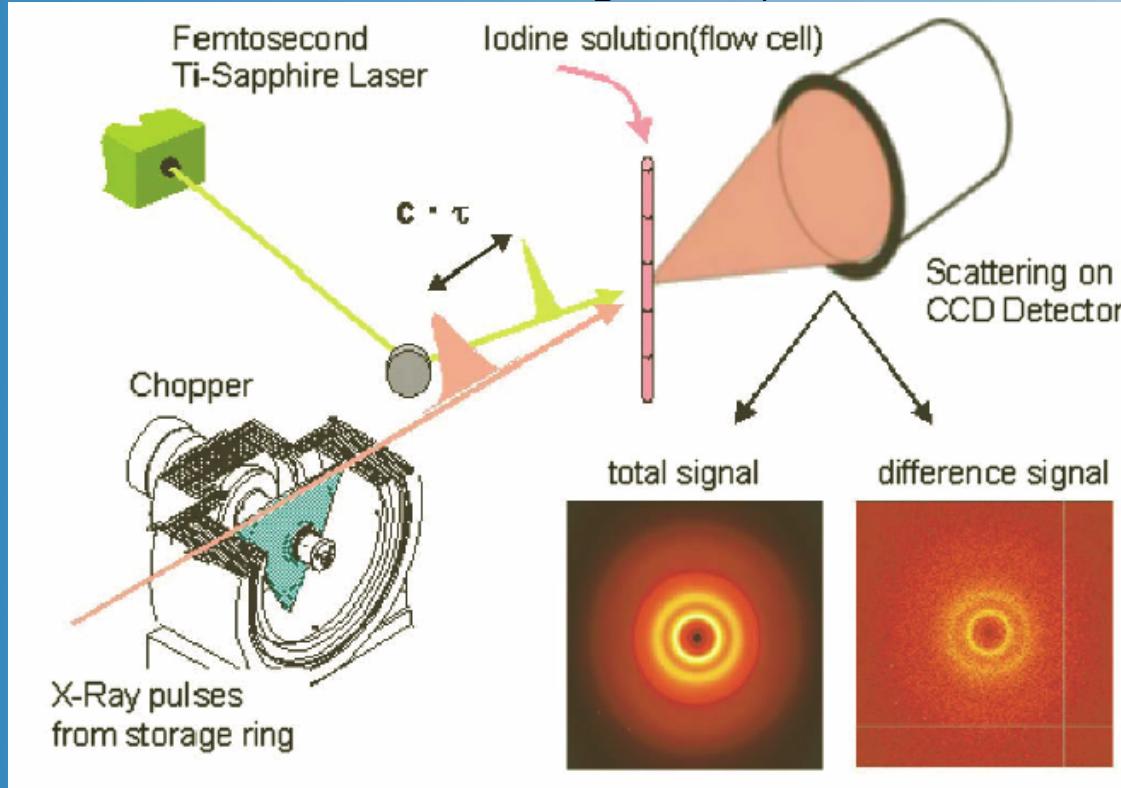
R. Mitric, M. Hartmann, J. Pittner, and V. Bonacic-Koutecky, *J. Phys. Chem.* **106**, 10477 (2002)

Disadvantage of time-resolved laser spectroscopy methods: no direct structural information.

Outlook: II. Time-resolved X-ray studies

Tracking of the motion of atoms possible

Example: recombination of I₂ in CCl₄



A. Plech, M. Wulff, S. Bratos, F. Mirloup, R. Vuilleumier, F. Schotte, and P. Anfinrud,
Phys. Rev. Lett. **92**, 125505 (2004)

Candidate model systems/processes:

- Study and control of photoinduced structural/phase changes of small clusters/molecules in the gas phase and on surfaces.

Relevance:

- nanocatalysis
- photochemistry



- The research was performed in the research group of Prof. Ludger Wöste, Freie Universität Berlin



group photo,
summer 2002

- Pump-probe and control group

- Undergraduate students

Bernd Baptist

Filip Budzyn

Cristina Kaposta

Cosmin Lupulescu

- Collaborations

- Experiment

Thomas Feurer (currently Friedrich-Schiller Universität Jena/MIT, from Sep.1 2004 Universität Bern)

Marcel Krenz (currently Quantronix)

Thomas Leisner (currently Professor at the Technische Universität Ilmenau)

- Theory

Prof. Vlasta Bonačić-Koutecký and coworkers (Humboldt Universität Berlin)

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- Graduate students

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DM/Euro: German Science Foundation – Deutsche Forschungsgemeinschaft, project SFB 450