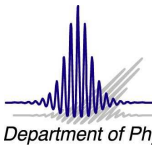


Optimal Control of Photochemistry in the Gas-Phase, Liquid-Phase and on Surfaces

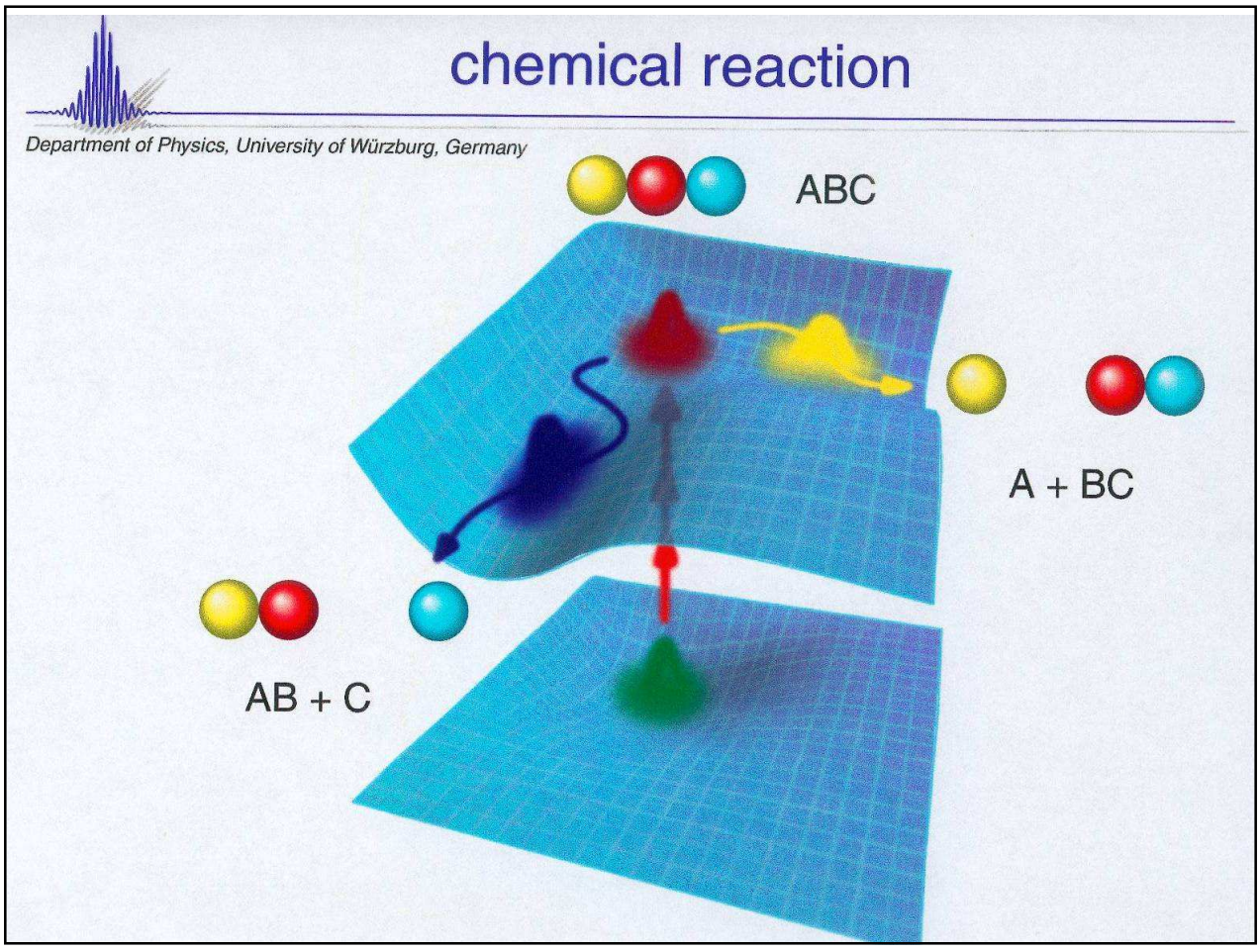
Department of Physics, University of Würzburg, Germany

Gustav Gerber
Physikalisches Institut, Universität Würzburg, Germany
gerber@physik.uni-wuerzburg.de

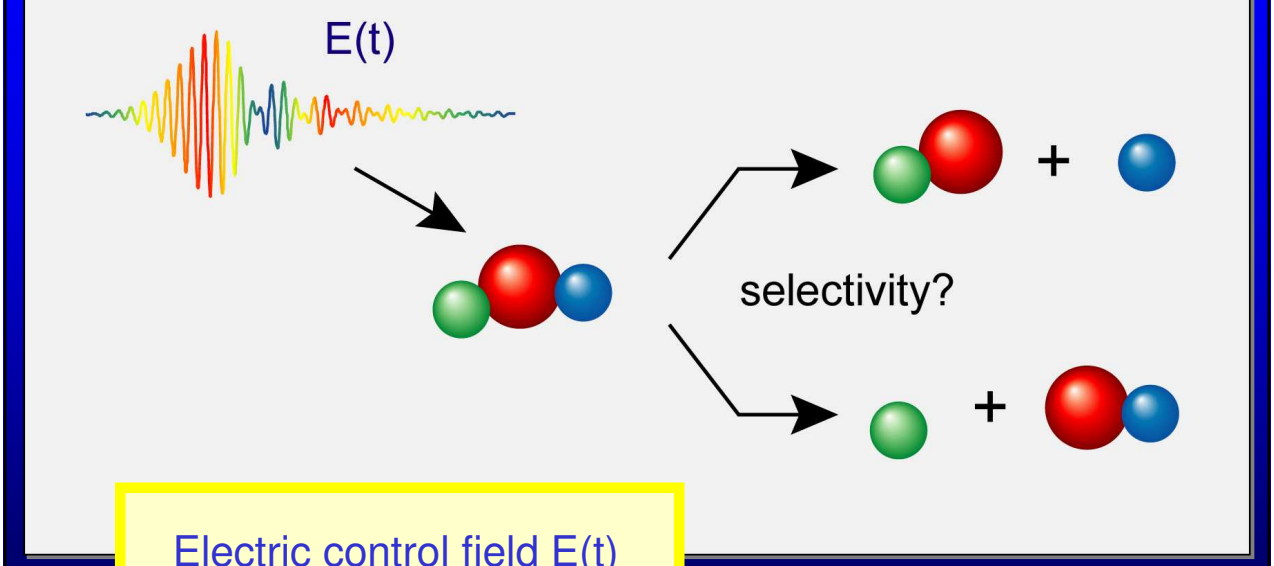
- **adaptive femtosecond pulse shaping**
- **optimal control of molecular dynamics**
  - **- gas phase: photodissociation reactions (bond-cleavage)**
  - **- liquid phase: selective excitation and photoisomerization**
  - **- surface: bond-forming catalytic reactions**
- **optimal control of electron dynamics**
  - **- high harmonic generation**

A. Assion, T. Baumert, T. Brixner, N. Damrauer, G. Krampert, P. Niklaus, P. Nuernberger, V. Seyfried, T. Pfeifer, G. Vogt, D. Walter, C. Winterfeldt, D. Wolpert

DFG: SFB 347 and SPP "Femtosecond Spectroscopy"
EU-Network on Coherence and Control (COCOMO)
Fonds der Chemischen Industrie, BASF AG


chemical reaction
Department of Physics, University of Würzburg, Germany
ABC
A + BC
AB + C

Optical control



Electric control field E(t)

Which one to use?
How to generate it?

Optimal laser control

optimal control theory (OCT)
"electric field design"

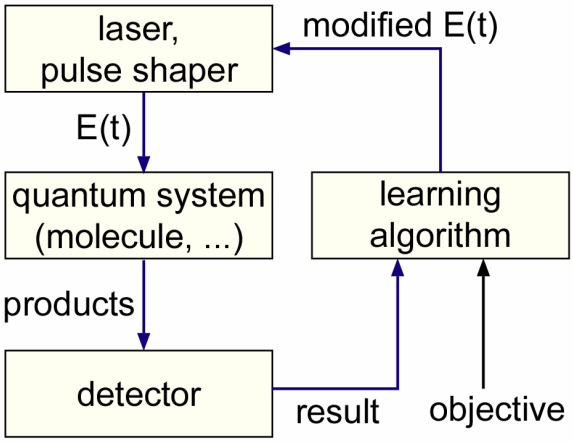
$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = H(t)|\psi(t)\rangle$$

$$H(t) = H_0 - \vec{\mu}\cdot\vec{E}(t)$$

find optimal $\vec{E}(t)$ such that
$|\langle\psi_{\text{target}}|\psi(T)\rangle|$ maximized

Hamiltonian required

optimal control experiment (OCE)
"teaching lasers to control molecules"

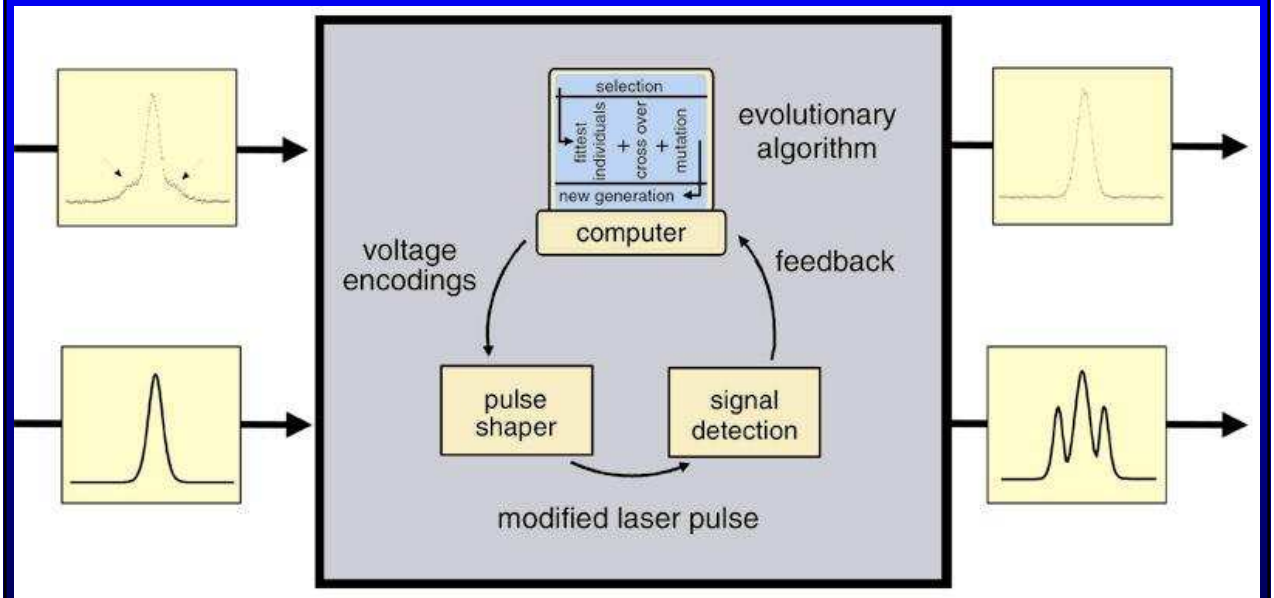


Hamiltonian not required

Tannor and Rice: *JCP* **83**, 5013 (1985)
Rabitz et al.: *PRA* **37**, 4950 (1988)
Kosloff et al.: *CP* **139**, 201 (1989)

Judson and Rabitz:
Phys. Rev. Lett. **68**, 1500 (1992)

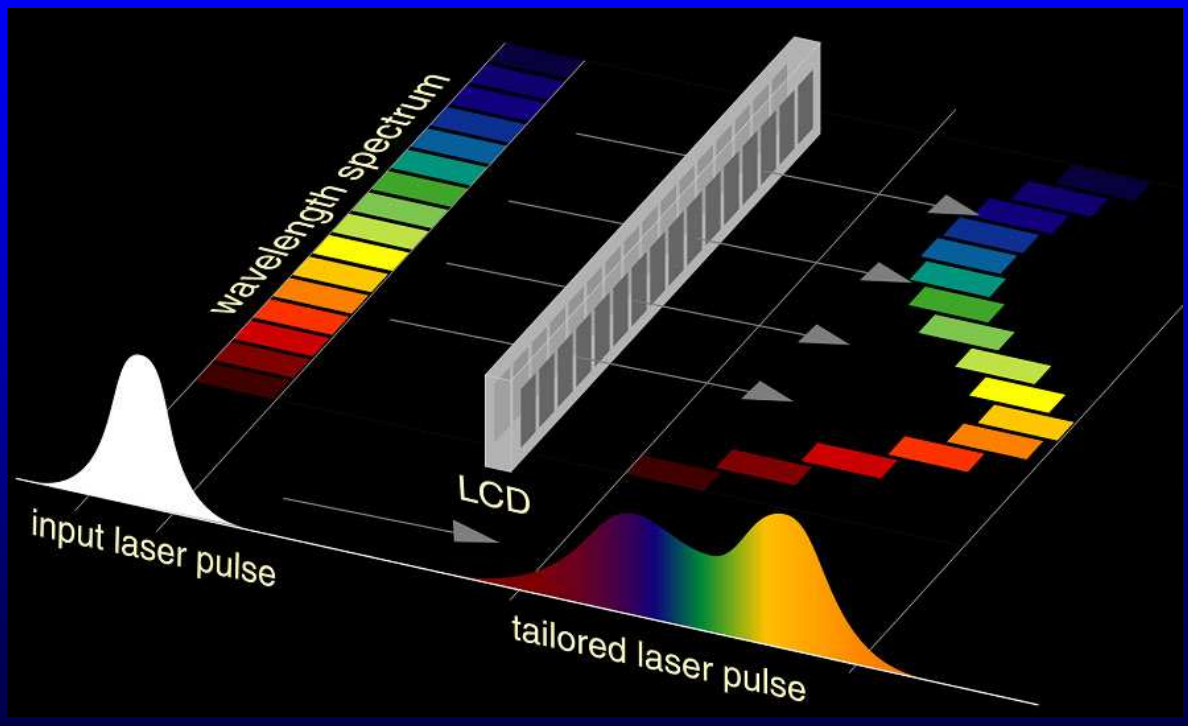
Adaptive pulse shaping



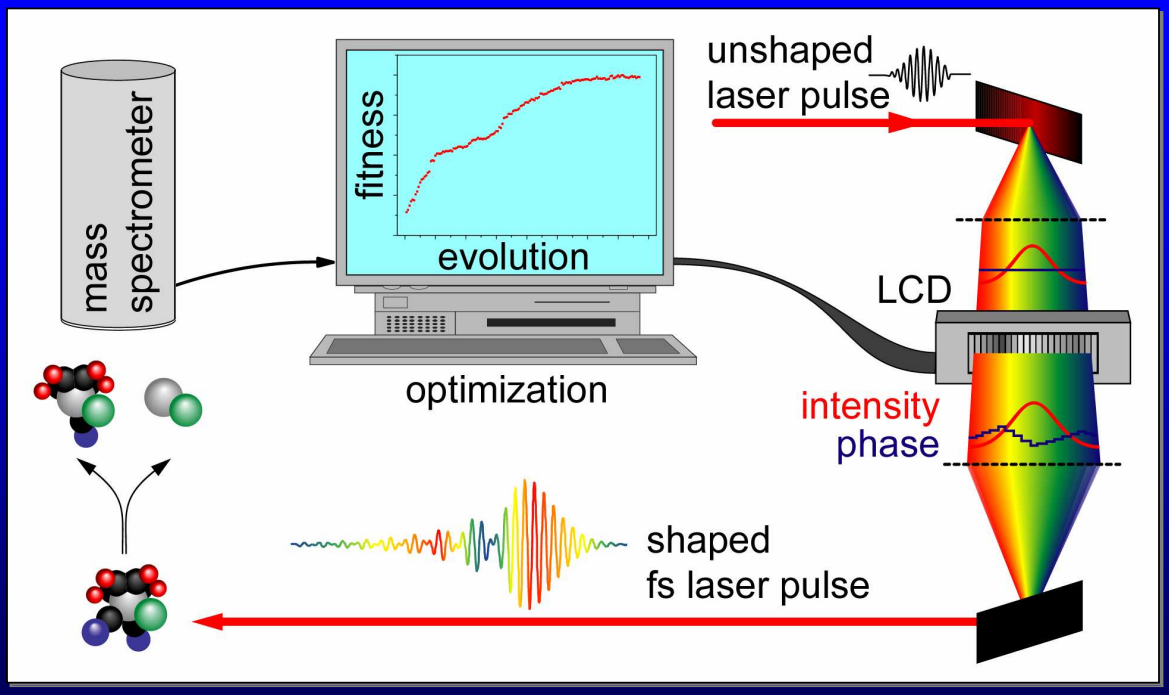
T. Baumert, T. Brixner, V. Seyfried, M. Strehle and G. Gerber: Appl. Phys. B **65**, 779 (1997)
idea of feedback: R.S. Judson and H. Rabitz: Phys. Rev. Lett. **68**, 1500 (1992)

D. Yelin et al.: Opt. Lett. **22**, 1793 (1997)
C.J Bardeen et al.: CPL **280**, 151 (1997)

Femtosecond pulse shaping

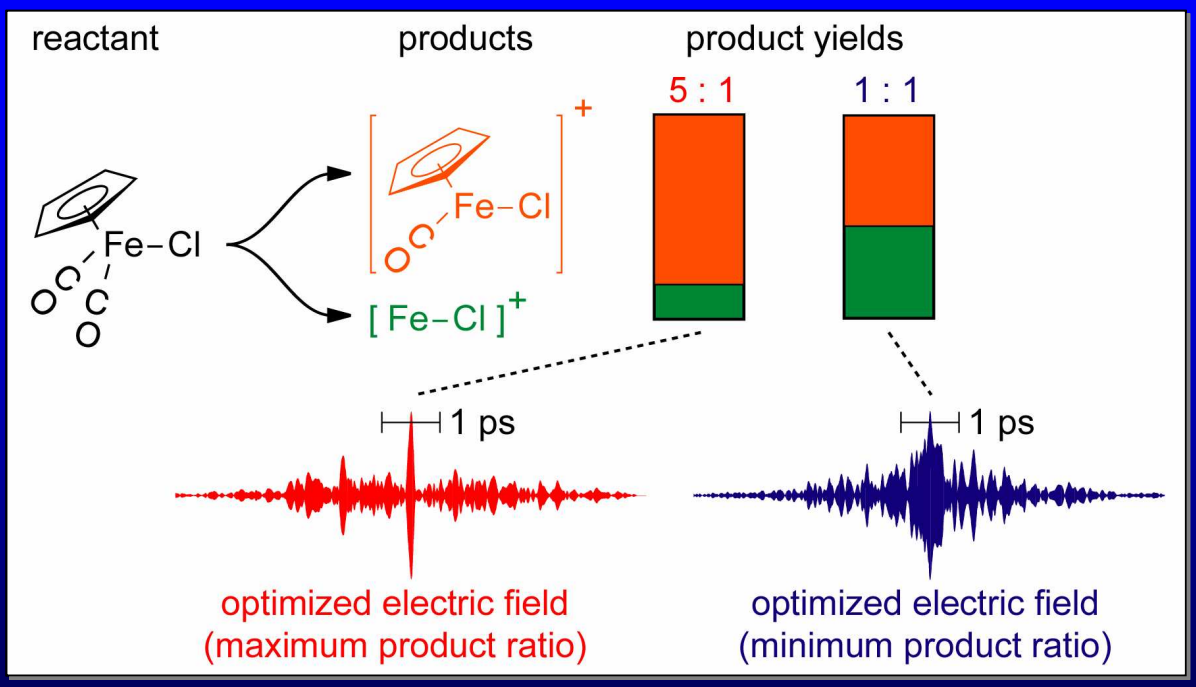


Learning loop with feedback



suggestion: Rabitz: *PRL* **68**, 1500 (1992) initial exp. (tech.): *APB* **65**, 779 (1997)
(gas): *Science* **282**, 919 (1998)
(liquid): *Nature* **414**, 57 (2001)

A laser-controlled molecule

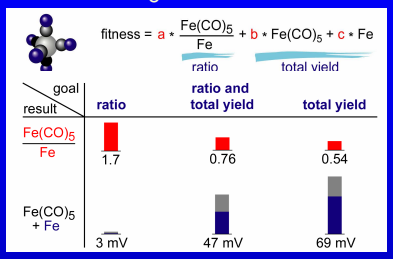


Fully automated control

Science **282**, 919 (1998)
cited >500×

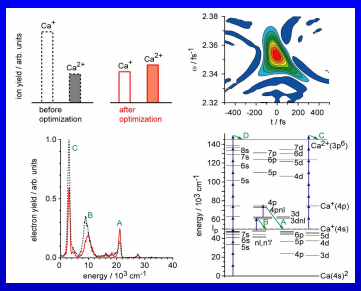
Adaptive gas-phase control

$Fe(CO)_5$ general fitness



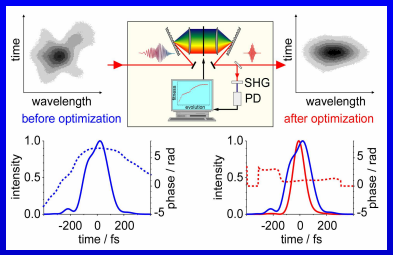
JPC A **103**, 10381 (1999)

Ca double ionization



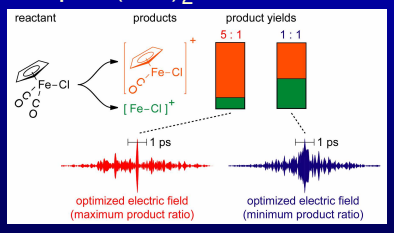
Chem. Phys. Lett. **408**, 65 (2005)

SHG pulse compression



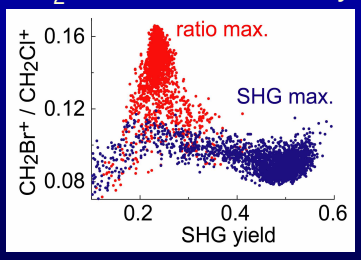
Appl. Phys. B **65**, 779 (1997)
Appl. Phys. B **68**, 281 (1999)

$CpFe(CO)_2X$, X=Cl,Br



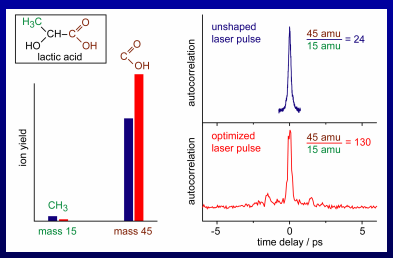
Science **282**, 919 (1998)
Chem. Phys. **267**, 241 (2001)
J. Org.met. Chem. **661**, 199 (2002)

CH_2ClBr bond selectivity



Eur. Phys. J. D **20**, 71 (2002)

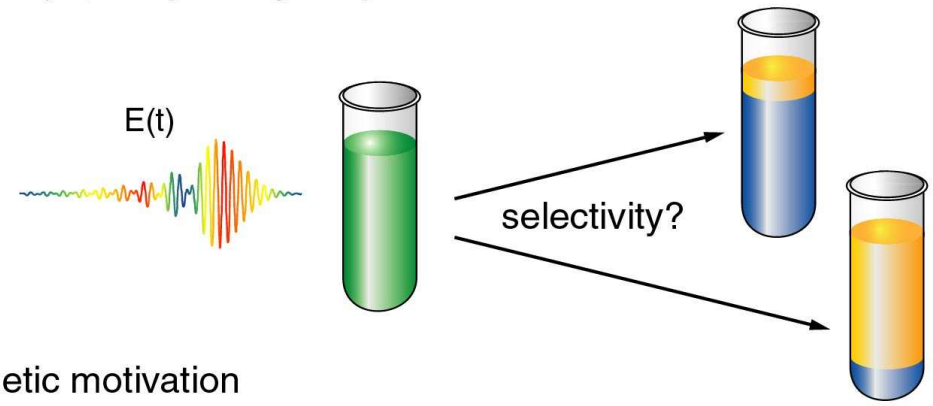
lactic acid conversion



J. Mod. Opt. **50**, 539 (2003)

Quantum control in the liquid phase

Department of Physics, University of Würzburg, Germany



Synthetic motivation

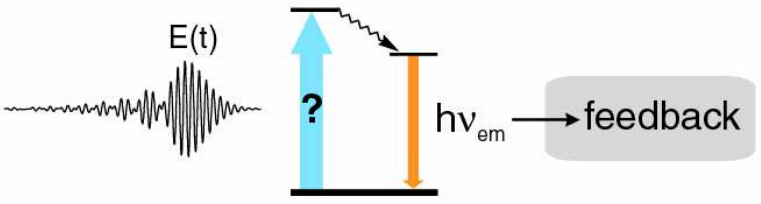
- If control of photochemistry is to become useful to chemists, it must be viable in solution

Physical motivation

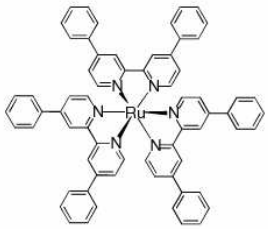
- Can photochemical control be achieved in the presence of solvent/solute interactions?
- Can control results provide insight into solution-phase dynamics?

Photophysical Emission for Feedback Control of Molecules in Solution

Department of Physics, University of Würzburg, Germany

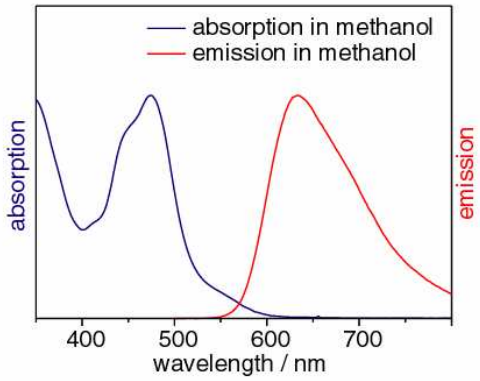


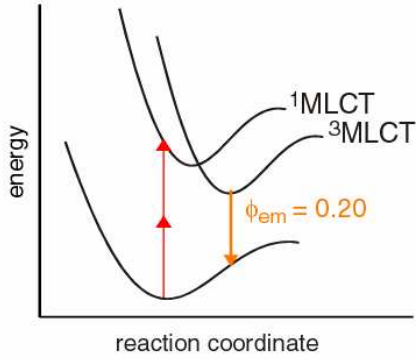
- Emission yield provides information about excited-state population.
- Used as a feedback signal for *control* of excitation.



$[Ru(dpb)_3]^{2+}$

dpb = 4,4'-diphenyl-2,2'-bipyridine





Optimization of emission/SHG ratio

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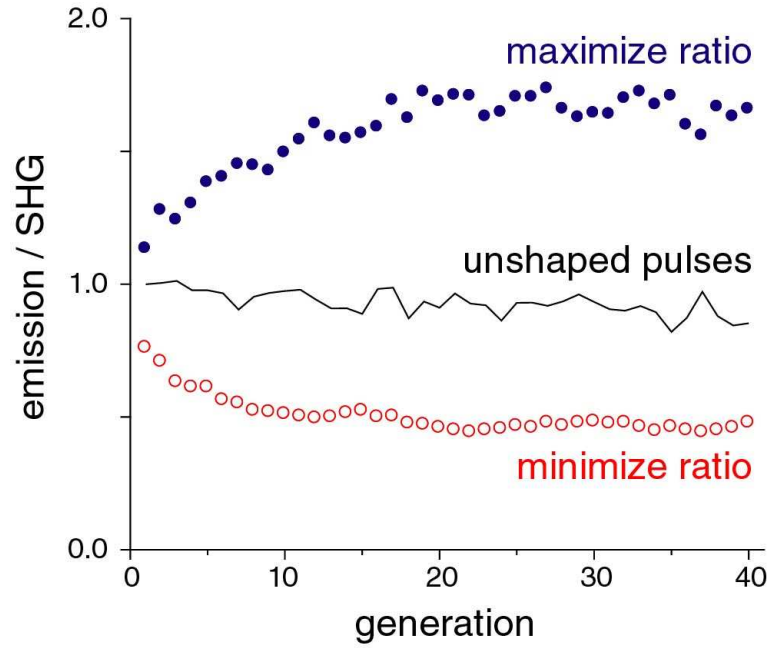


ratio as feedback removes dominant intensity dependence

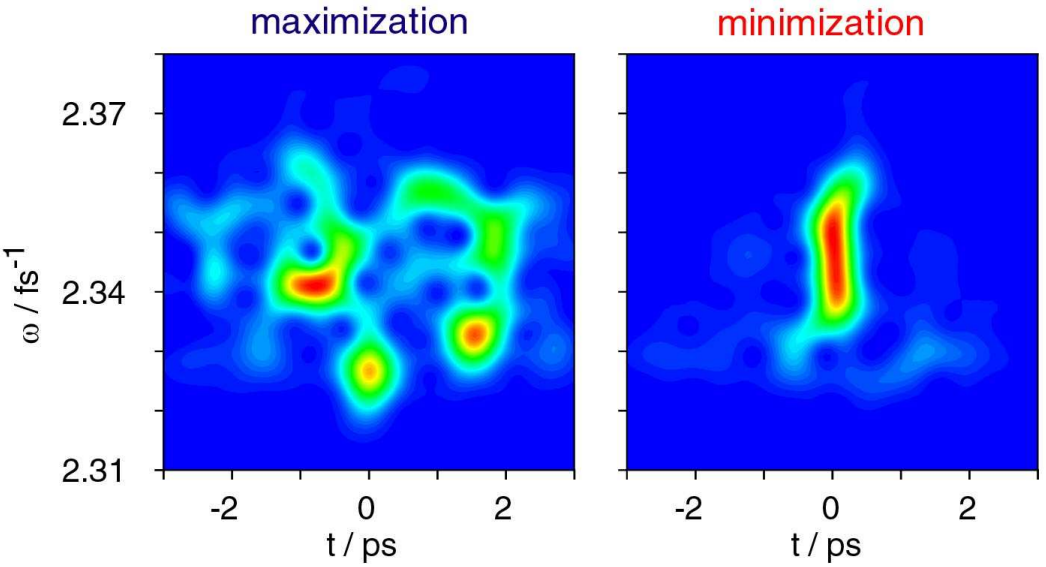
provides sensitivity to molecular properties

J.Chem.Phys. **118**, 3692 (2003)

Optimized Electric Fields for Maximization and Minimization of Emission/SHG for $[Ru(dpb)_3]^{2+}$

Department of Physics, University of Würzburg, Germany

Optimized electric fields in husimi representation:

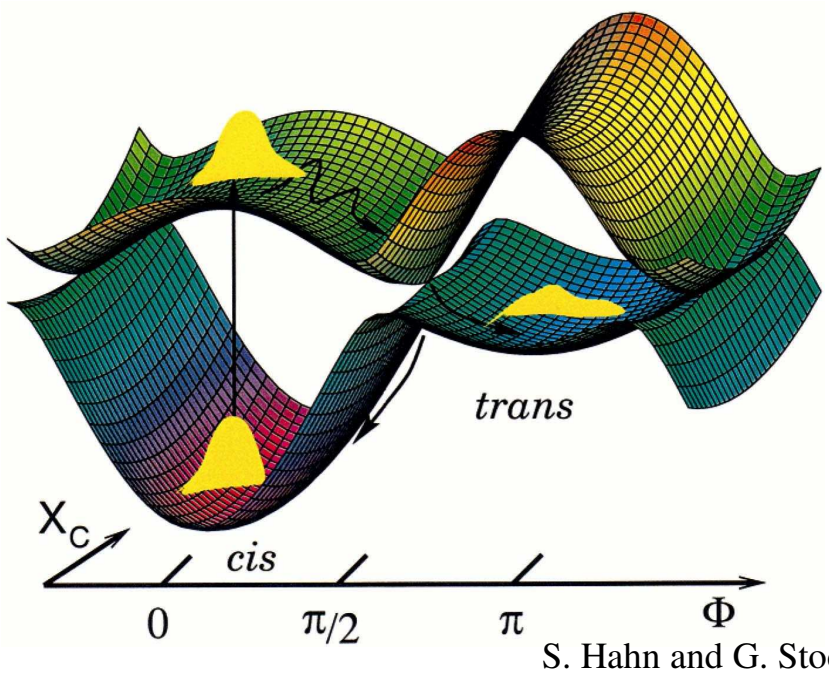


- Result shows selectivity between excitation pathways has been achieved

J.Chem.Phys. **118**, 3692 (2003)

cis-trans Isomerization in rhodopsin

Department of Physics, University of Würzburg, Germany

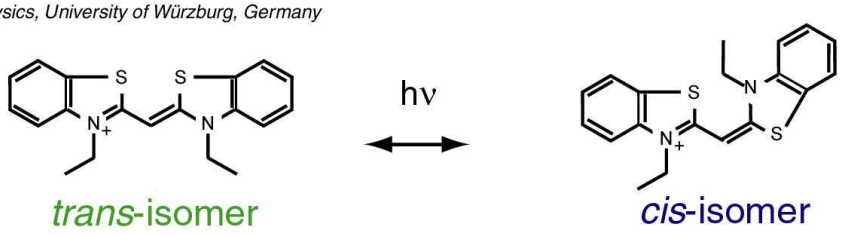


S. Hahn and G. Stock

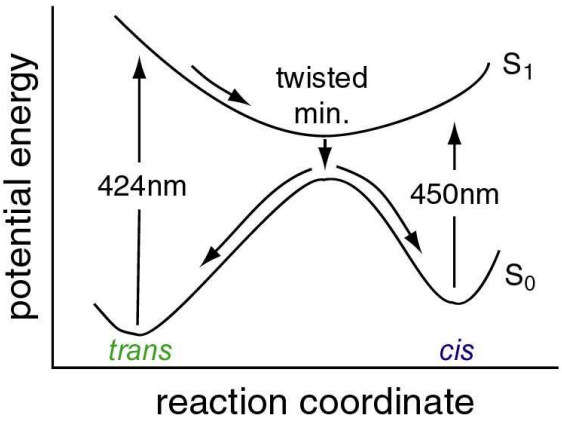
J. Phys. Chem. B, 104, 1146 (2000)

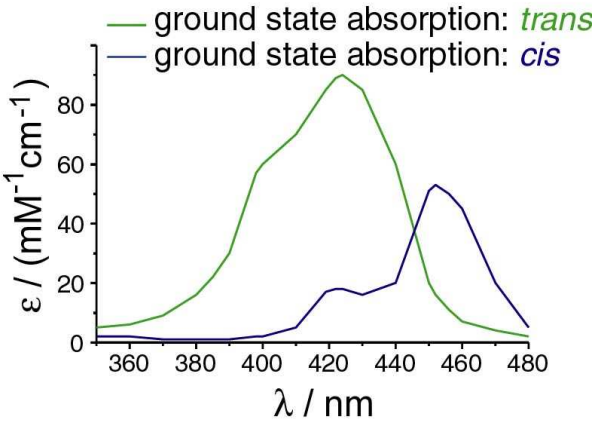
3,3 diethyl-2,2 thiacyanine iodide - NK88

Department of Physics, University of Würzburg, Germany



trans-isomer ⟷ *cis*-isomer





Experimental setup

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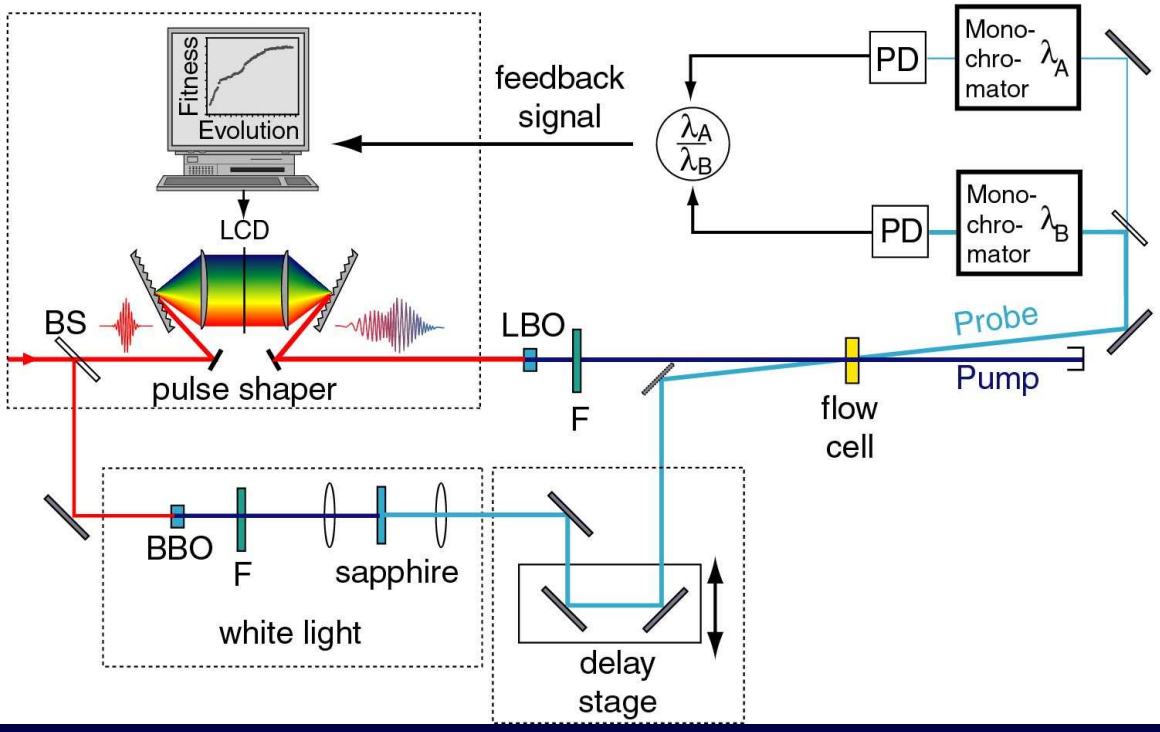
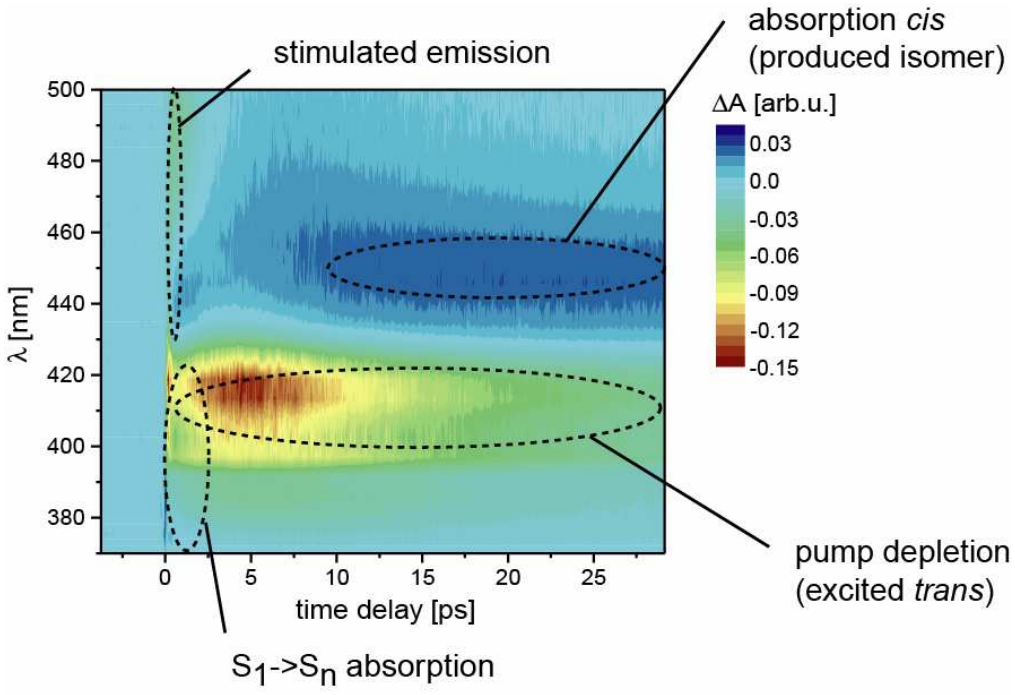


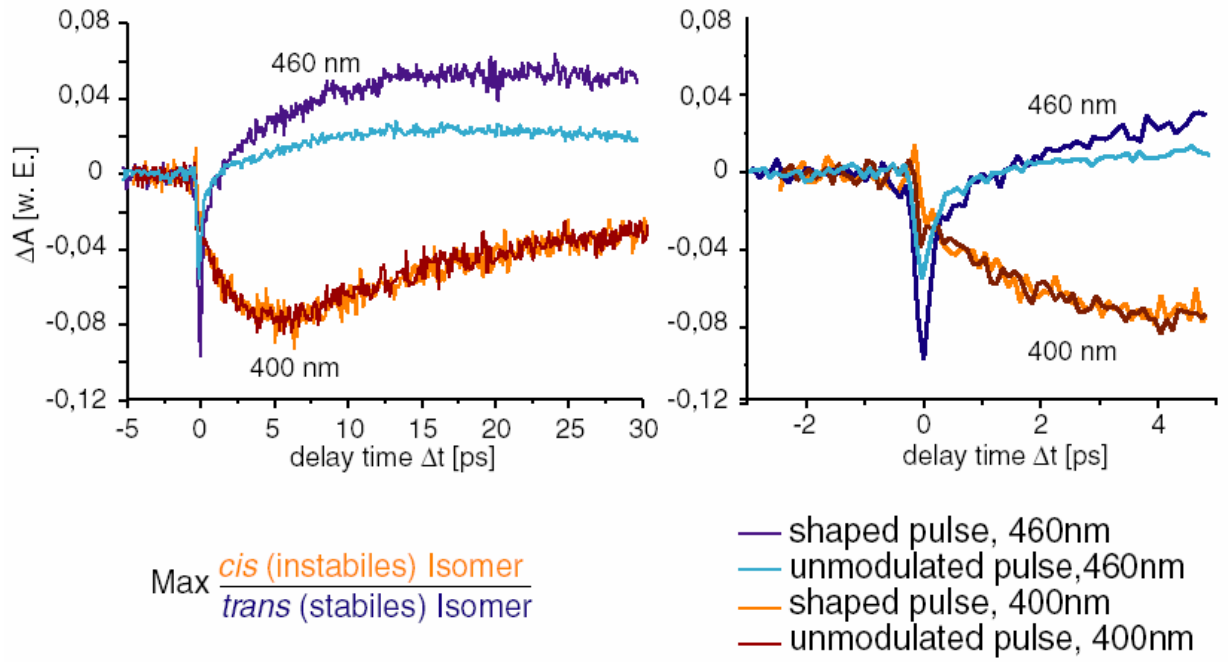
NK88 – transient absorption, 370nm to 500nm

Department of Physics, University of Würzburg, Germany



NK88 - optimization results

Department of Physics, University of Würzburg, Germany



$$\text{Max}\ \frac{\textit{cis}\ \text{(instabiles) Isomer}}{\textit{trans}\ \text{(stabiles) Isomer}}$$

NK88 - control of photoisomerization

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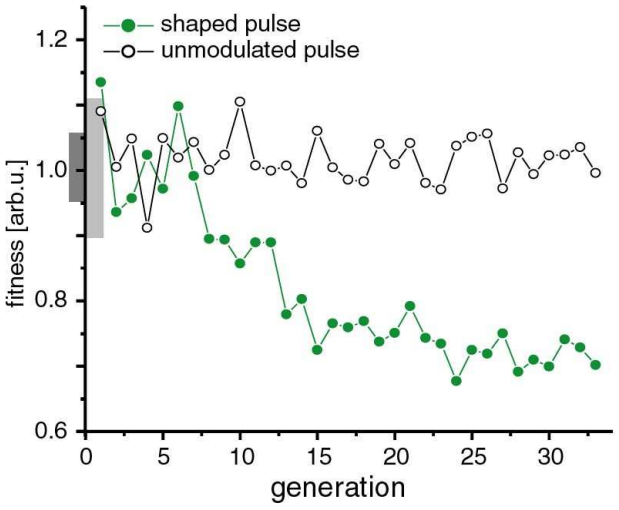
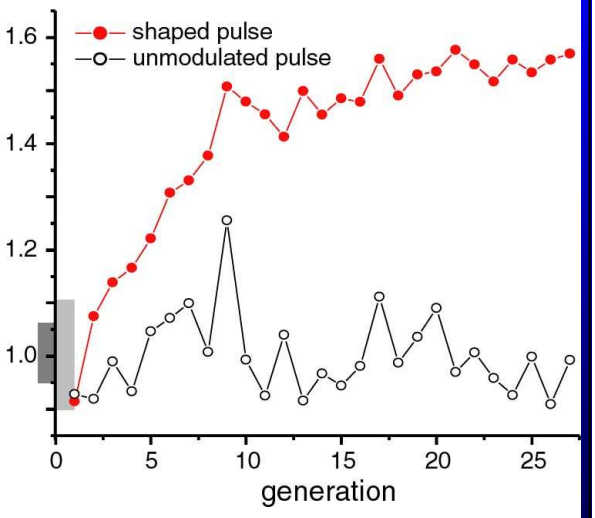
suppression of isomerization



enhancement of isomerization

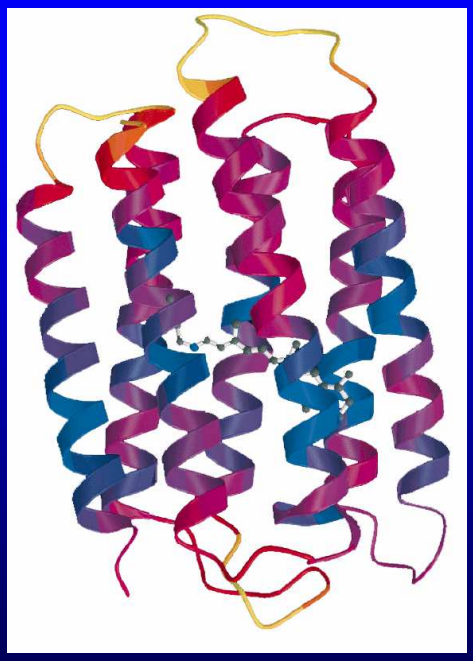


Min. $\frac{\text{cis-isomer}}{\text{trans-isomer}}$

intensity
chirp

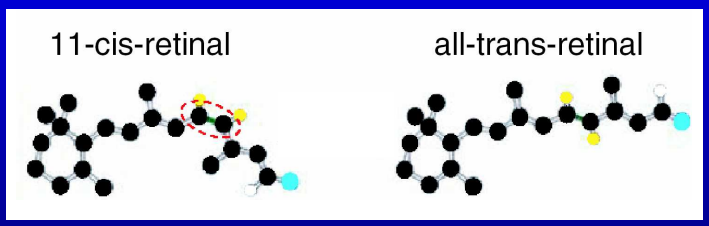
Max. $\frac{\text{cis-isomer}}{\text{trans-isomer}}$

Retinal in bacteriorhodopsin



C. Shank: *Science* **254**, 412 (1991)
R. Henderson: *J. Mol. Biol.* **259**, 393 (1996)

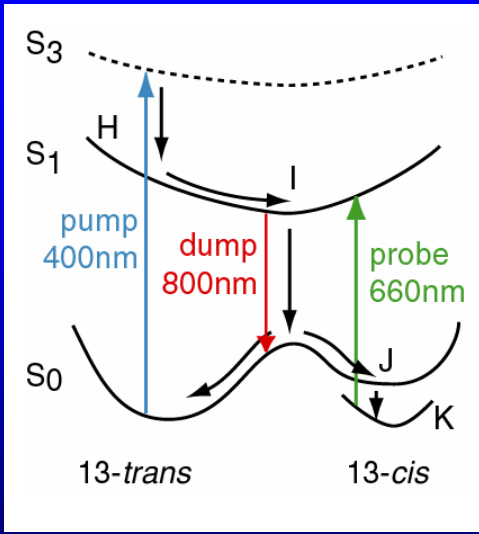
Primary step of vision:
cis-trans isomerization

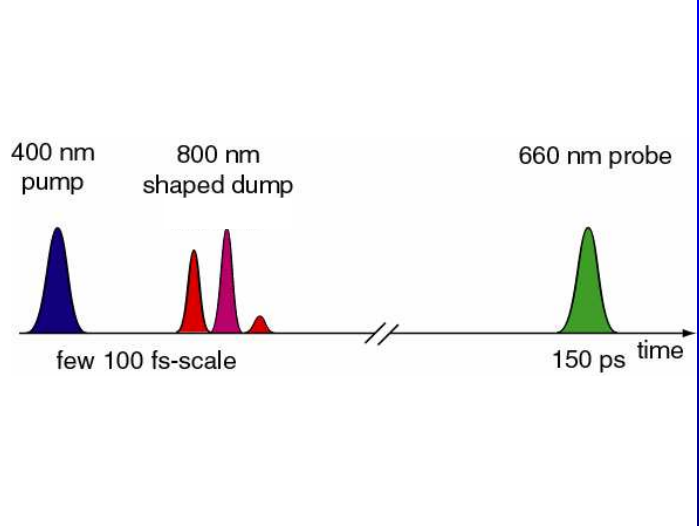


Femtosecond spectroscopy:

C. Shank: *Science* **240**, 777 (1988)
R.M. Hochstrasser: *Chem. Phys. Lett.* **261**, 389 (1996)
D. Oesterhelt: *Annu. Rev. Biophys. Biomol. Struct.* **28**, 367 (1999)
S. Ruhman: *J. Phys. Chem B.* **103**, 5122 (1999)
M.A. El-Sayed: *PNAS* **98**, 8675 (2001)

Learning from optimal control

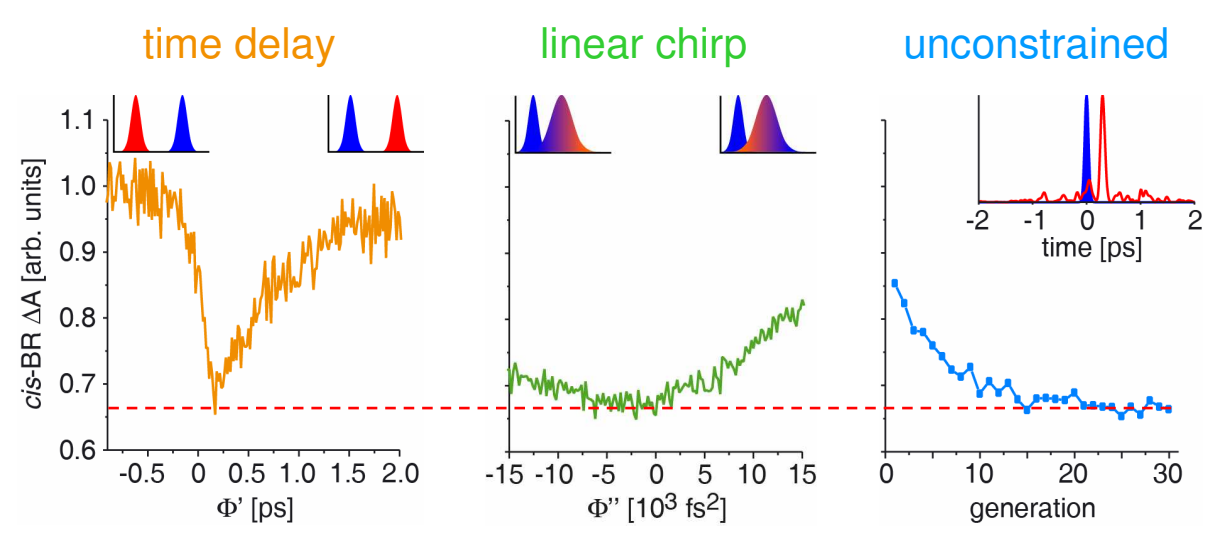




What is the most efficient dump pulse?

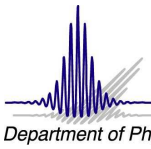
→ Information on S_1 wave packet and PES

Reverse control



optimum de-excitation: short NIR pulse at 200 fs delay

→ compact S_1 wave packet



Optimal Control Experiments

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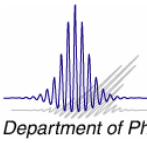
- molecular gas phase photodissociation
  (selective bond-cleavage)
- selective excitation of complex molecules
  in the liquid phase
- photoisomerization of complex molecules
  in the liquid phase

- selective bond-forming reactions



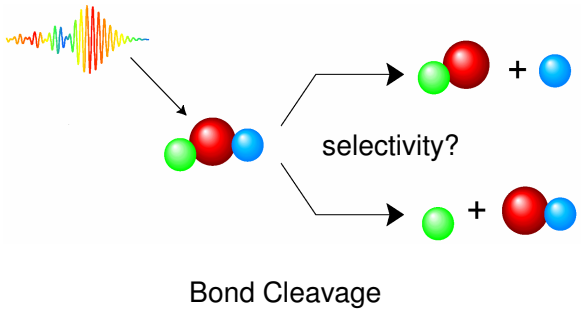
Department of Physics, University of Würzburg, Germany

Femtosecond Laser-Assisted Catalytic Surface Reactions of Syngas ($CO+H_2$) and their Optimization by Tailored Laser Pulses

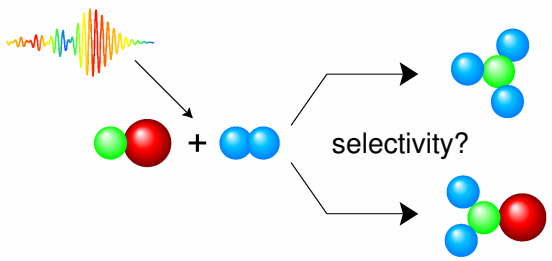
Patrick Nuernberger[1], Daniel Wolpert[1], Horst Weiss[2], and Gustav Gerber[1]

[1] Physikalisches Institut, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

[2] BASF AG, Polymer Research Division, 67056 Ludwigshafen, Germany



Bond Cleavage



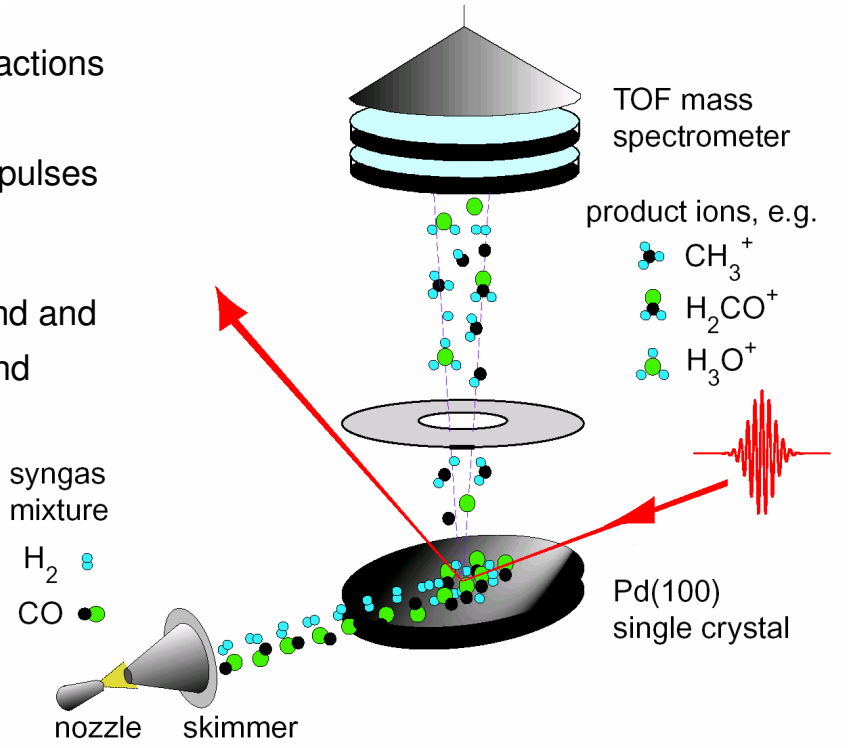
Bond Formation

bond-forming catalytic surface reaction

Department of Physics, University of Würzburg, Germany

catalytic surface reactions
assisted by
femtosecond laser pulses

bond-formation:
- ions with C-H bond and
- ions with O-H bond



syngas stream onto the Pd surface

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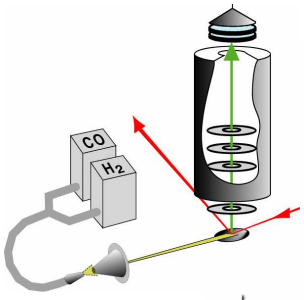
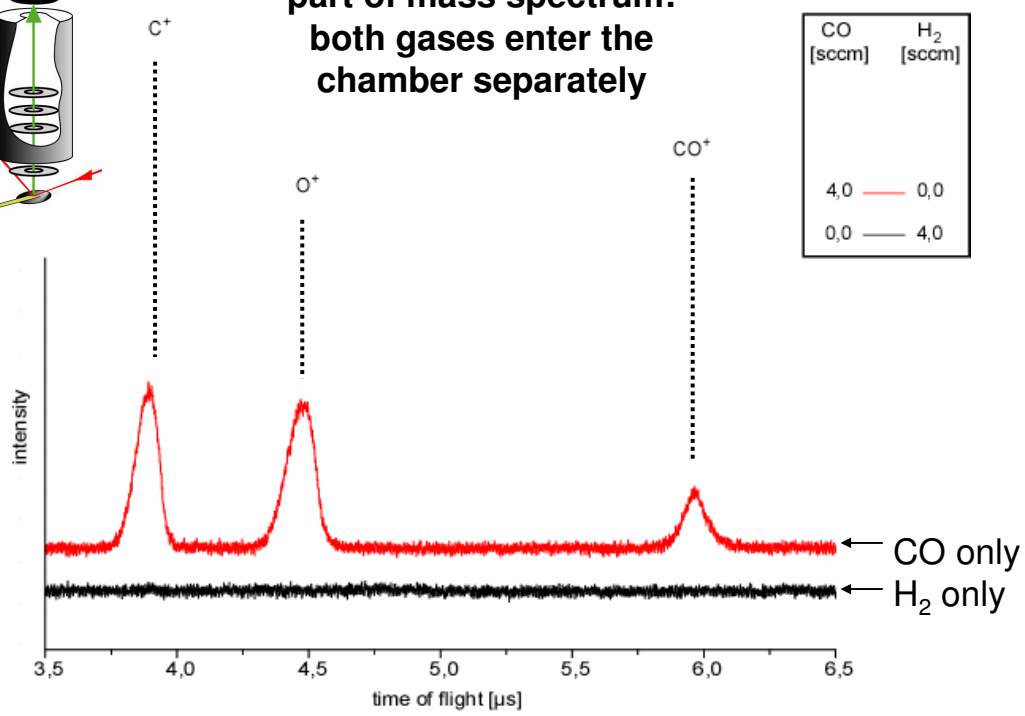
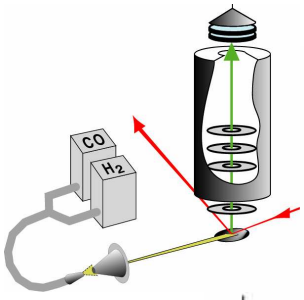


part of mass spectrum: both gases enter the chamber separately

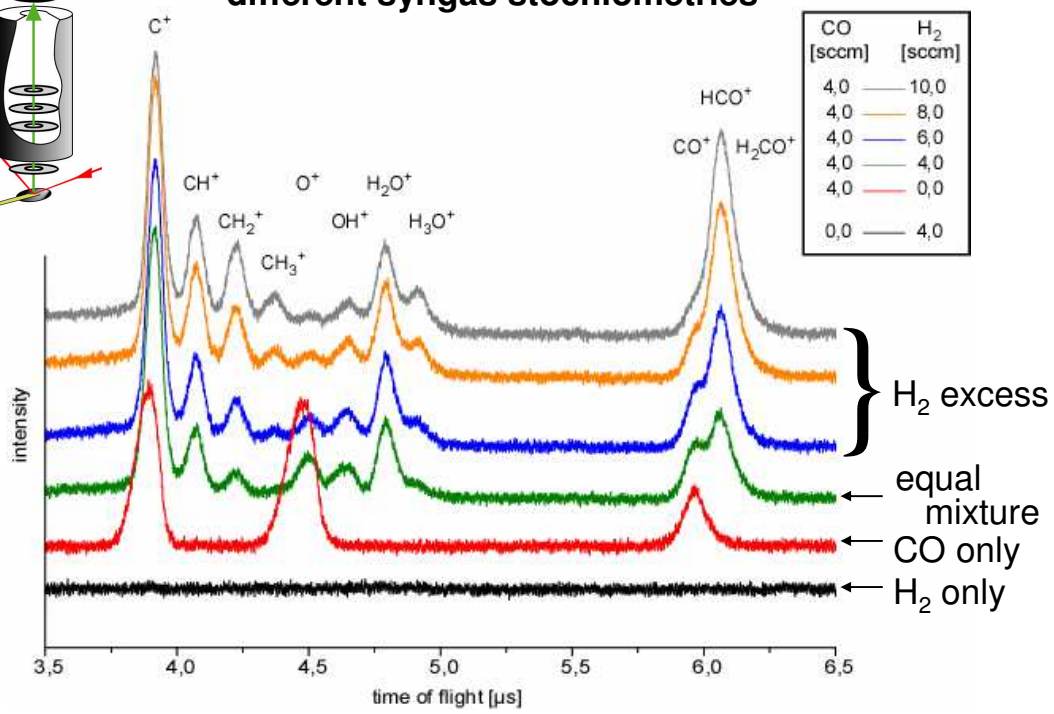


syngas stream onto the Pd surface

Department of Physics, University of Würzburg, Germany



different syngas stochiometries

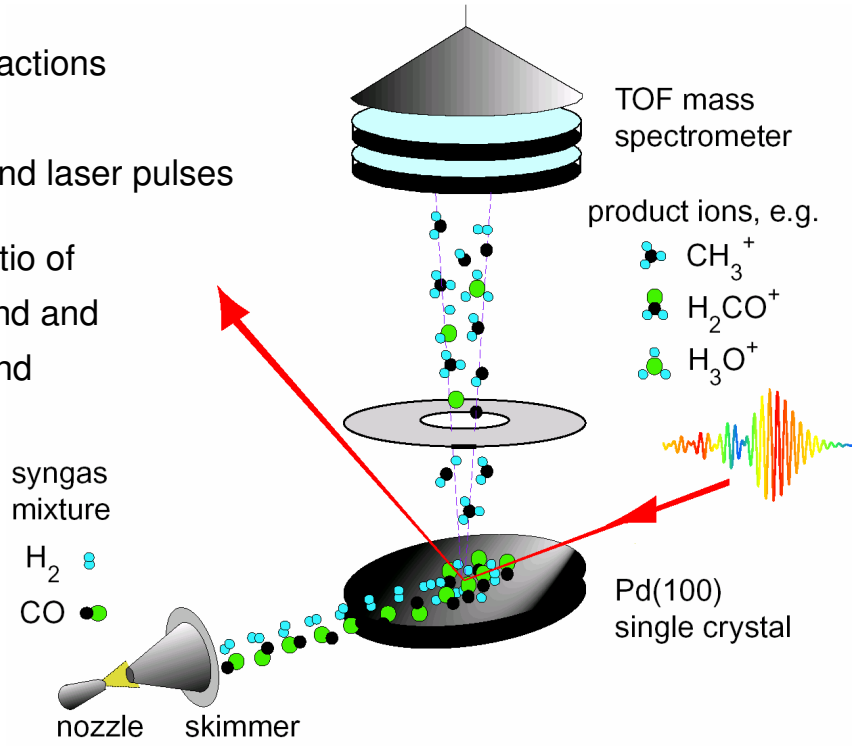


bond-forming catalytic surface reaction

Department of Physics, University of Würzburg, Germany

catalytic surface reactions
steered by
shaped femtosecond laser pulses

control over the ratio of
- ions with C-H bond and
- ions with O-H bond



experimental setup

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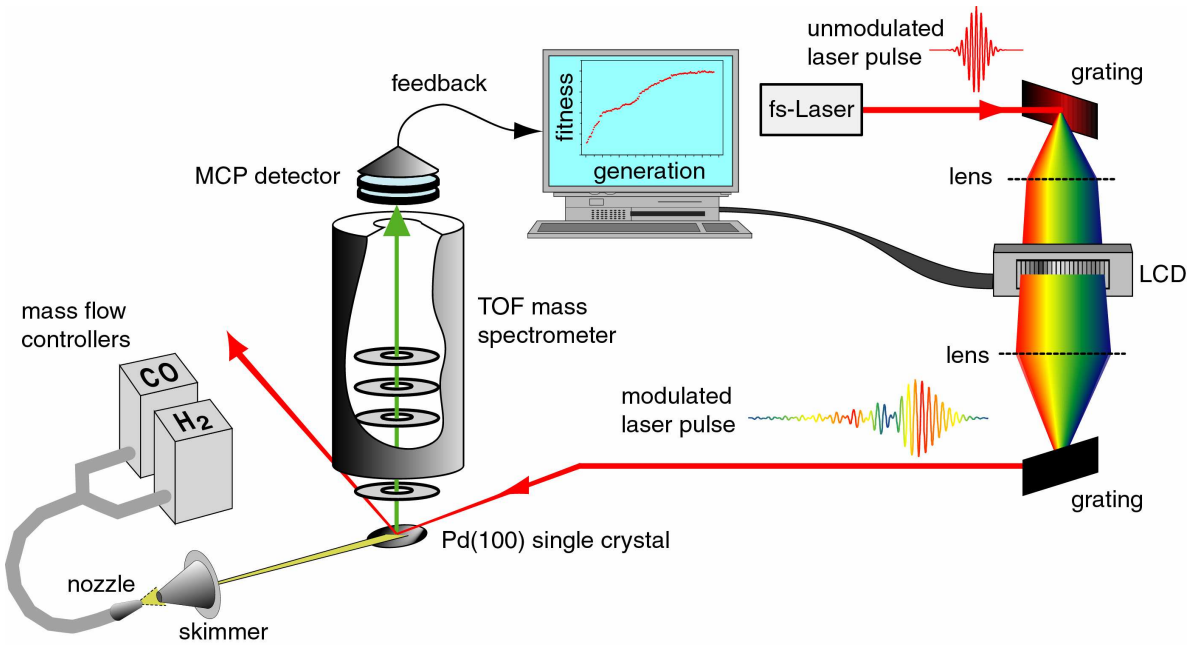

optimization of different reaction channels

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closed-loop optimal control experiment:
ratio CH^+ / H_2O^+ as fitness function

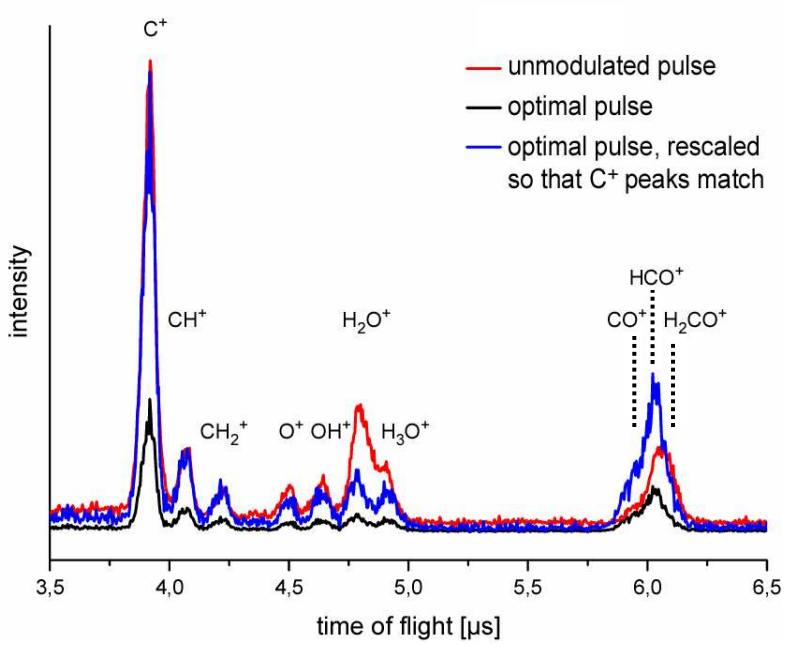
- H_2O^+ signal initially is higher than CH^+

  reversed with optimal laser pulse shape

- overall signal drops due to smaller peak intensity

  but intensity variation fails to achieve an optimization effect

selectivity over different reaction channels



optimization of different reaction channels

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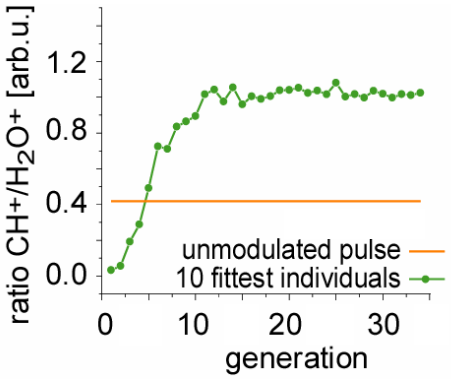
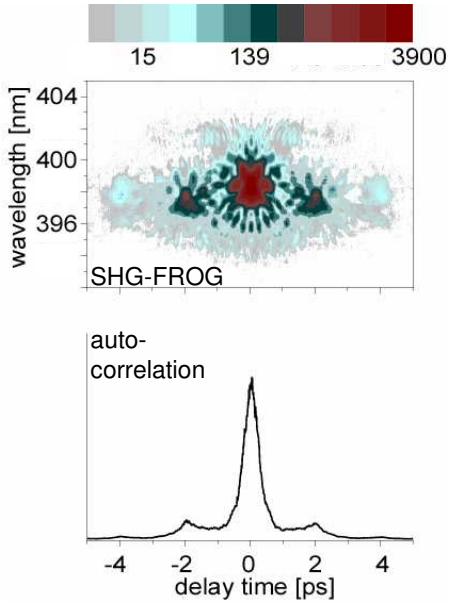
closed-loop optimal control experiment:
ratio CH^+ / H_2O^+ as fitness function

- equal syngas mixture
- ratio is greatly increased with modulated laser pulse





peak shape analysis

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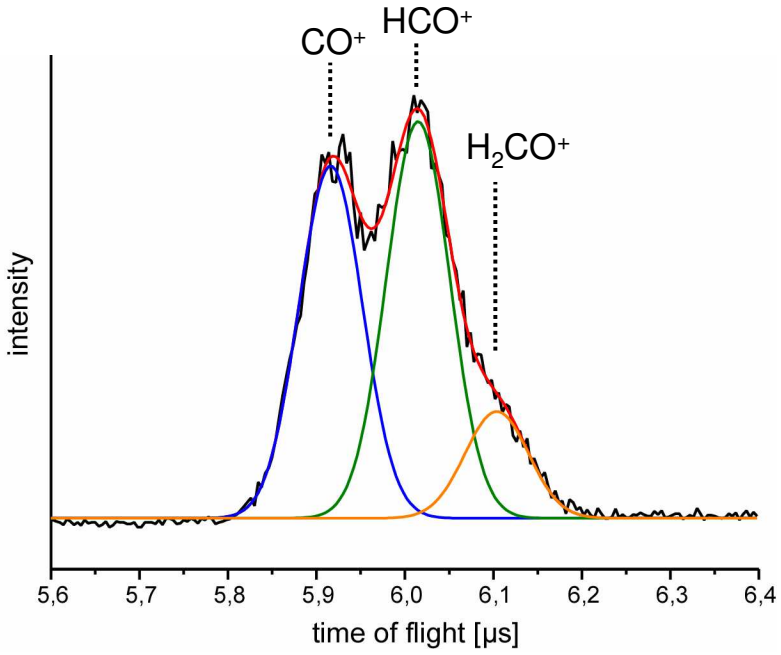
mass peaks of hydrogenated CO

- data indicates three underlying signals
- Gaussian fit matches well with data set
- peak positions from fit coincide well with mass calibration
- 3 contributing species: CO^+, HCO^+ and H_2CO^+



Summary

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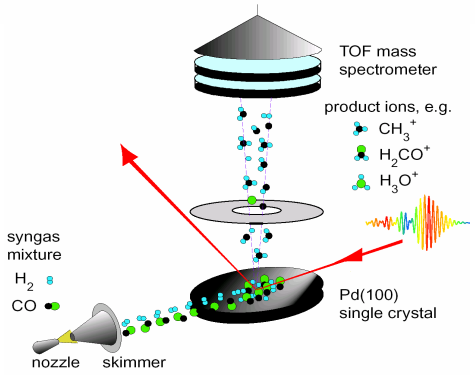
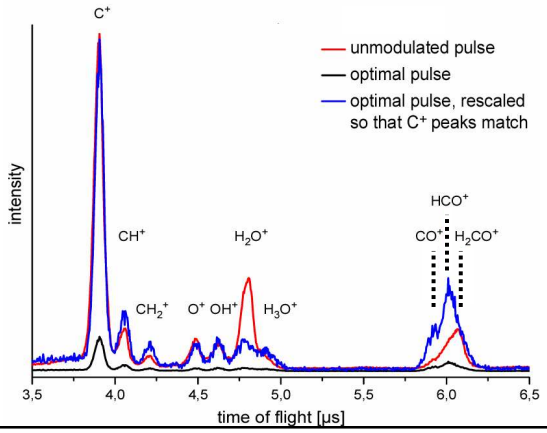
Laser-assisted surface chemistry:

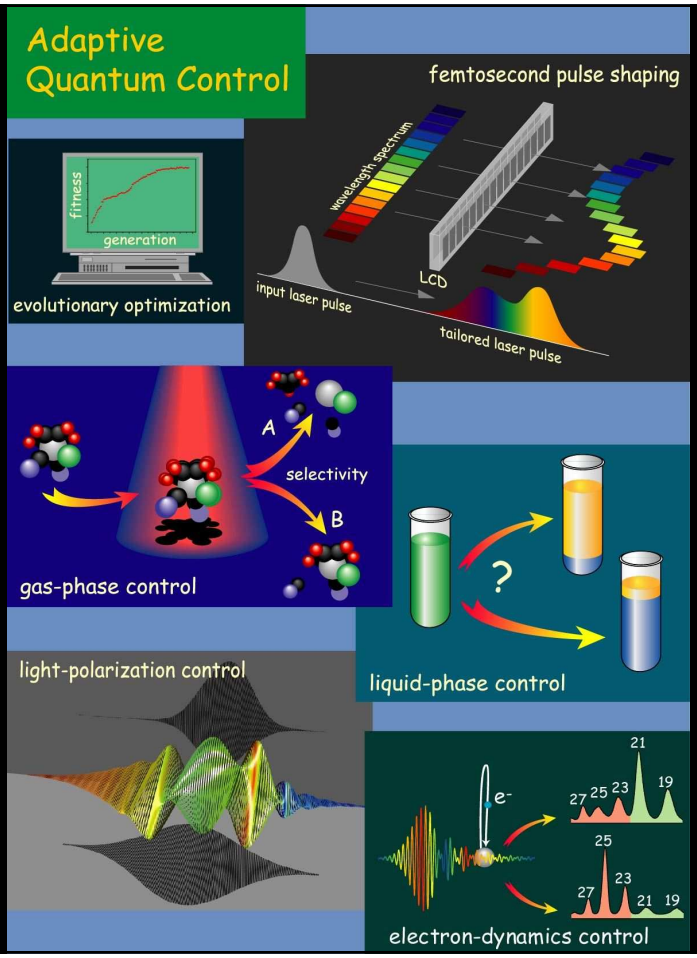
- successful catalytic reaction of syngas on a Pd single crystal surface
- synthesis of species for whose formation two or more particles have to meet e.g. CH_3^+, H_3O^+ or H_2CO^+

Closed-loop femtosecond optimal control:

- selective manipulation of different product ion ratios
- reaction channels comprise bond **formation**, not only cleavage






Adaptive
Quantum Control
femtosecond pulse shaping
fitness
generation
evolutionary optimization
wavelength spectrum
LCD
input laser pulse
tailored laser pulse
A
selectivity
B
gas-phase control
?
liquid-phase control
light-polarization control
e-
21
27 25 23 19
25
27 23 21 19
electron-dynamics control

Applications of adaptive pulse shaping

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