Optimal control of molecular and electron dynamics by tailored femtosecond laser pulses

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- **adaptive femtosecond pulse shaping**
- **optimal control of molecular dynamics**
  - **gas phase**
  - **liquid phase**
- **optimal control of electron dynamics**
  - **high harmonics generation**
  - **electron wavepacket interference**

A. Assion, T. Baumert M. Bergt, T. Brixner, N. Damrauer, C. Dietl, B. Kiefer, G. Krampert P. Niklaus,
E. Papastathopoulus, R. Selle, V. Seyfried, M. Strehle, T. Pfeifer, G. Vogt, D. Walter

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

chemical reaction

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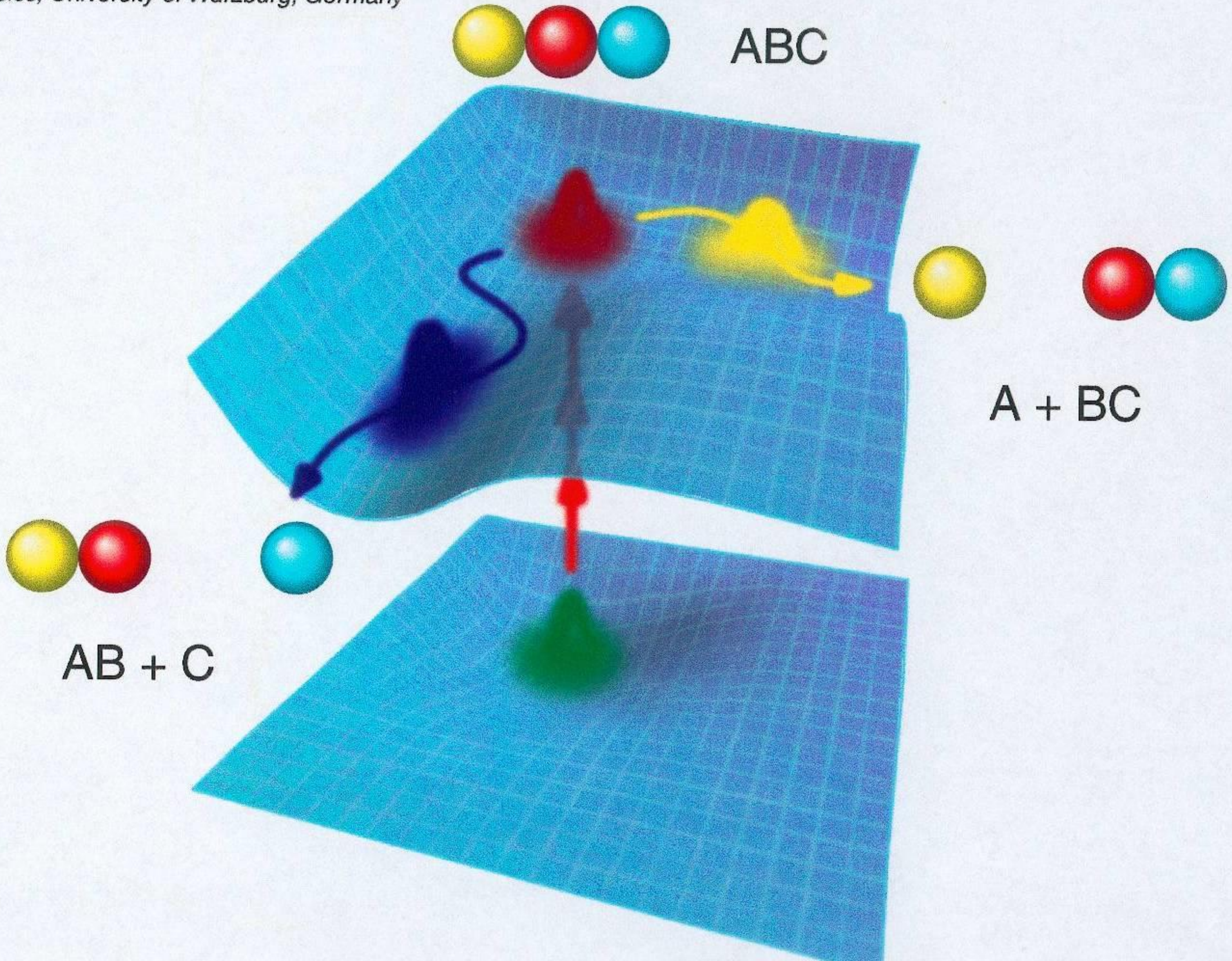

chemical reaction

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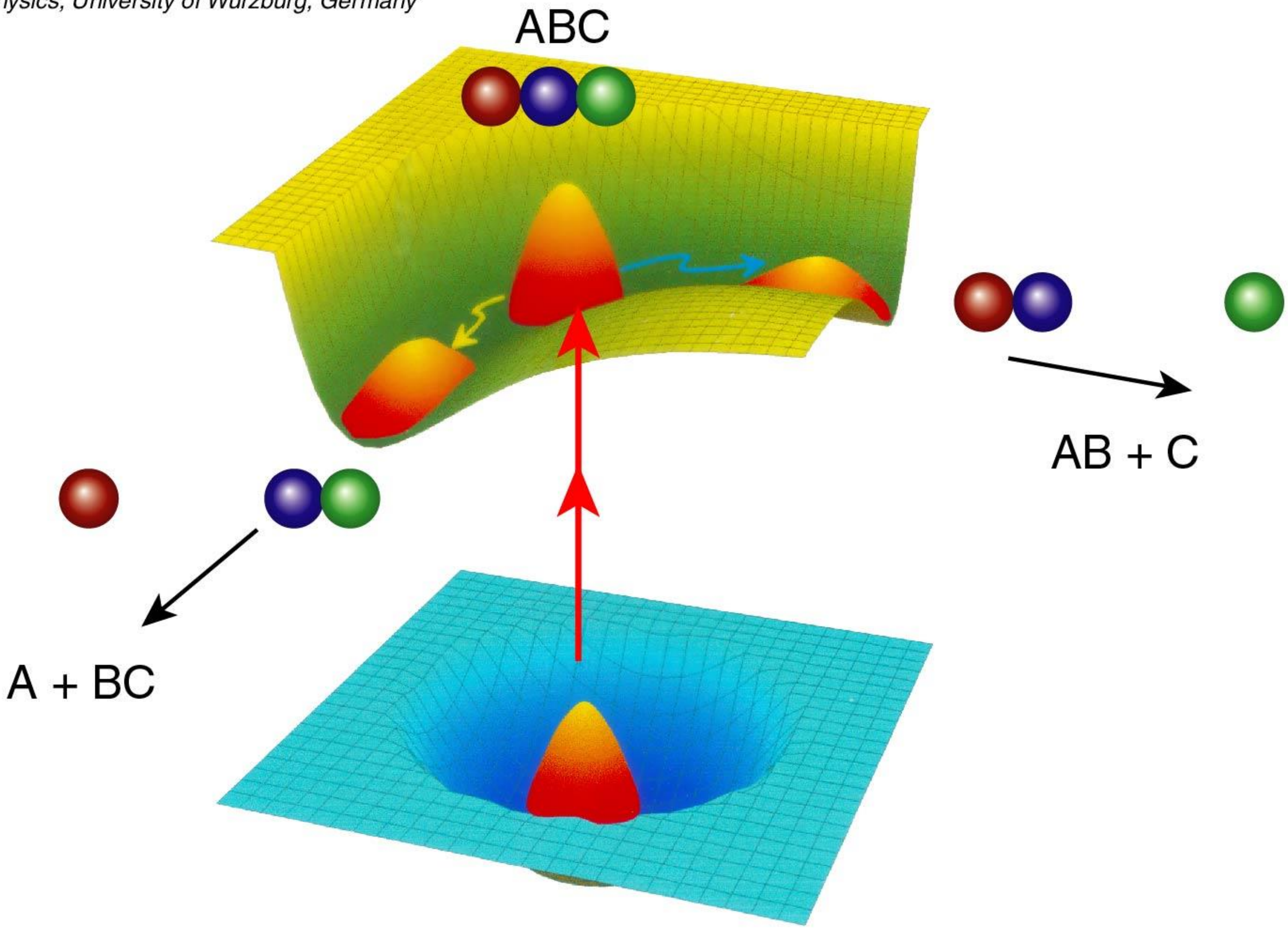

control of chemical reactions

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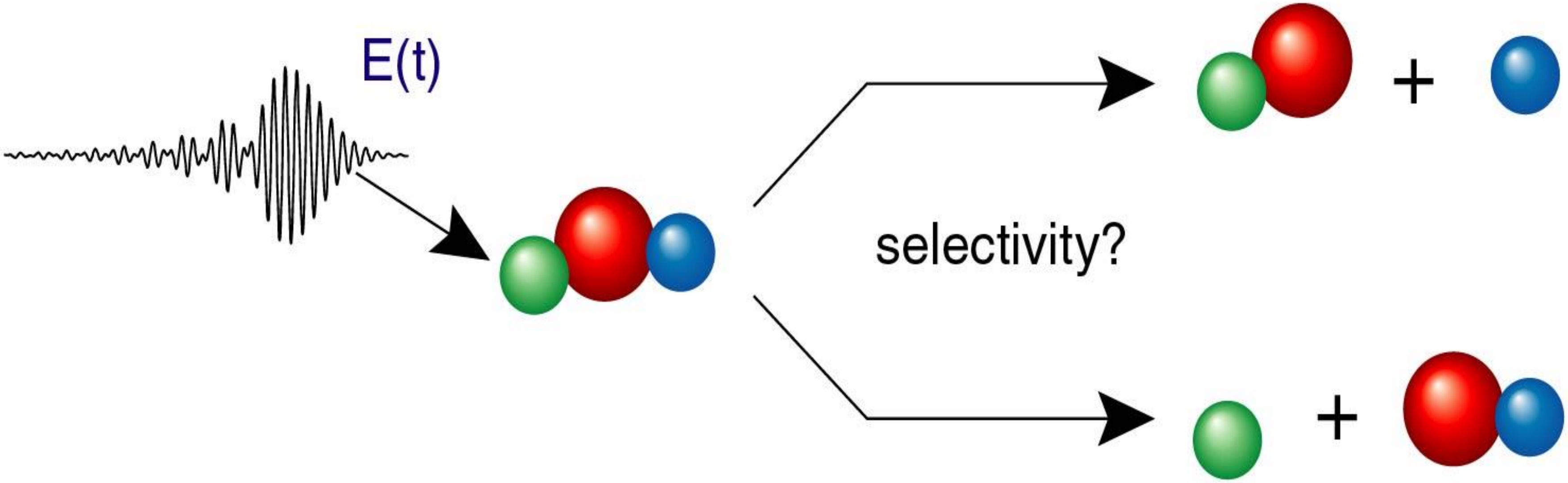

laser electric field E(t):

- calculation for real molecules extremely complicated (if not impossible)
- exact laboratory realization of predicted fields difficult

Single-parameter coherent control

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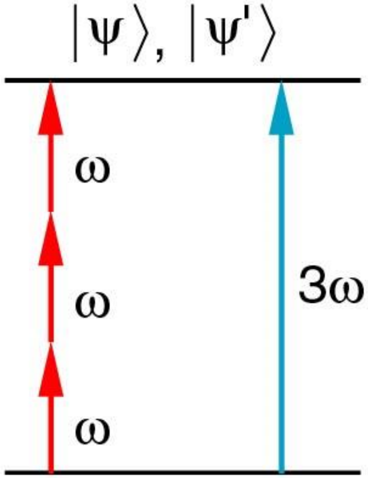
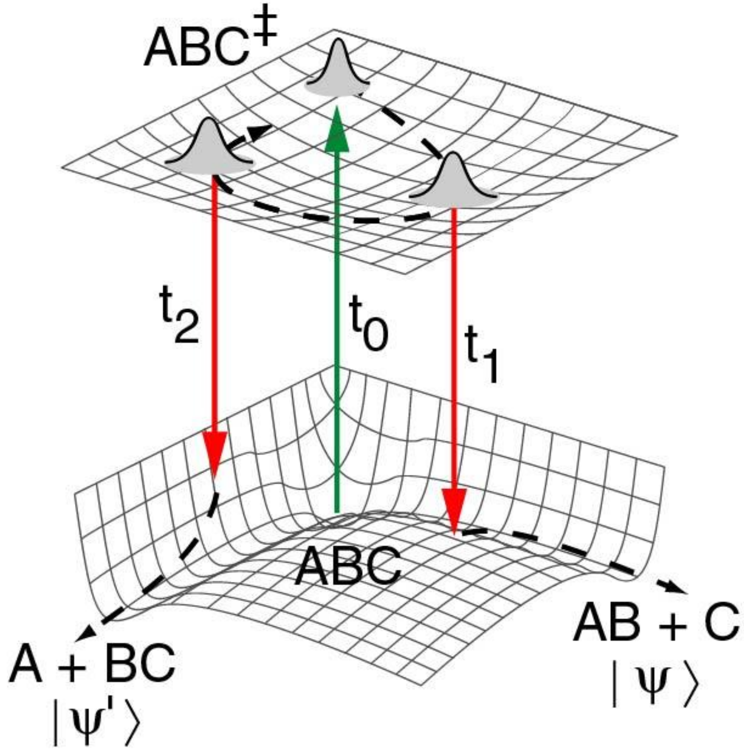
Brumer-Shapiro
"phase control"
$\Delta\Phi = \Phi_{\omega} - \Phi_{3\omega}$



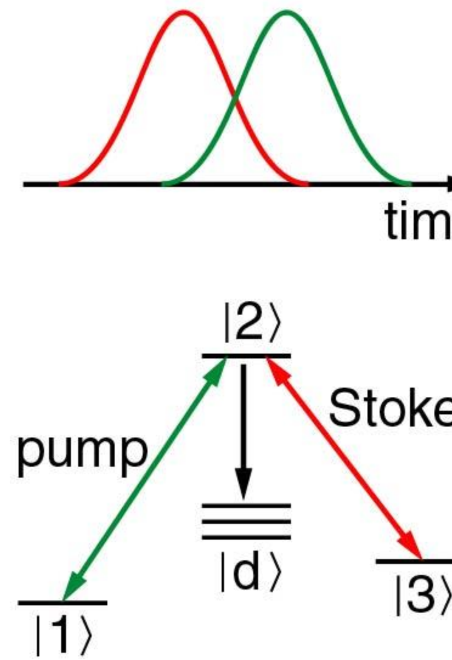
CPL **126**, 541 (1986)

Tannor-Kosloff-Rice
"pump-dump control"
$\Delta t = t_{1,2} - t_0$



JCP **85**, 5805 (1986)

Bergmann et al.
"STIRAP control"



CPL **149**, 463 (1988)

Rabitz

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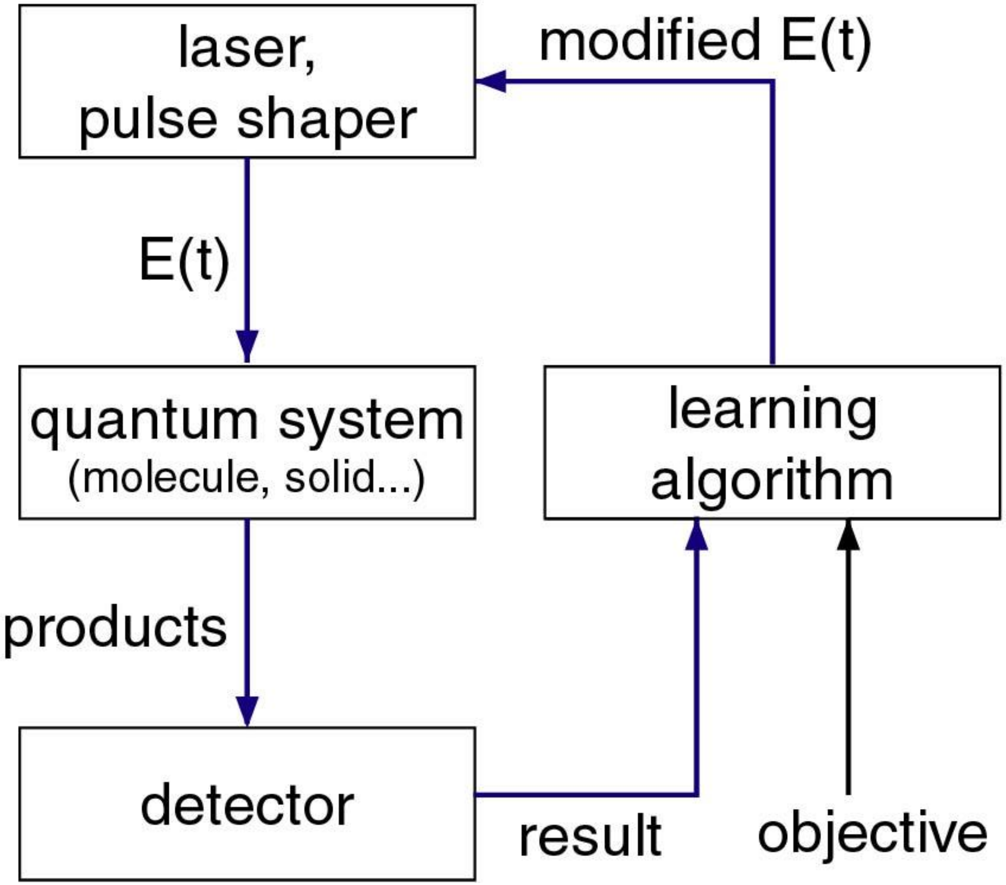
R.S. Judson, H. Rabitz, PRL 68, 1500 (1992)

"optimal control therory" used to design electric fields such that the yield of a specified reaction product is maximized by directly including the experimental output

"teaching lasers to control molecules"



Adaptive pulse shaping

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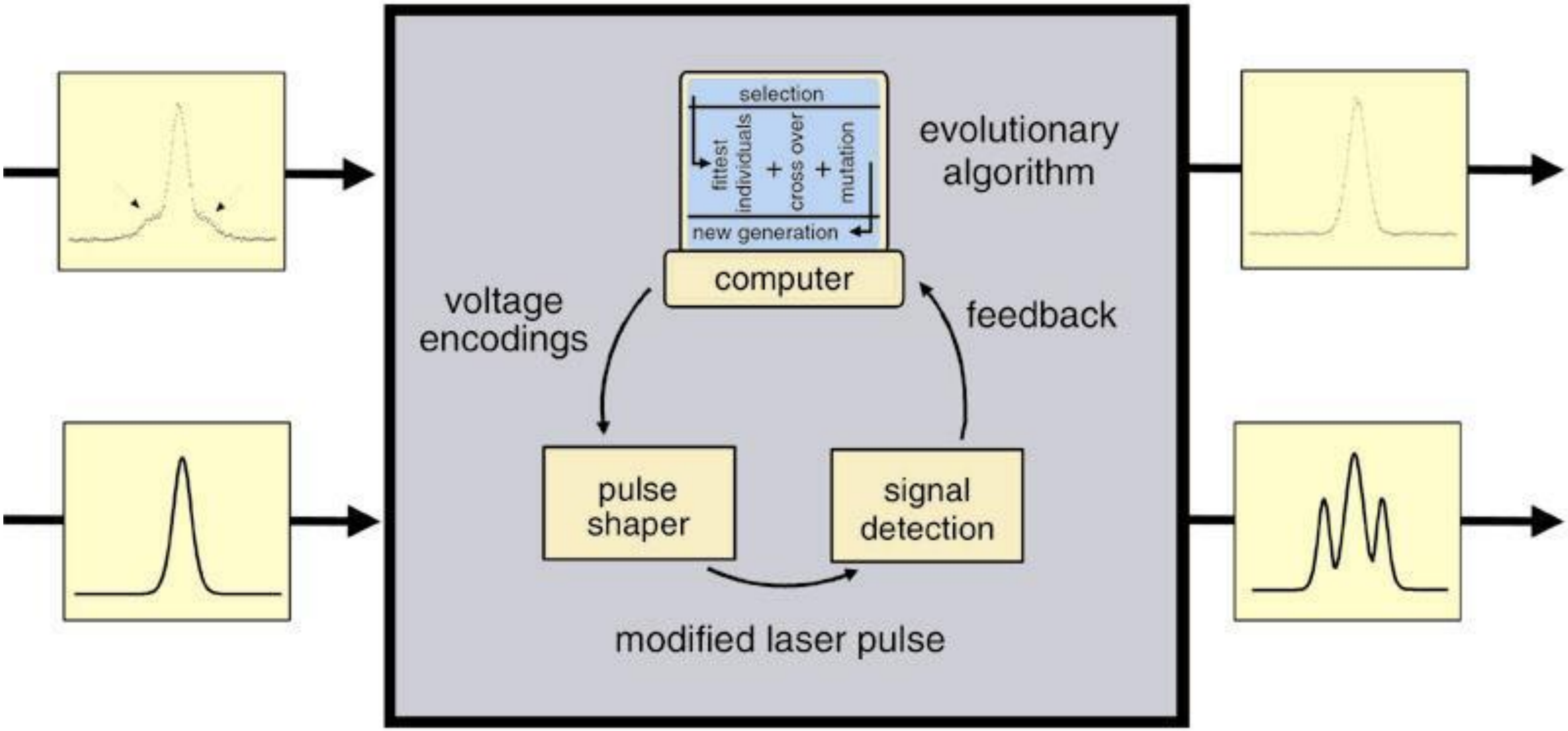

T. Baumert, T. Brixner, V. Seyfried, M. Strehle and G. Gerber: Appl. Phys. B **65**, 779 (1997)
idea of feedback: R.S. Judson and H. Rabitz: Phys. Rev. Lett. **68**, 1500 (1992)

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

Pulse shaper

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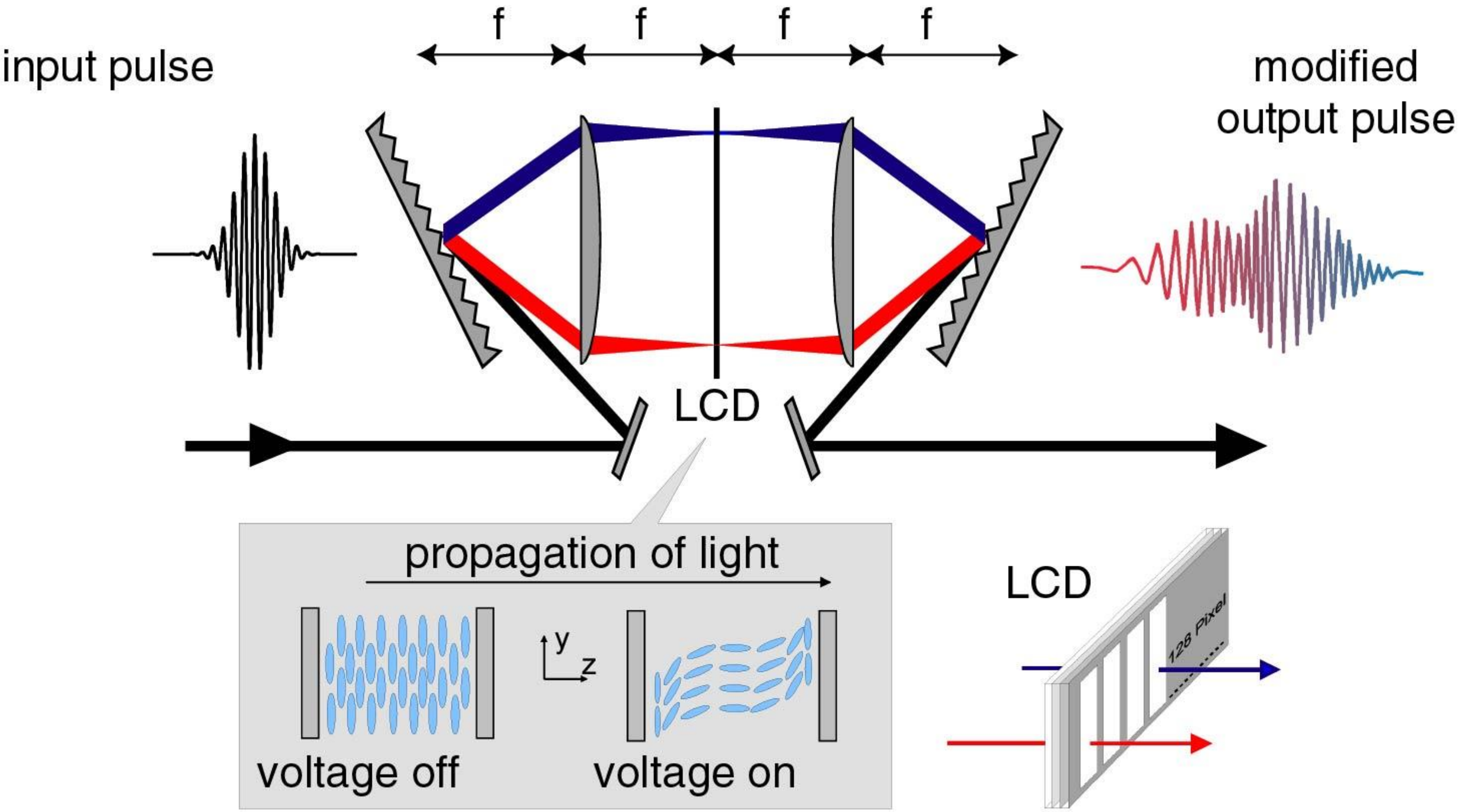

A. M. Weiner et al., IEEE J. Quantum Electron. **28**, 908 (1992)
A. M. Weiner et al., Opt. Lett. **15**, 326 (1990)

Femtosecond pulse shaping

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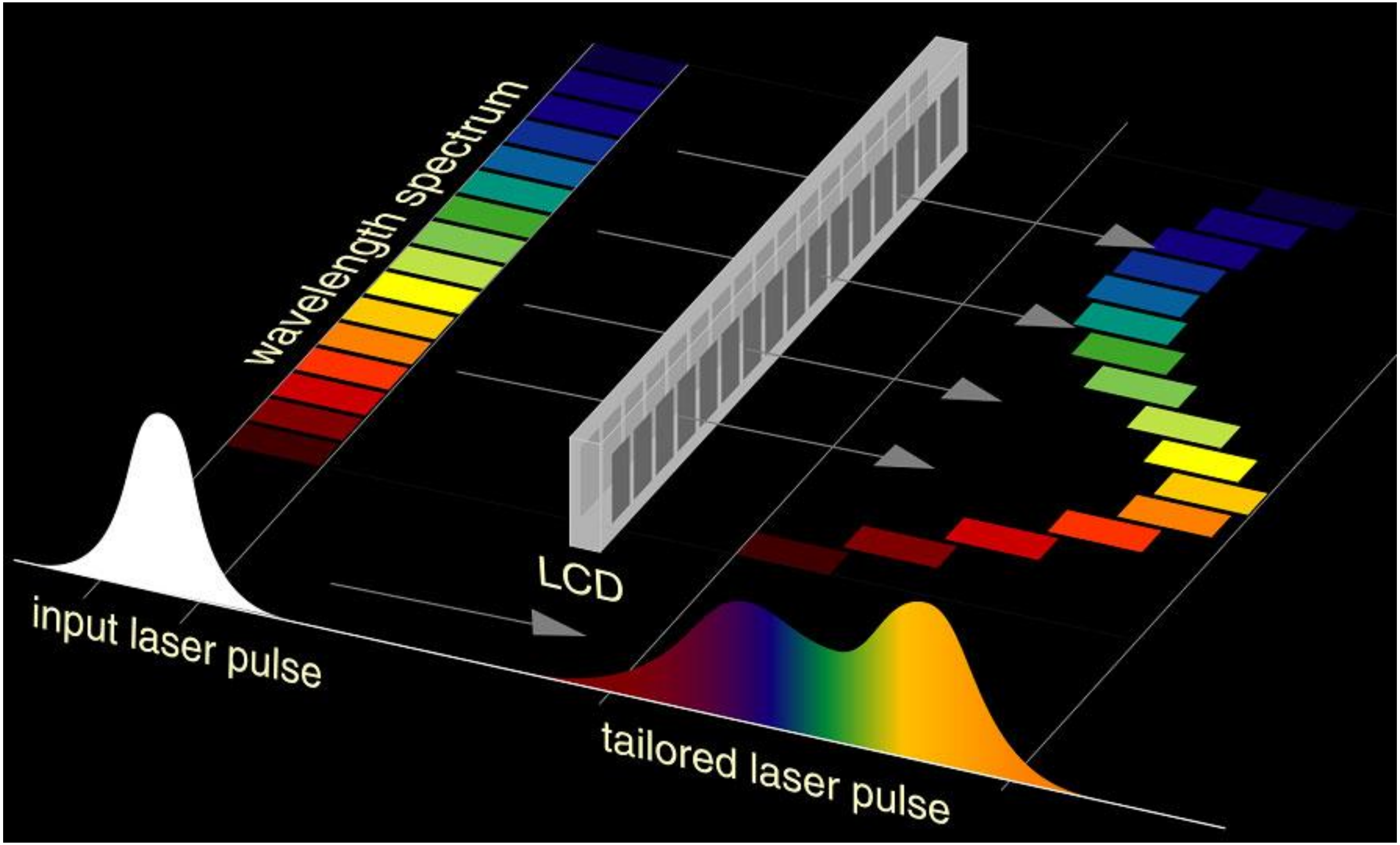

Evolutionary algorithm

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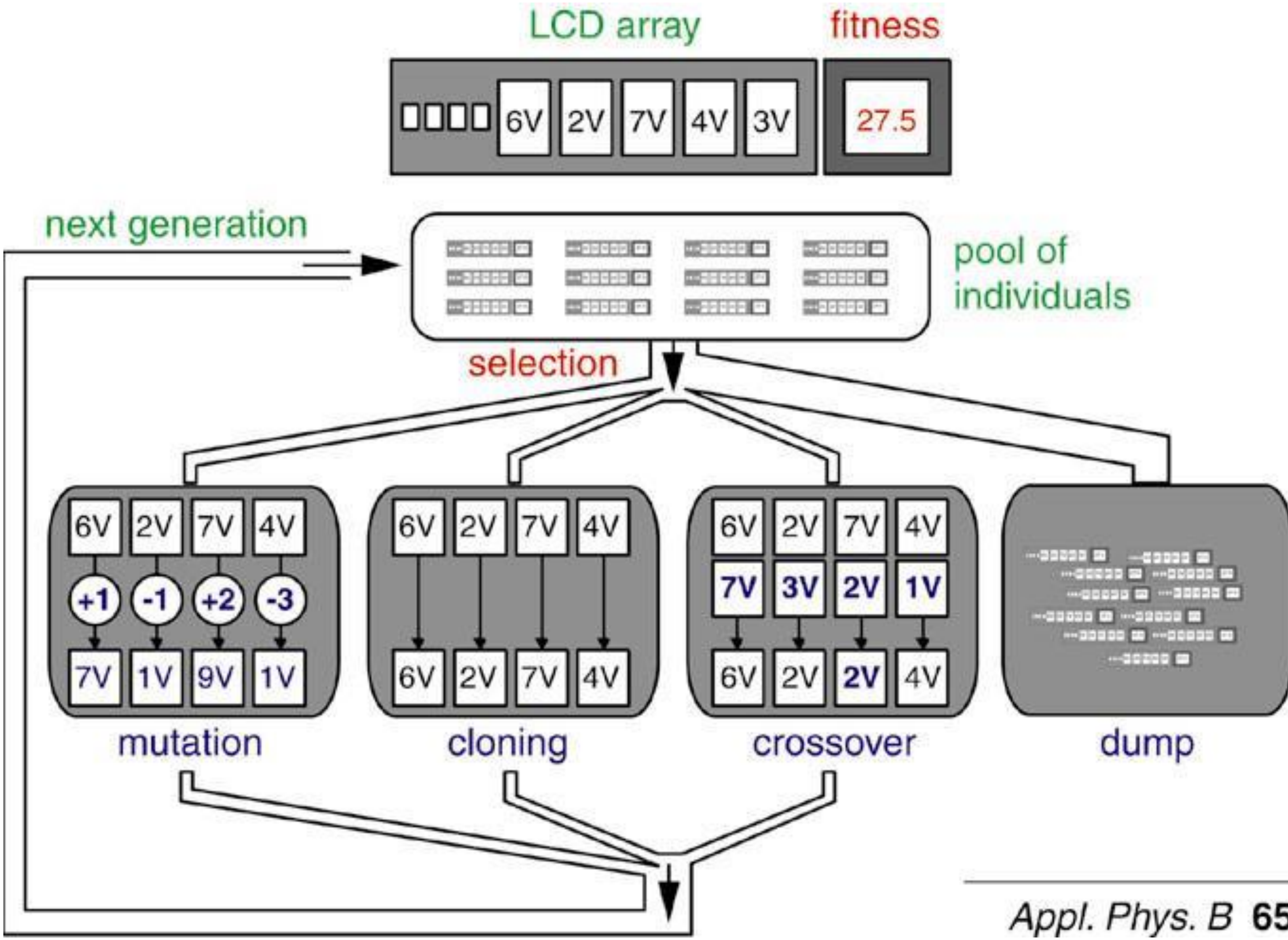

Appl. Phys. B **65**, 779 (1997)

Recompression of fs laser pulses: Compensation of material dispersion

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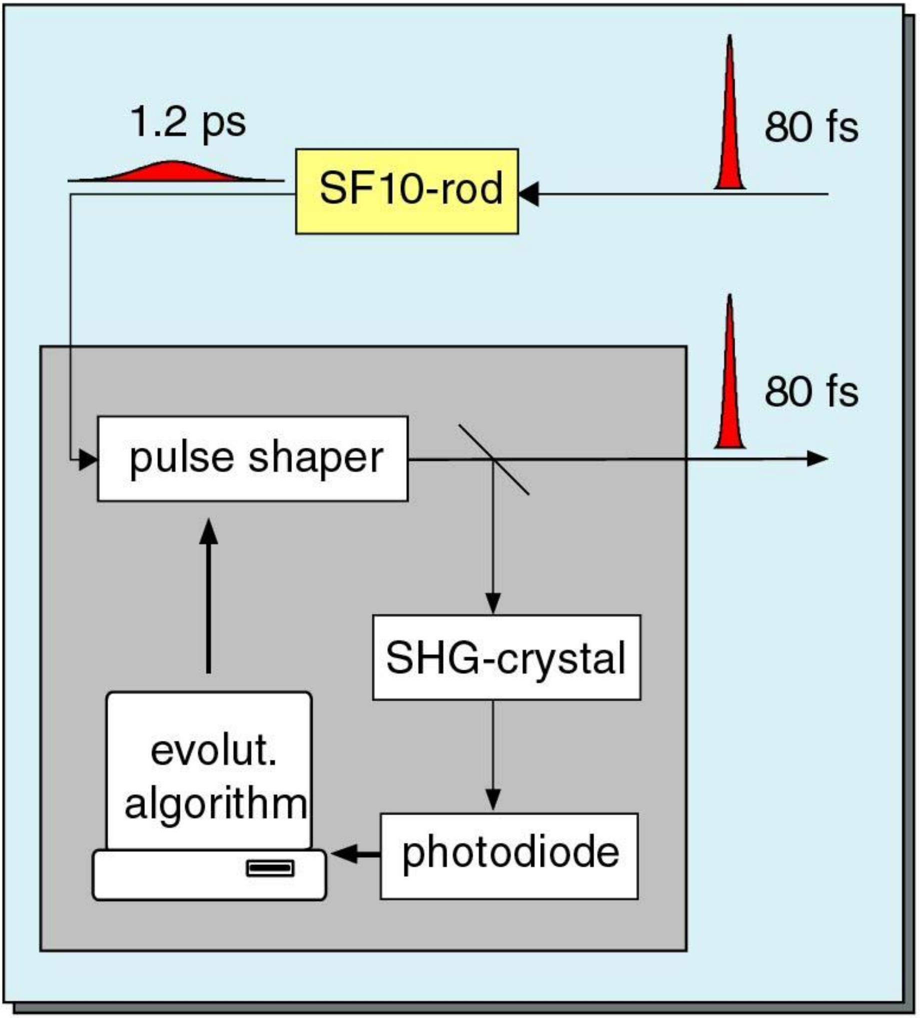

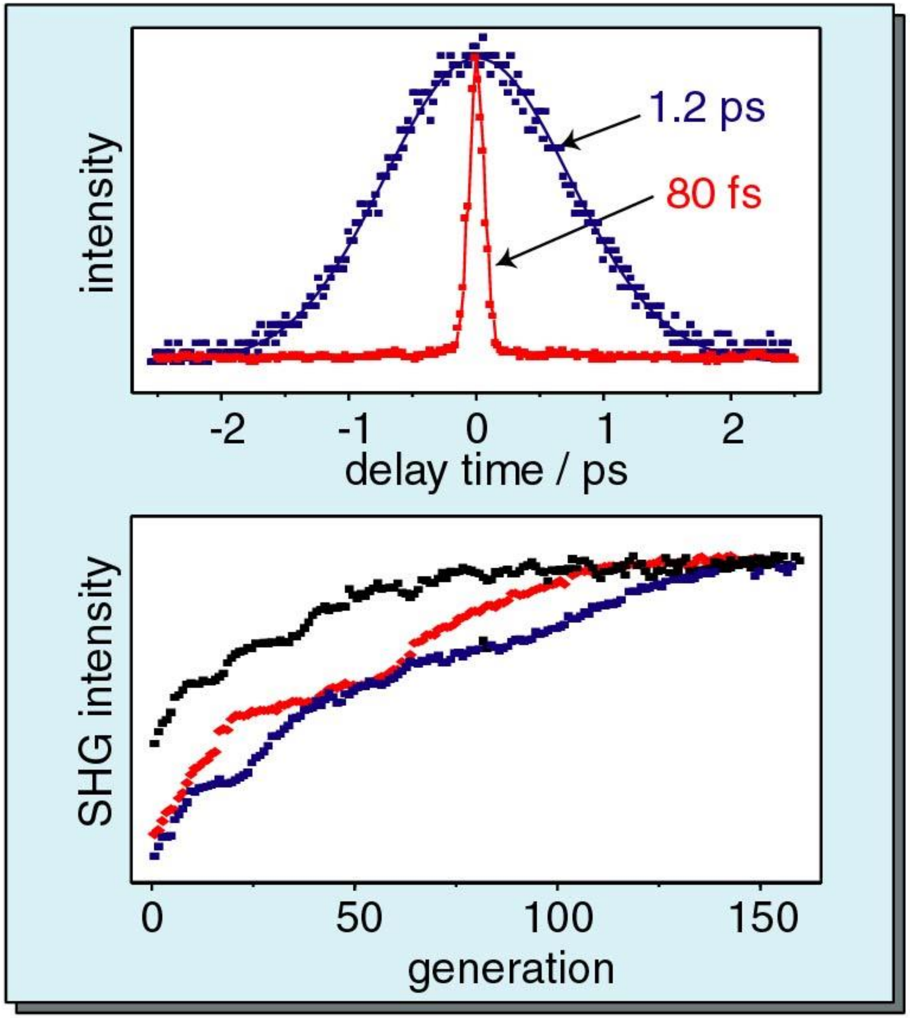

Appl. Phys. B **65**, 779 (1997)

Automated pulse compression

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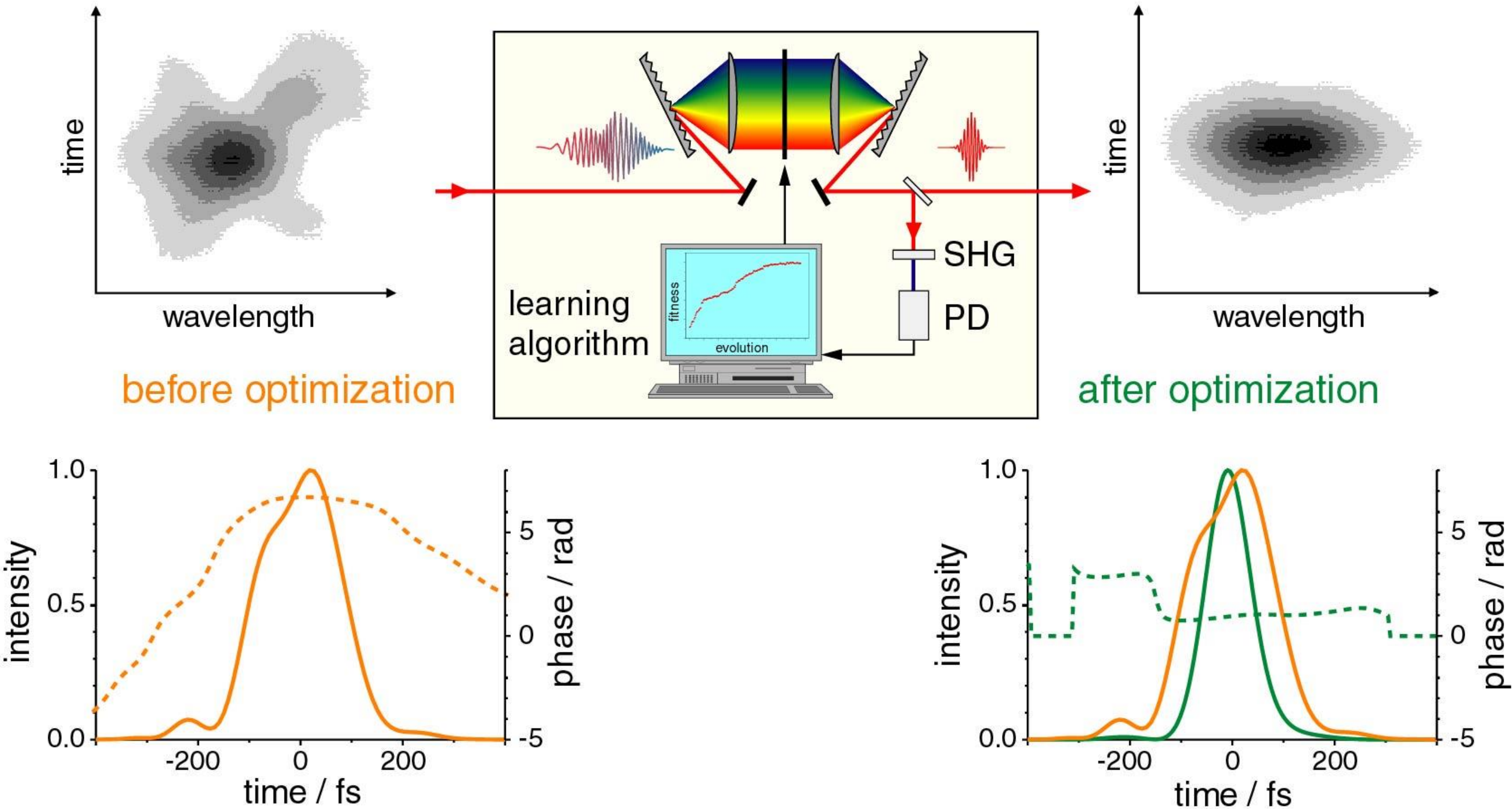

Appl. Phys. B **68**, 281 (1999)

Polarization-shaped laser pulse

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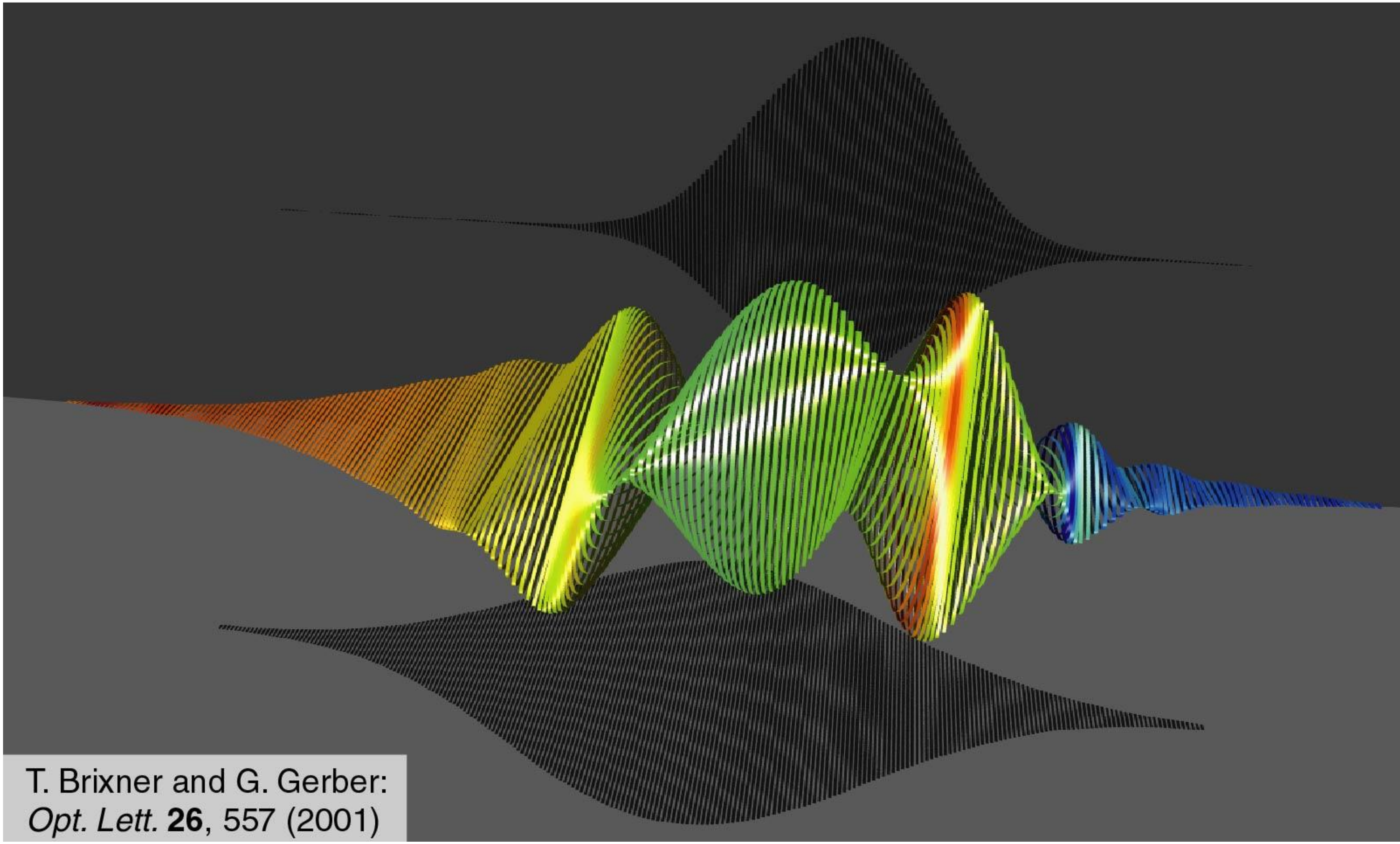

Adaptive femtosecond quantum control

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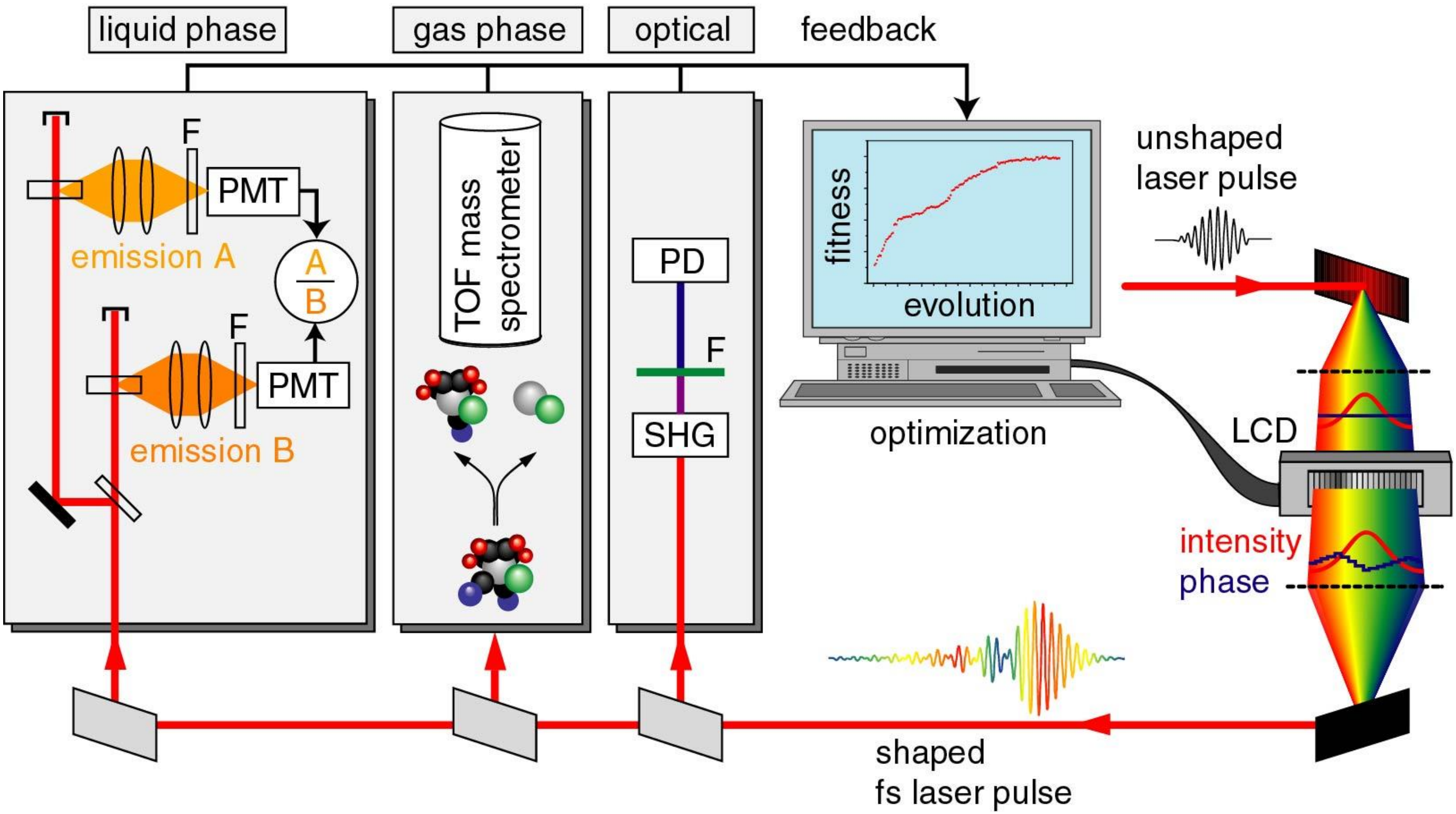

$CpFe(CO)_2Cl$ optimization

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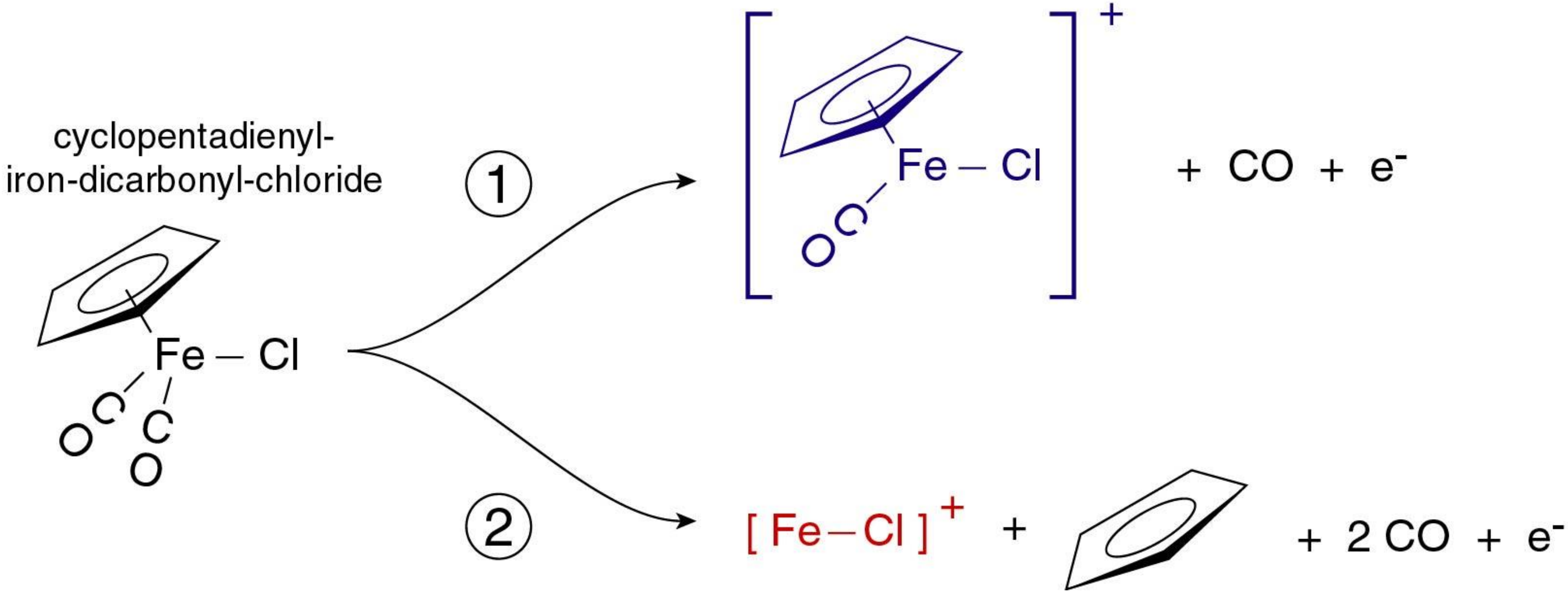

CpFe(CO)Cl⁺/FeCl⁺ optimization

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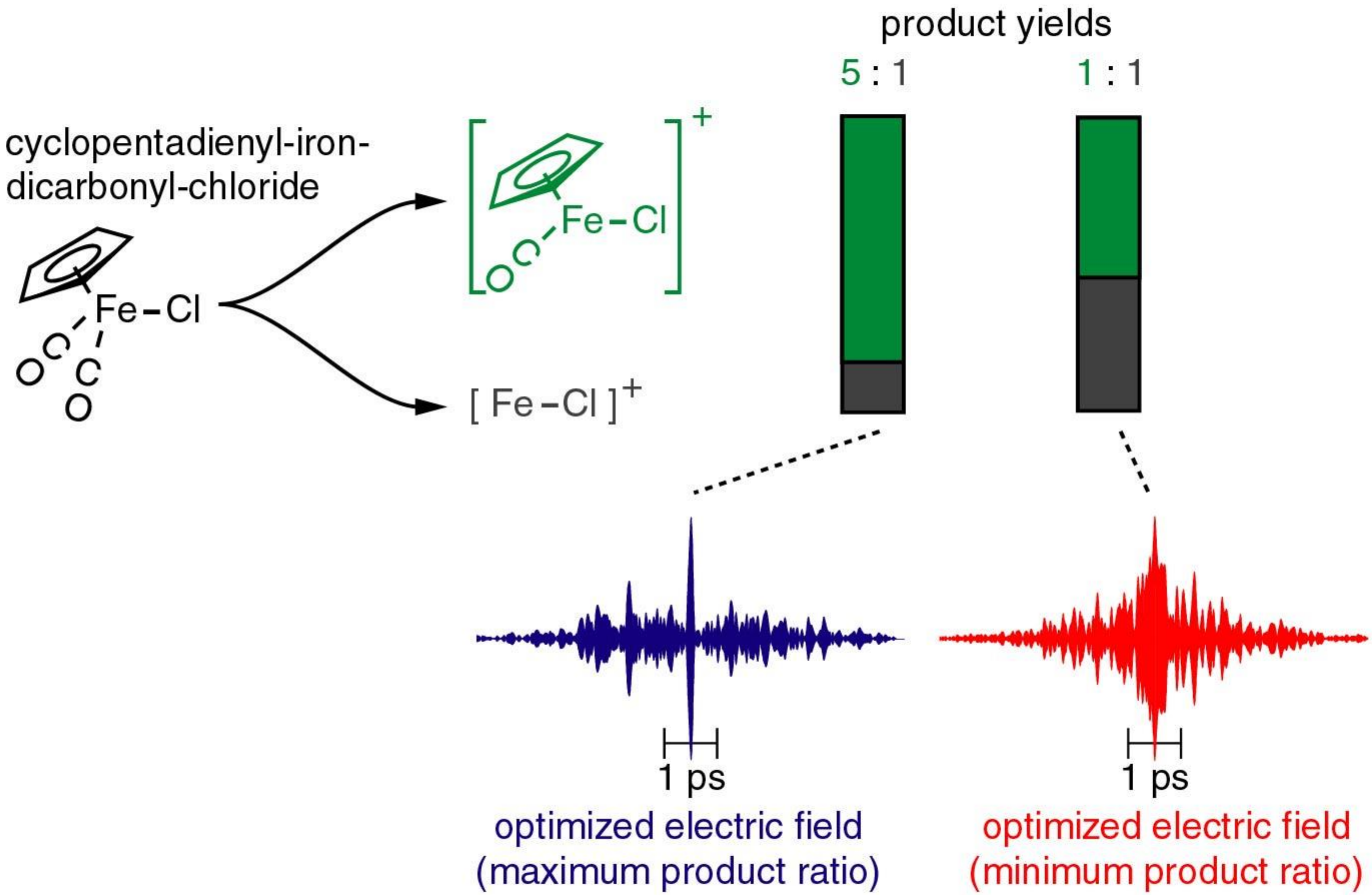

Science **282**, 919 (1998)

"Turning milk into alcohol"

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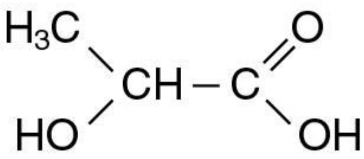
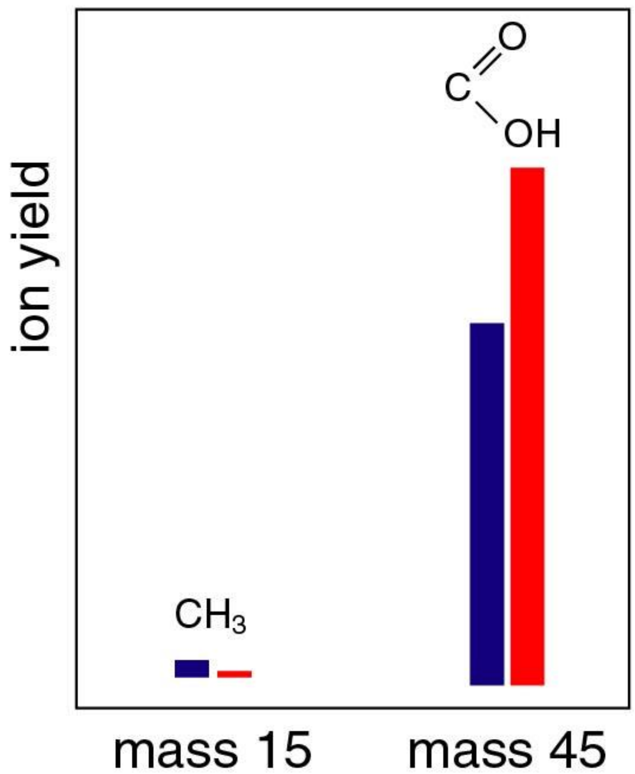
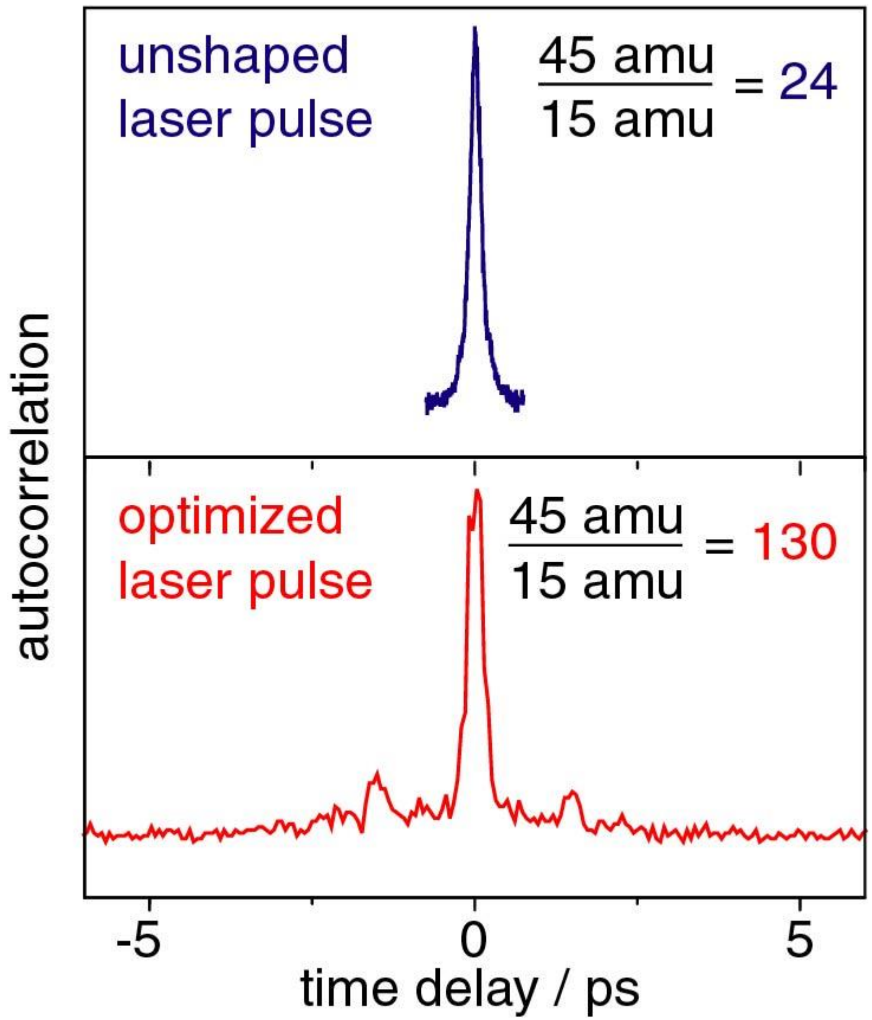
lactic acid:







J. Mod. Opt., **50**, 539-560 (2003)

Quantum control in the liquid phase

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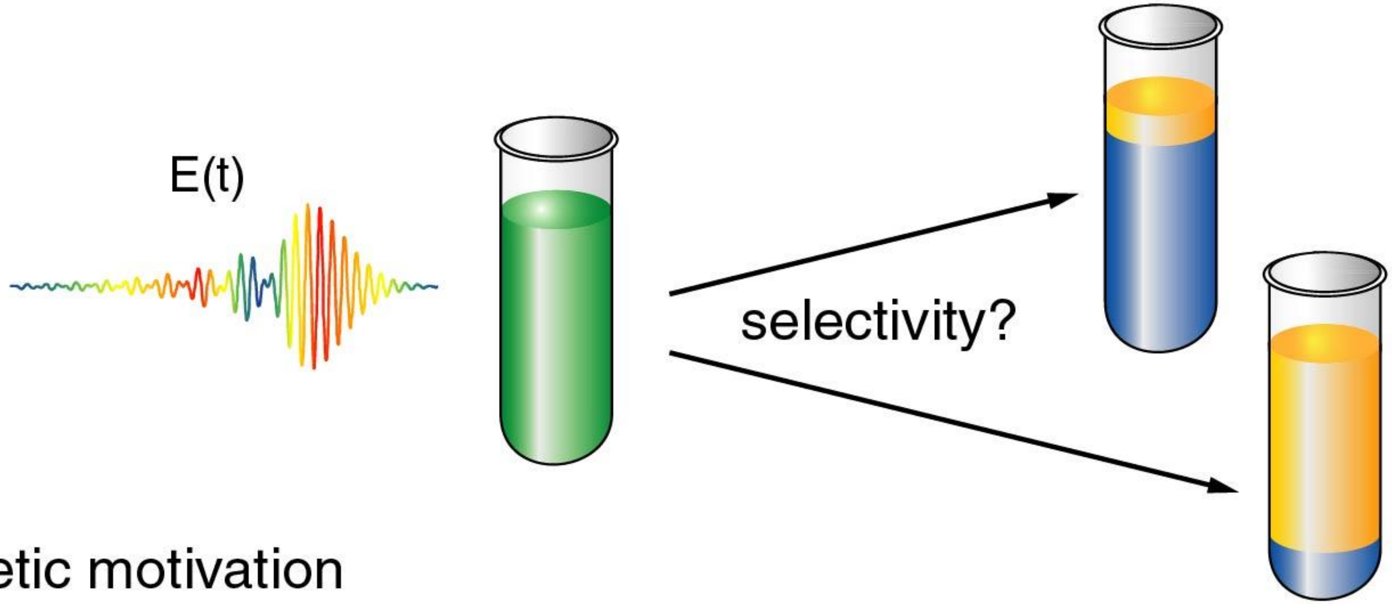

Synthetic motivation

- 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?

Intensity dependence of $[Ru(dpb)_3]^{2+}$ emission

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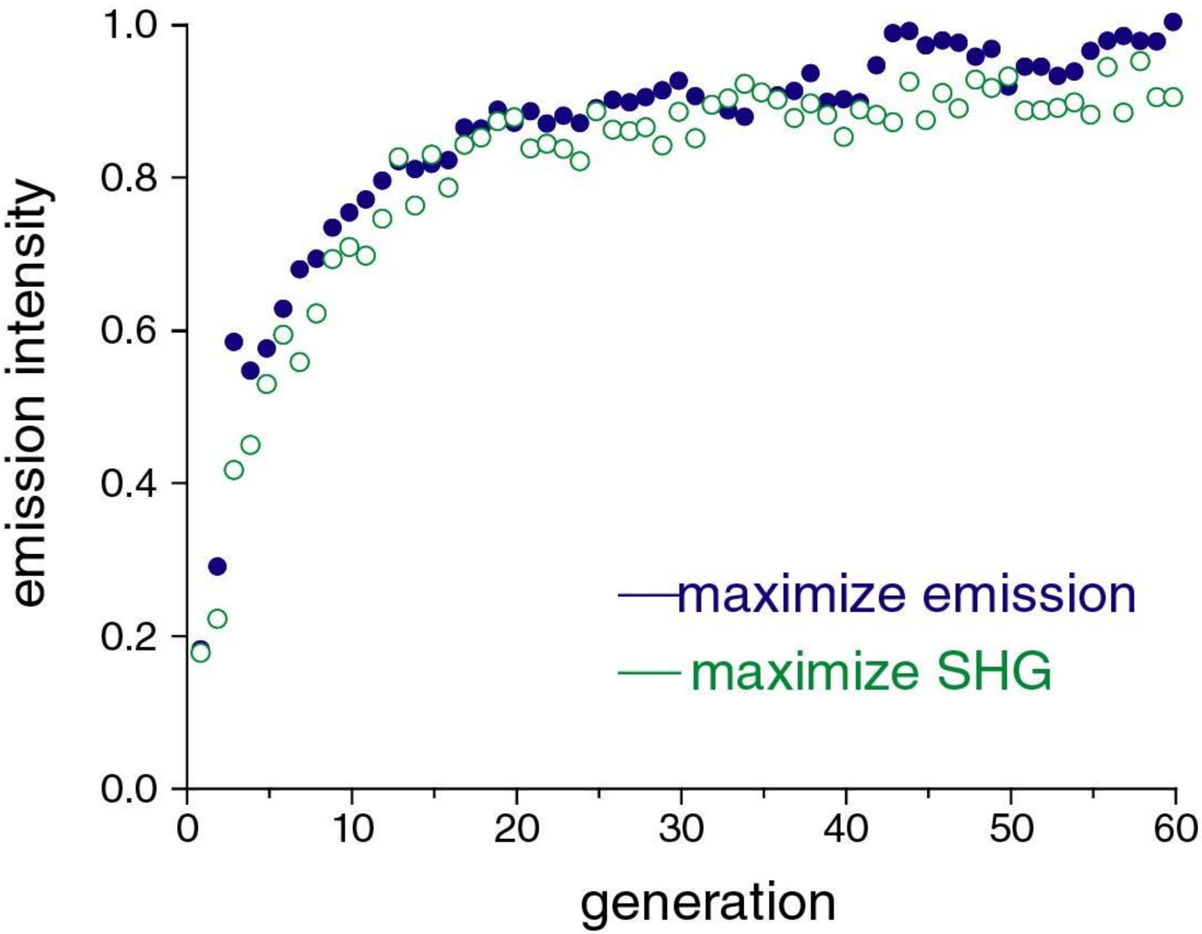
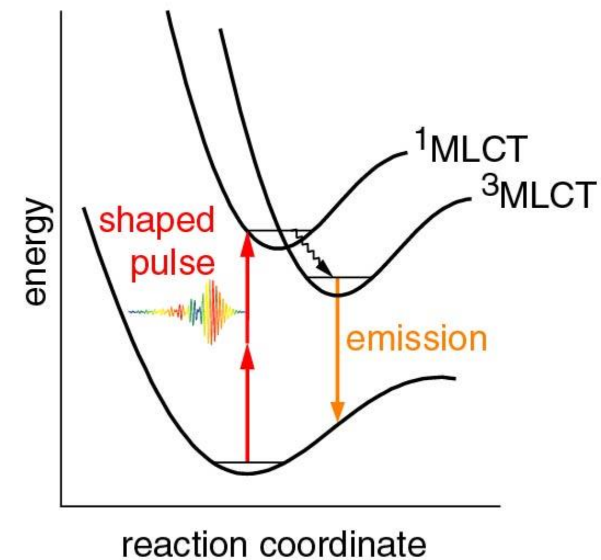


Absolute emission intensity is strongly governed by excited state population created in multi-photon excitation



Optimization of emission/SHG ratio

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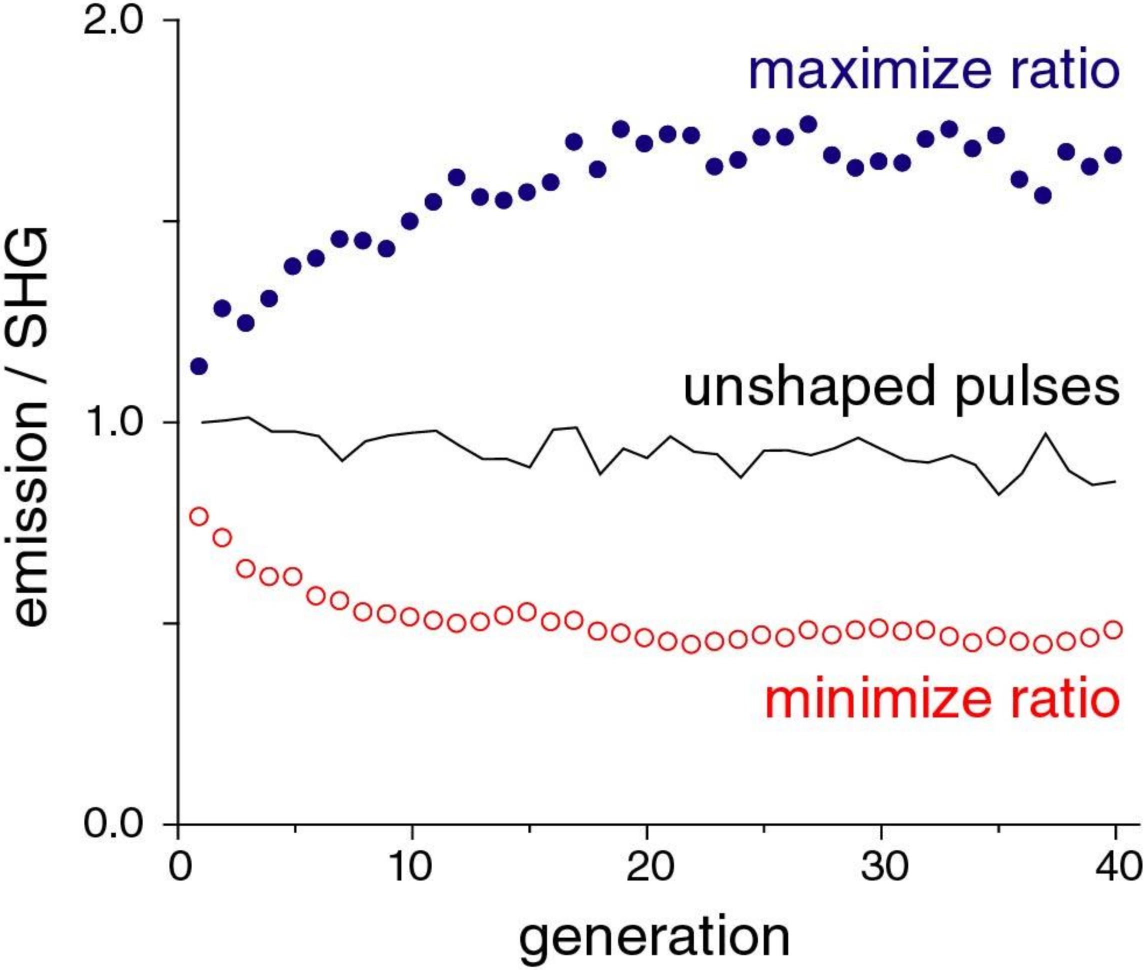

ratio as feedback removes dominant intensity dependence

provides sensitivity to molecular properties

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

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

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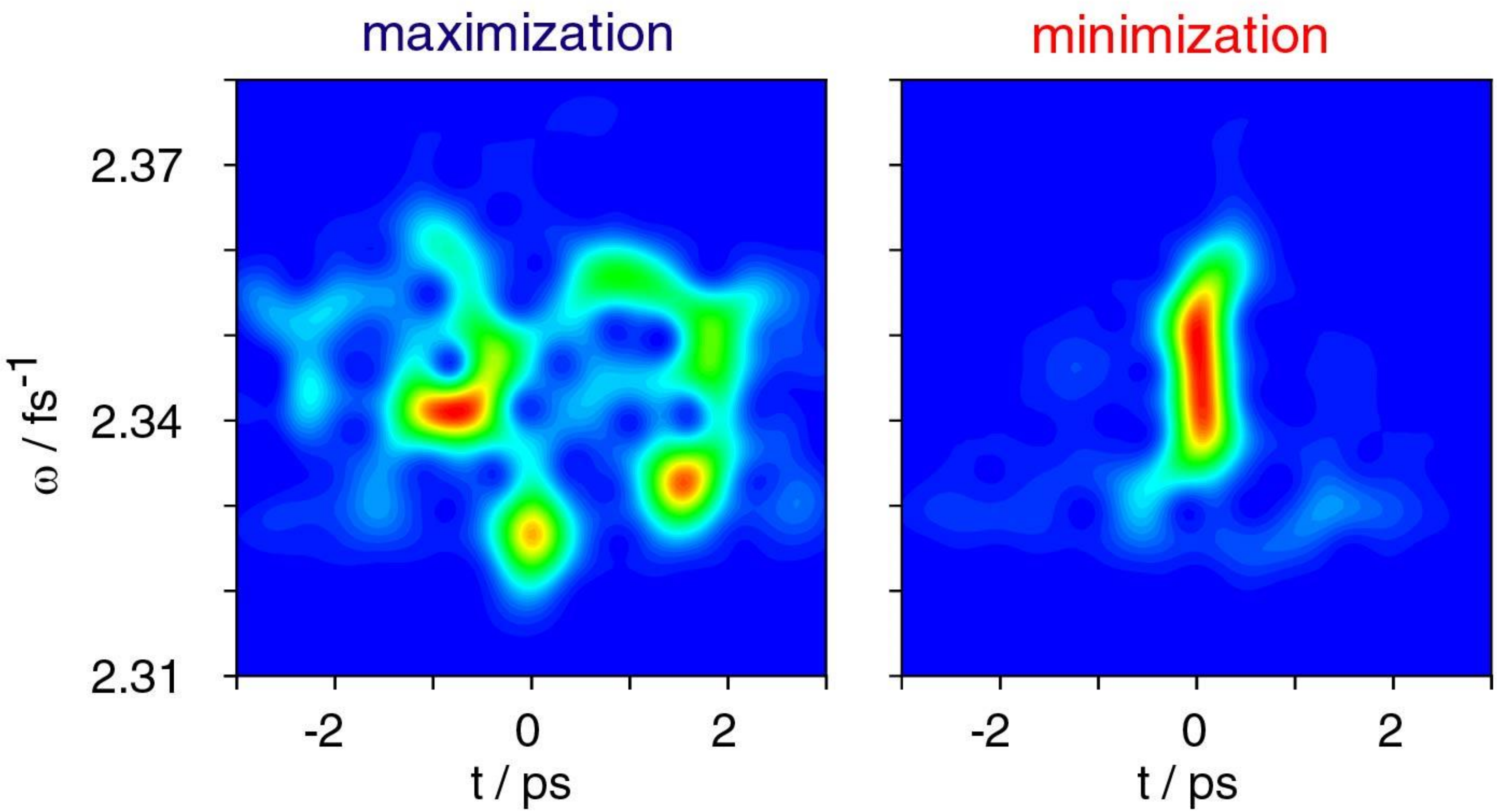
Optimized electric fields in husimi representation:



- Result shows selectivity between excitation pathways has been achieved

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

Selective excitation in liquids

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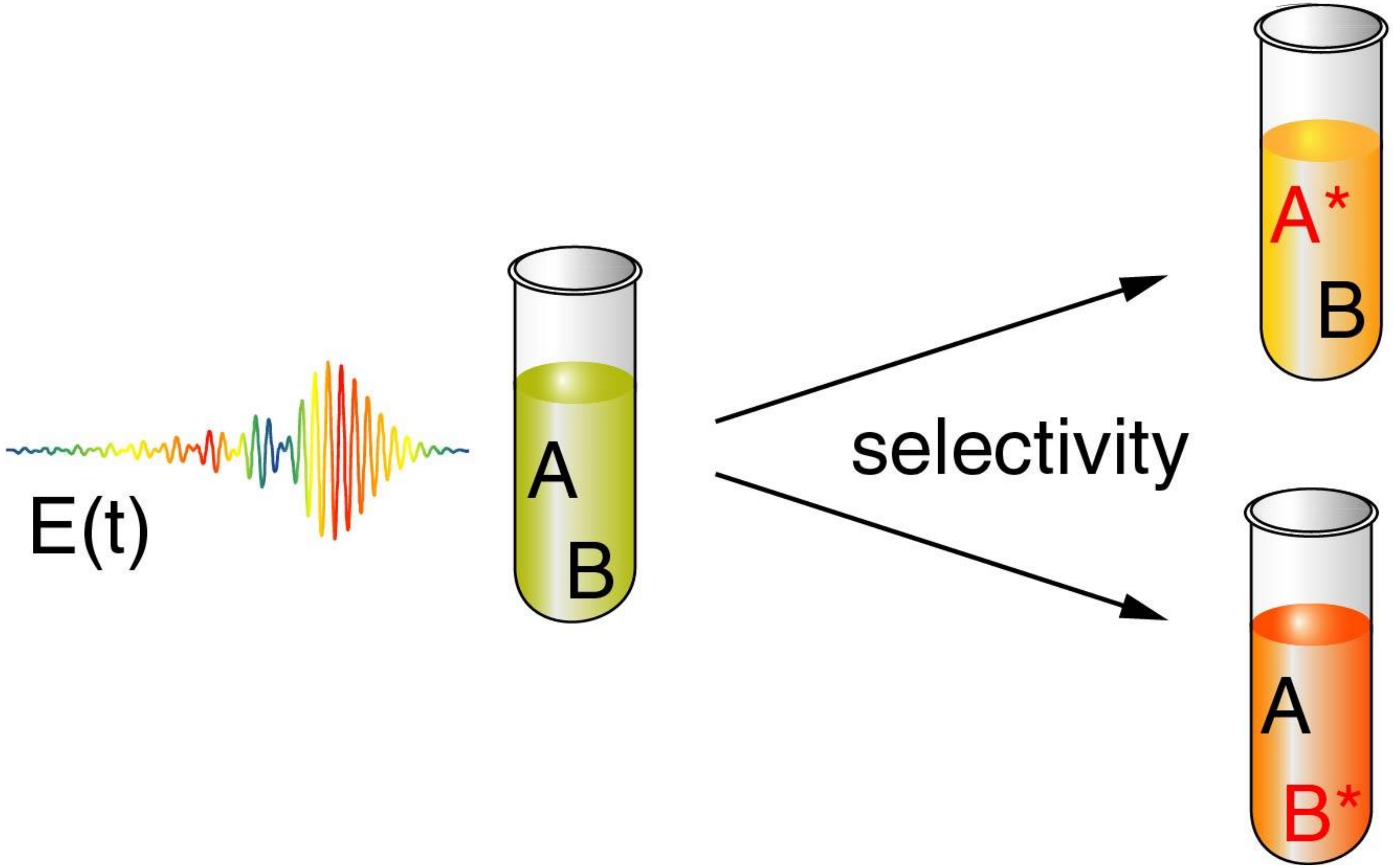

Quantum control in the liquid phase

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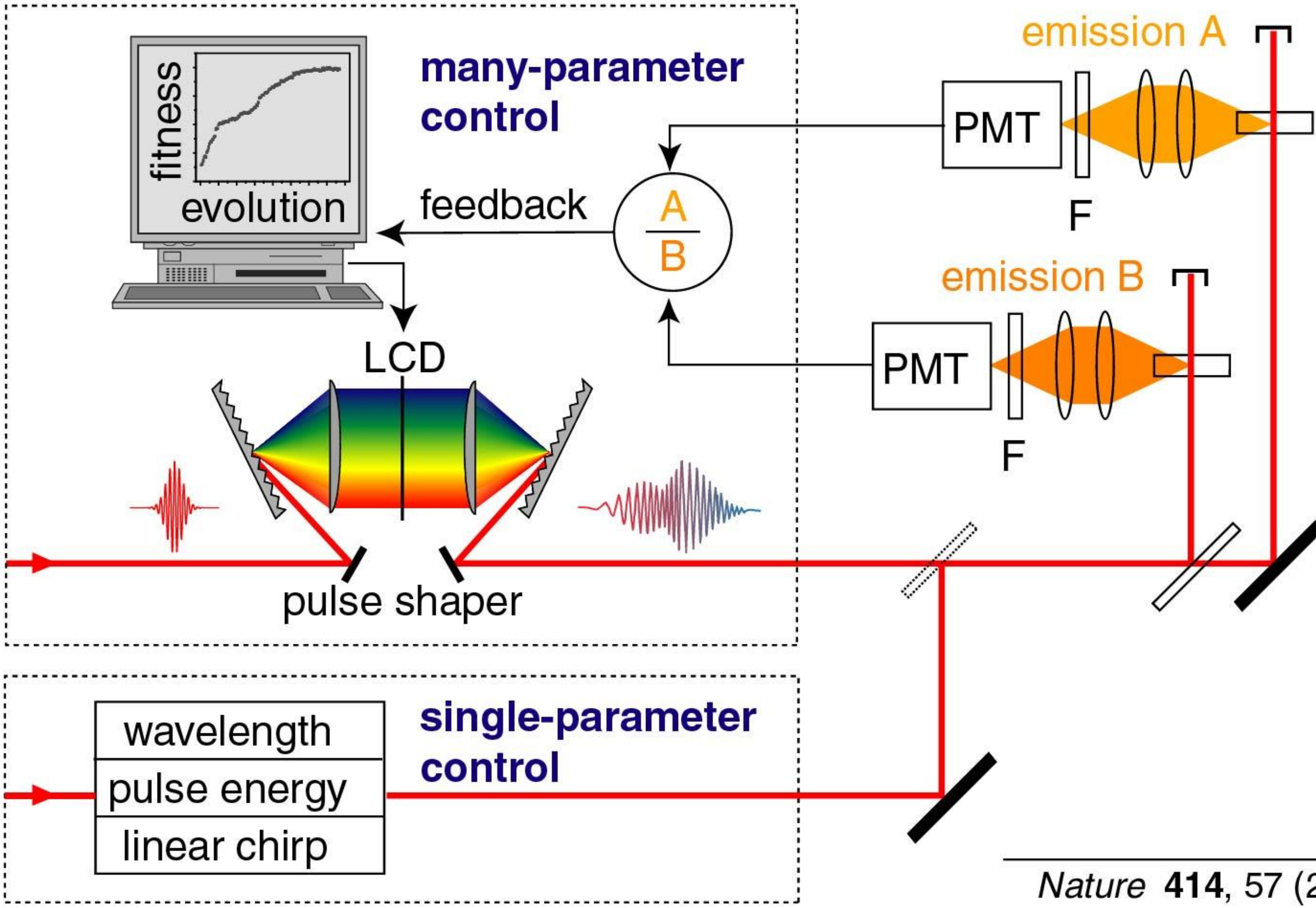

Nature **414**, 57 (2001)

Photochemically selective excitation

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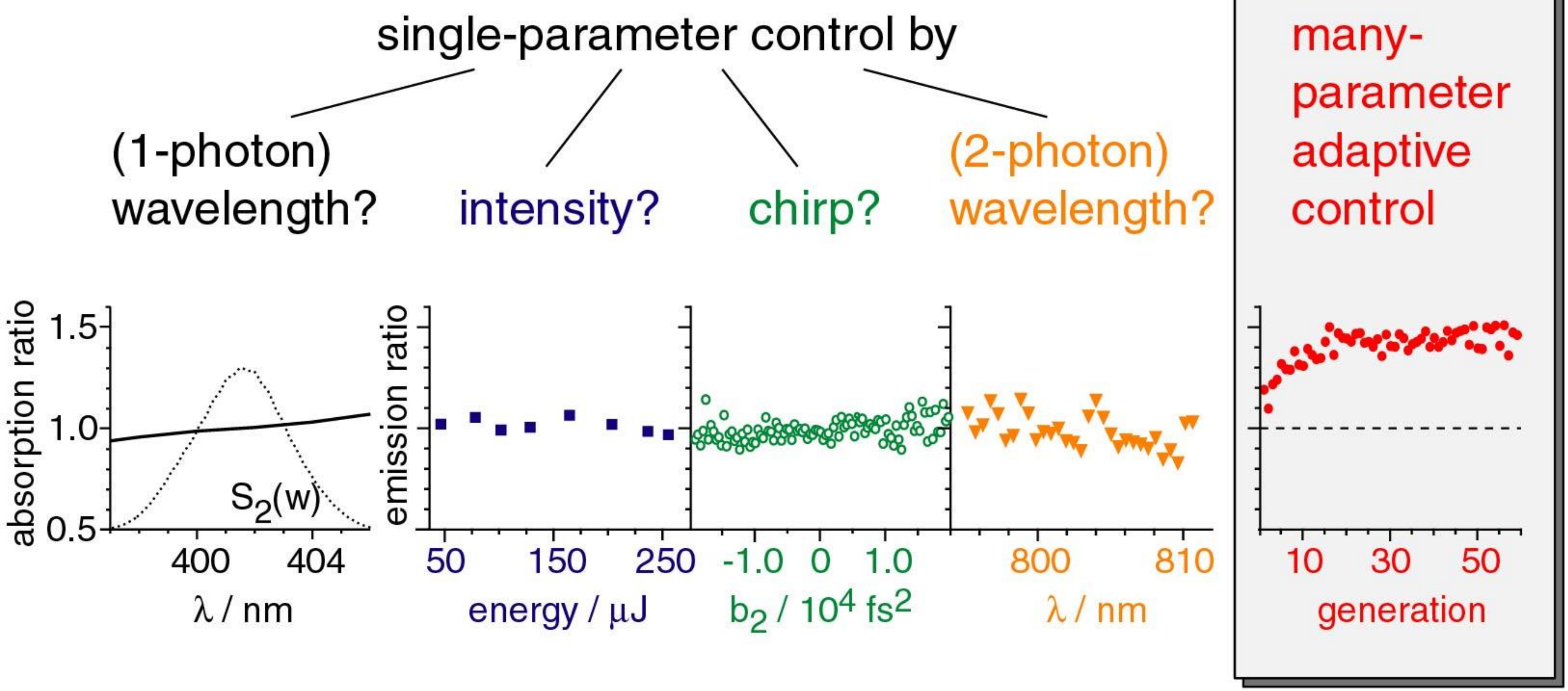

Nature **414**, 57 (2001)

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

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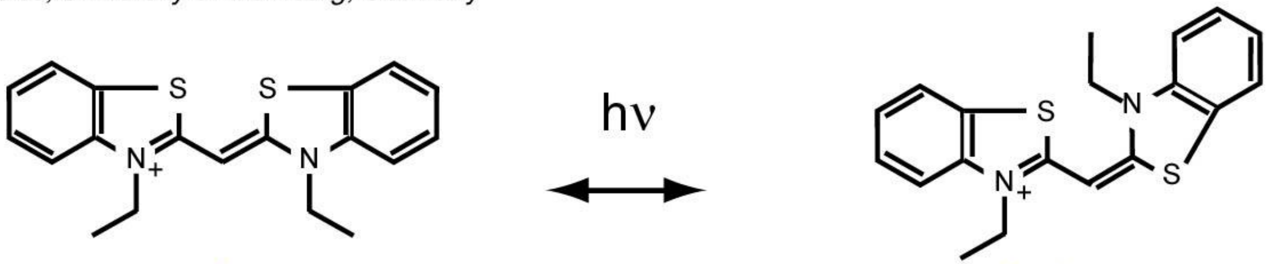
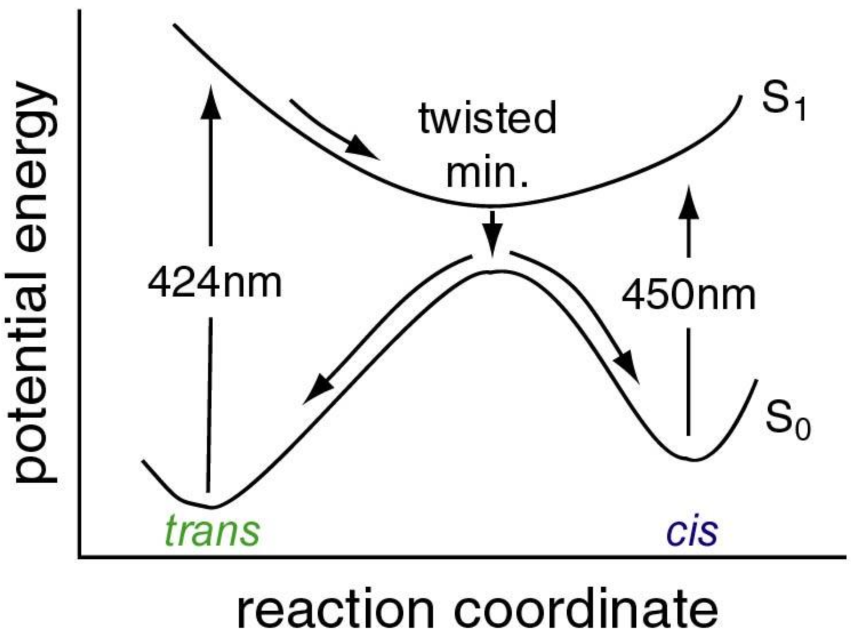
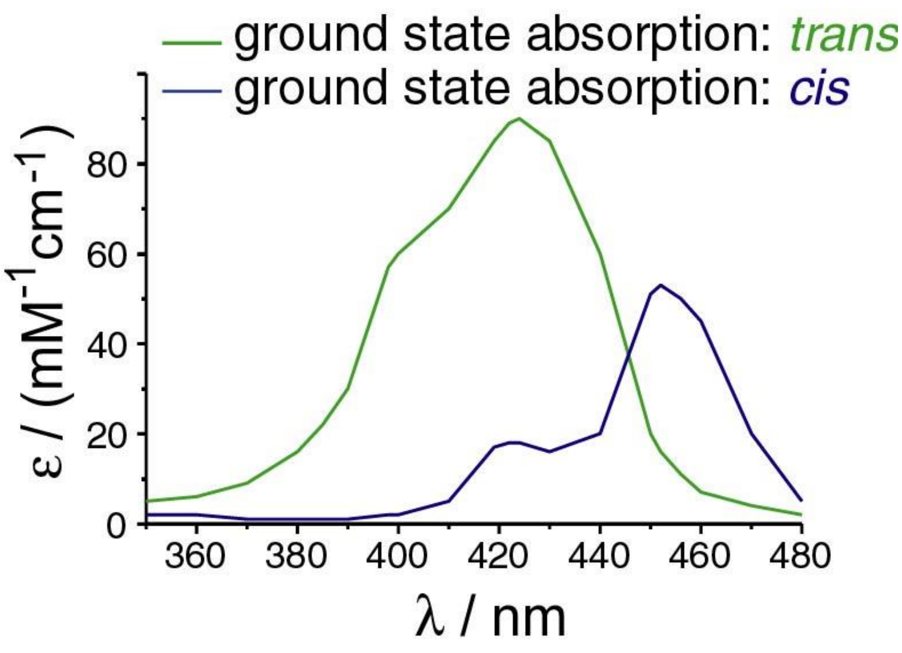


trans-isomer *cis*-isomer





Experimental setup

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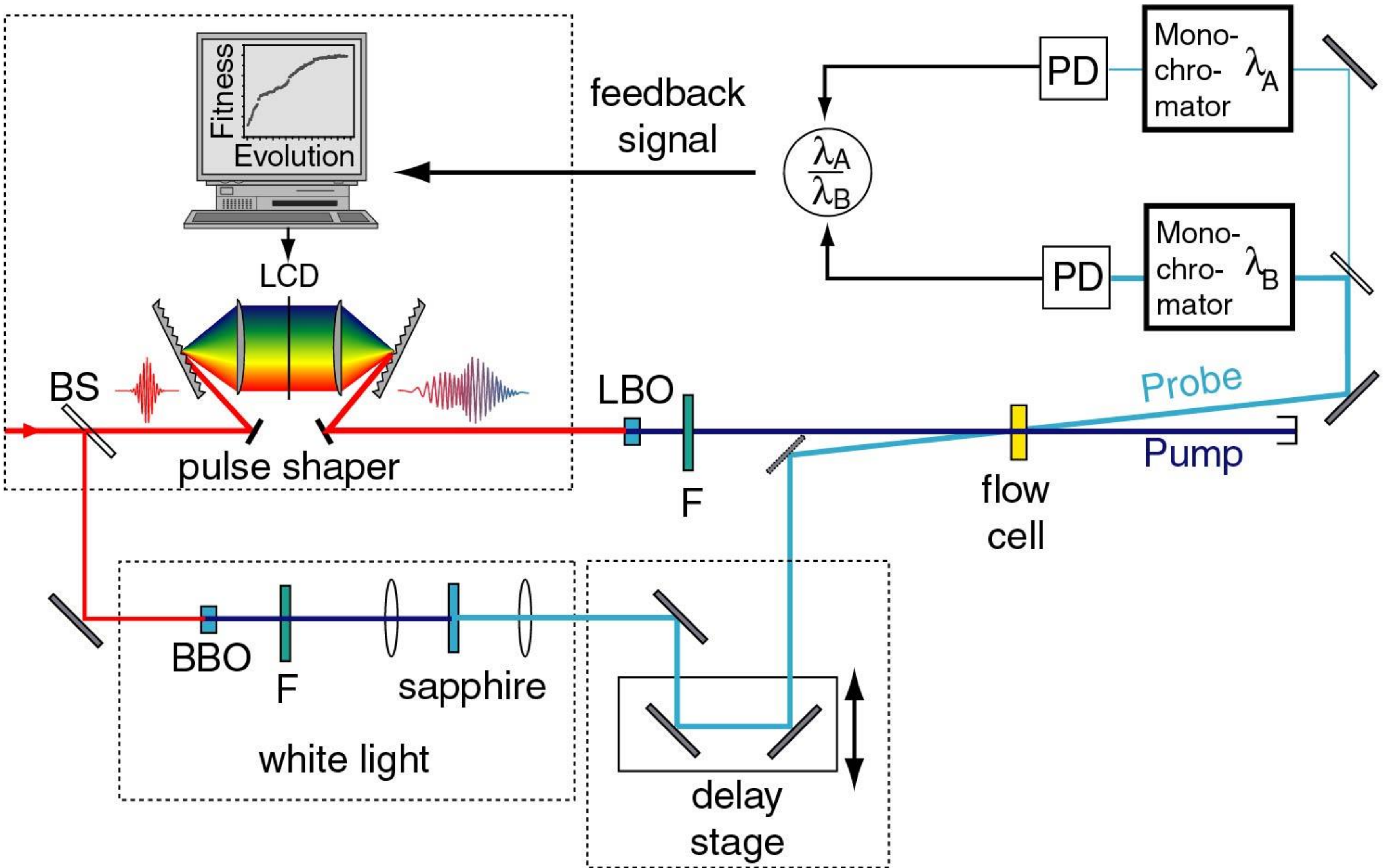

Transient Absorption - 3.3'-DiEthyl-2.2'-thiacyanine iodide - NK88

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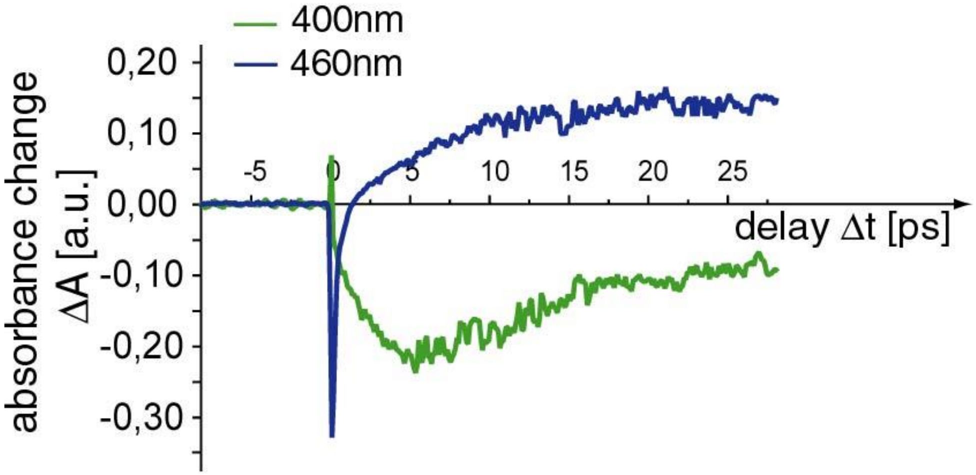
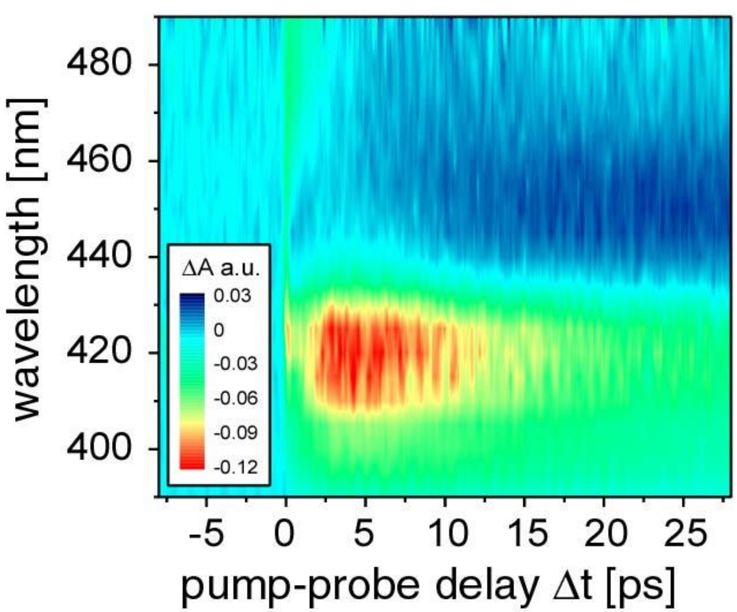
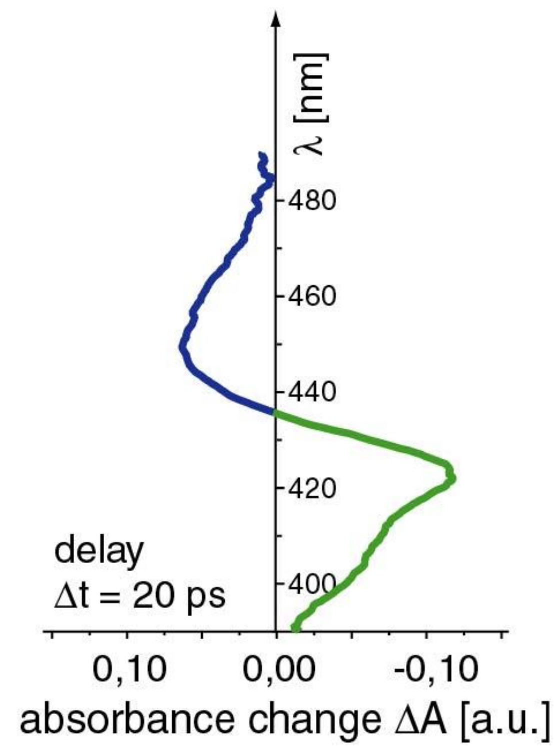


- 460nm: absorption *cis*
- 400nm: pump-depletion excited *trans*





NK88 - control of photoisomerization

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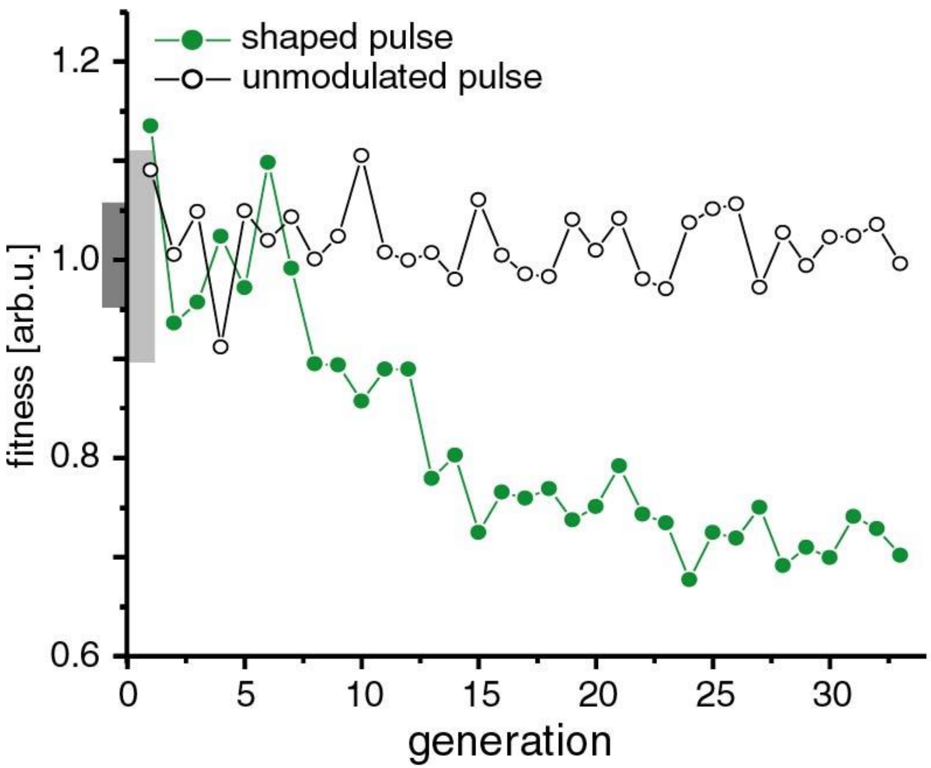
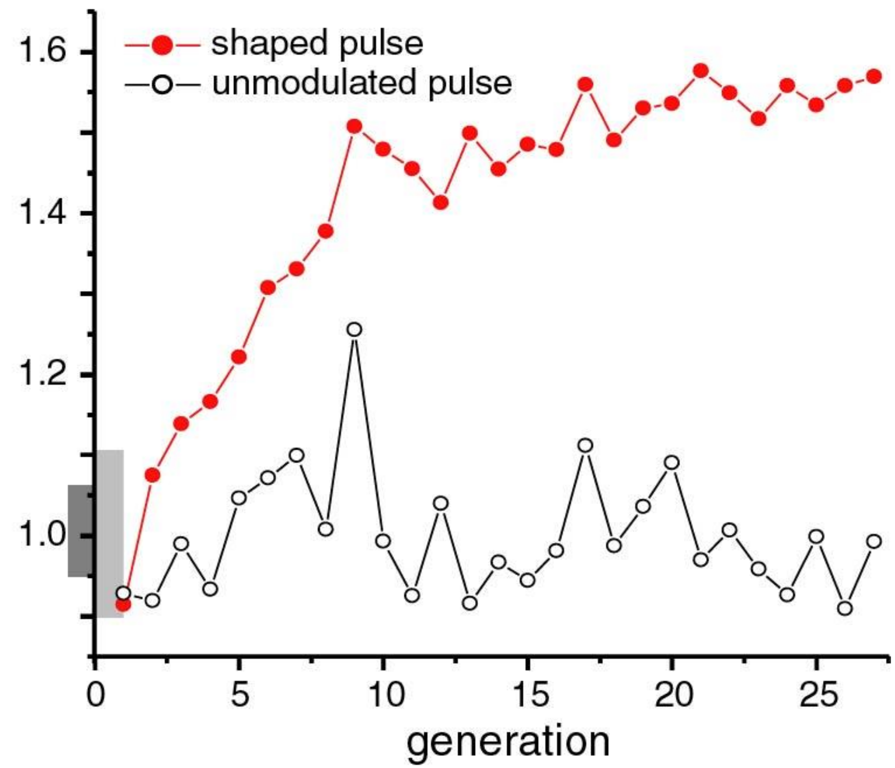
suppression of isomerization



enhancement of isomerization



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

■ intensity
■ chirp

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

NK88 - optimal pulse shapes

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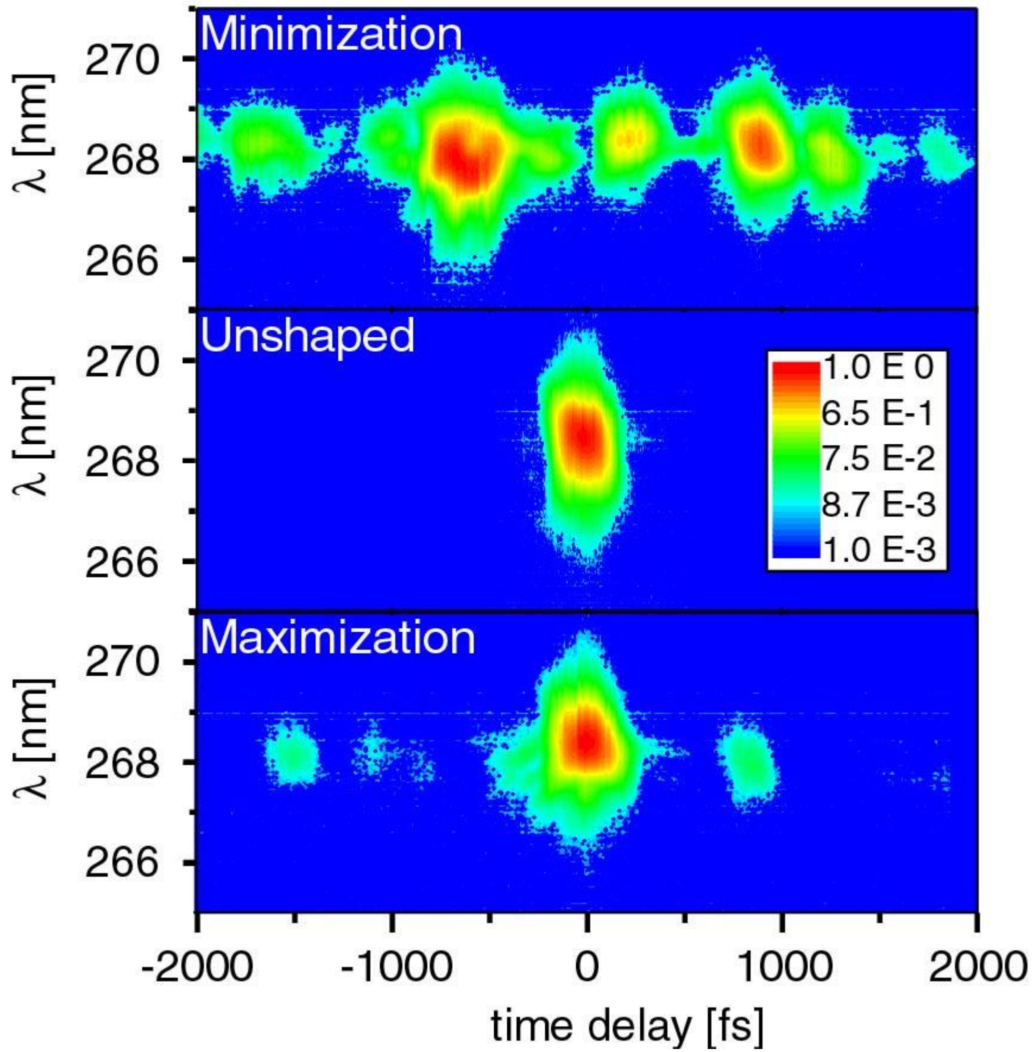
XFROG Traces:

- 800nm reference pulse: characterised by FROG
- 400nm pulse is cross-correlated with the known 800nm pulse



Applications of adaptive pulse shaping

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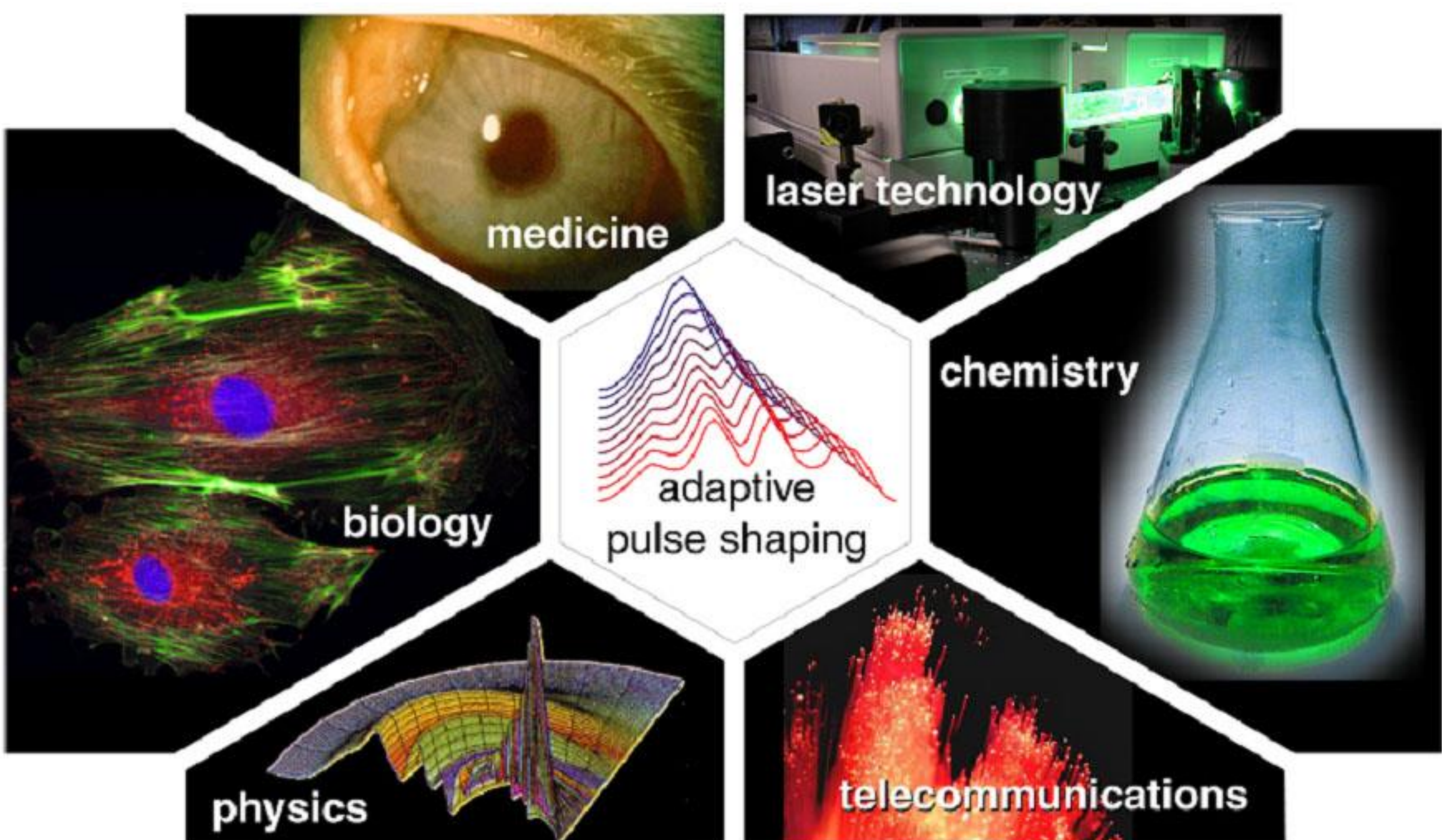

high harmonic generation

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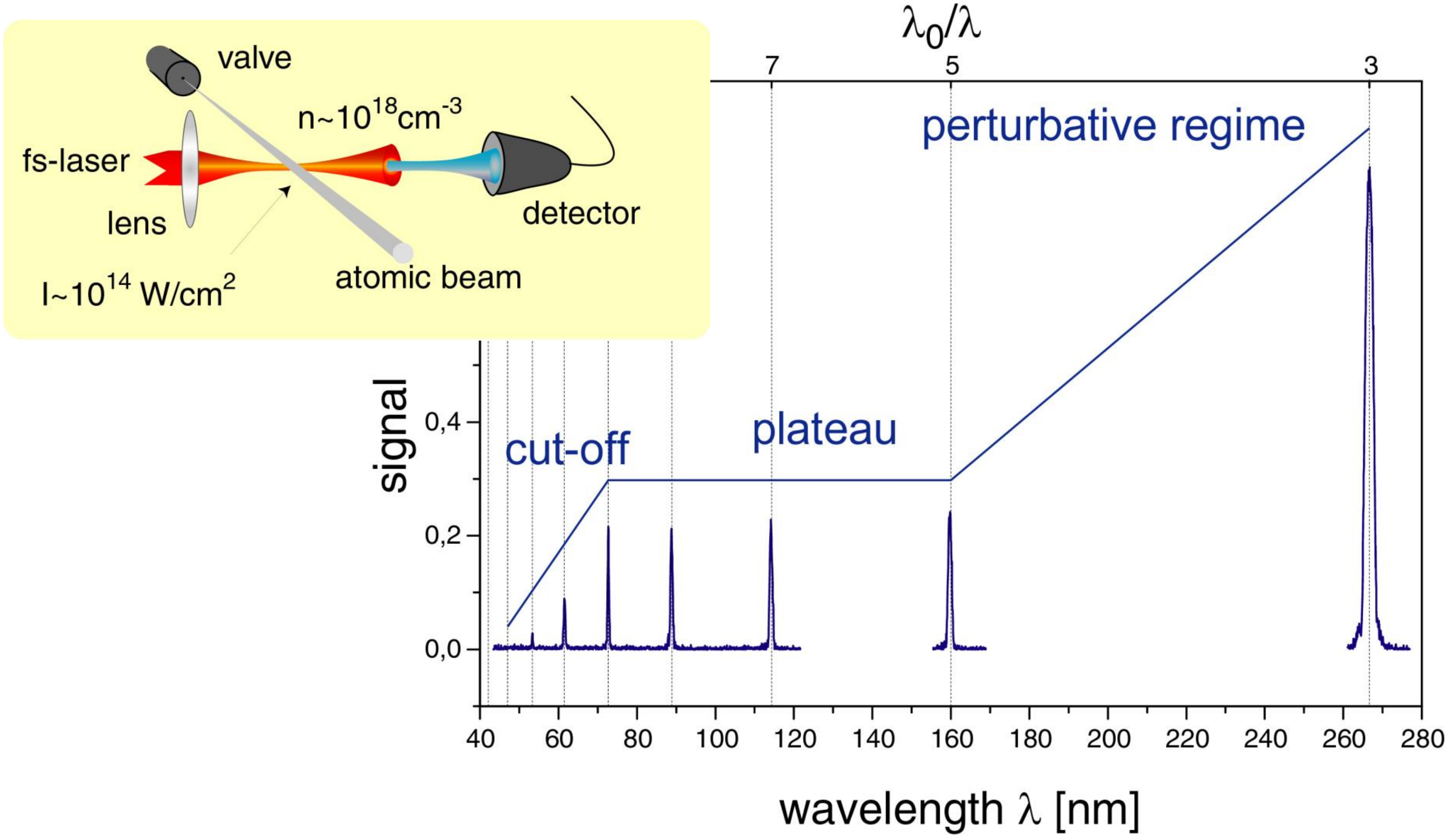

High-harmonics in Ne

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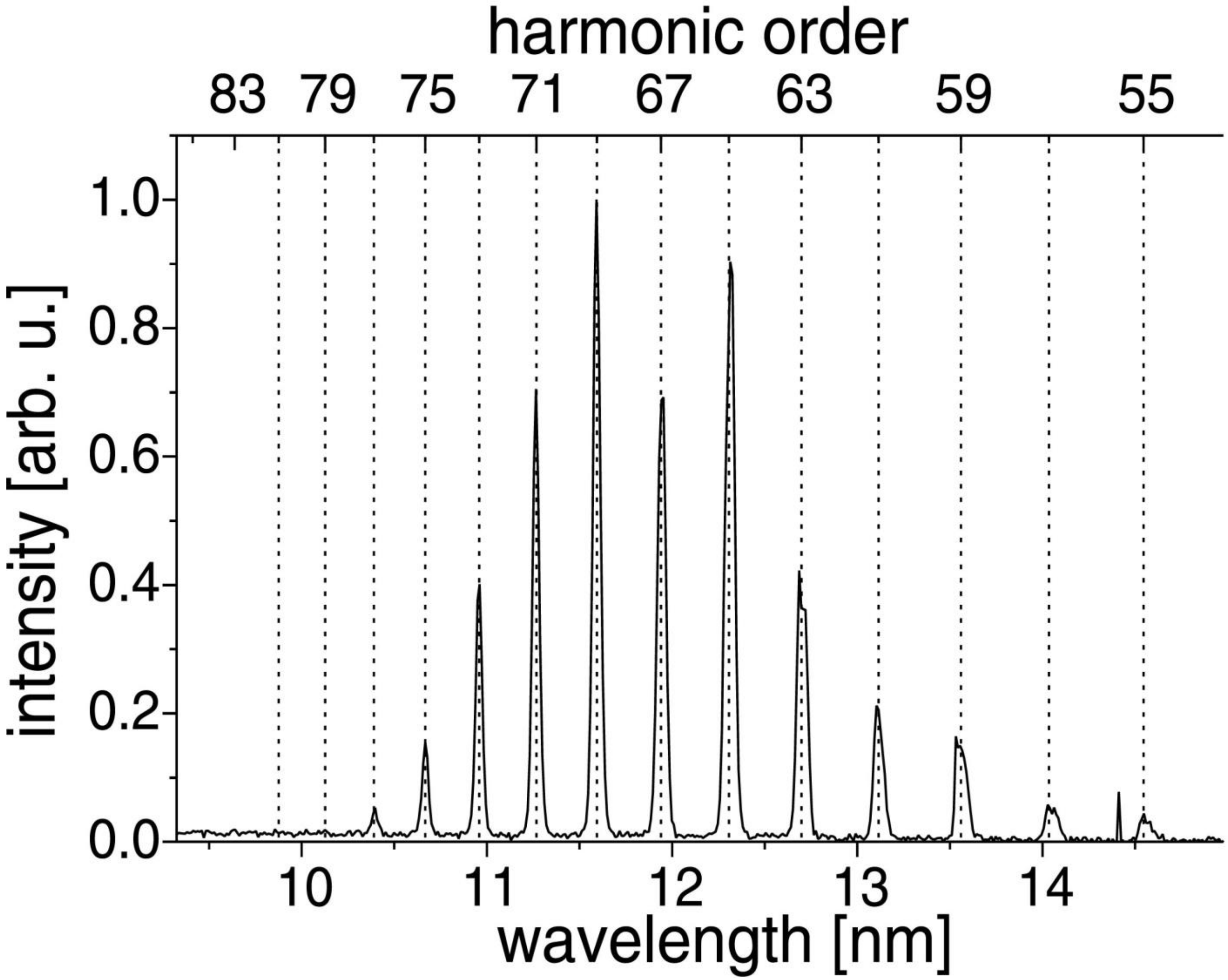

80 fs
800 nm
$5 \cdot 10^{14}$ W/cm^2
1 kHz

Zr + Parylene-N filter

Objective: Control HHG

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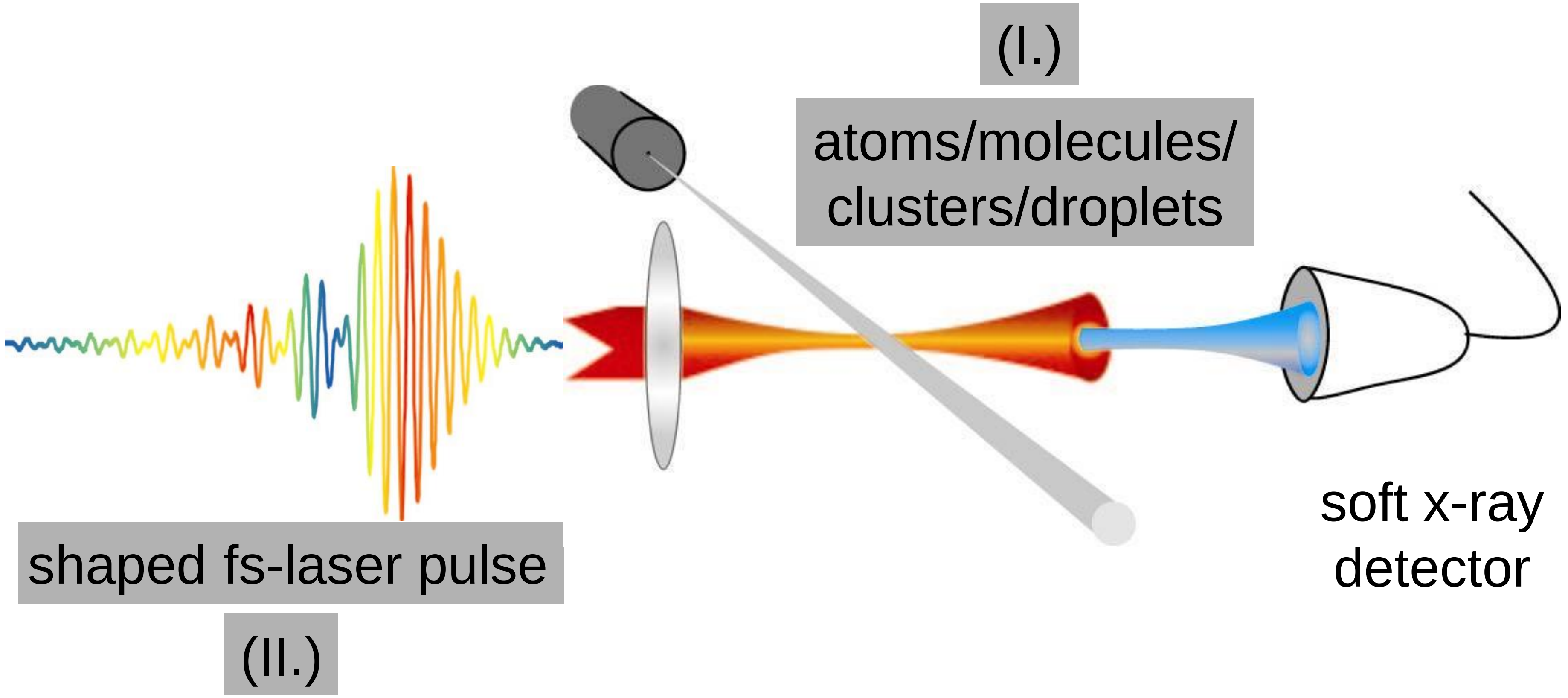

Three-step model

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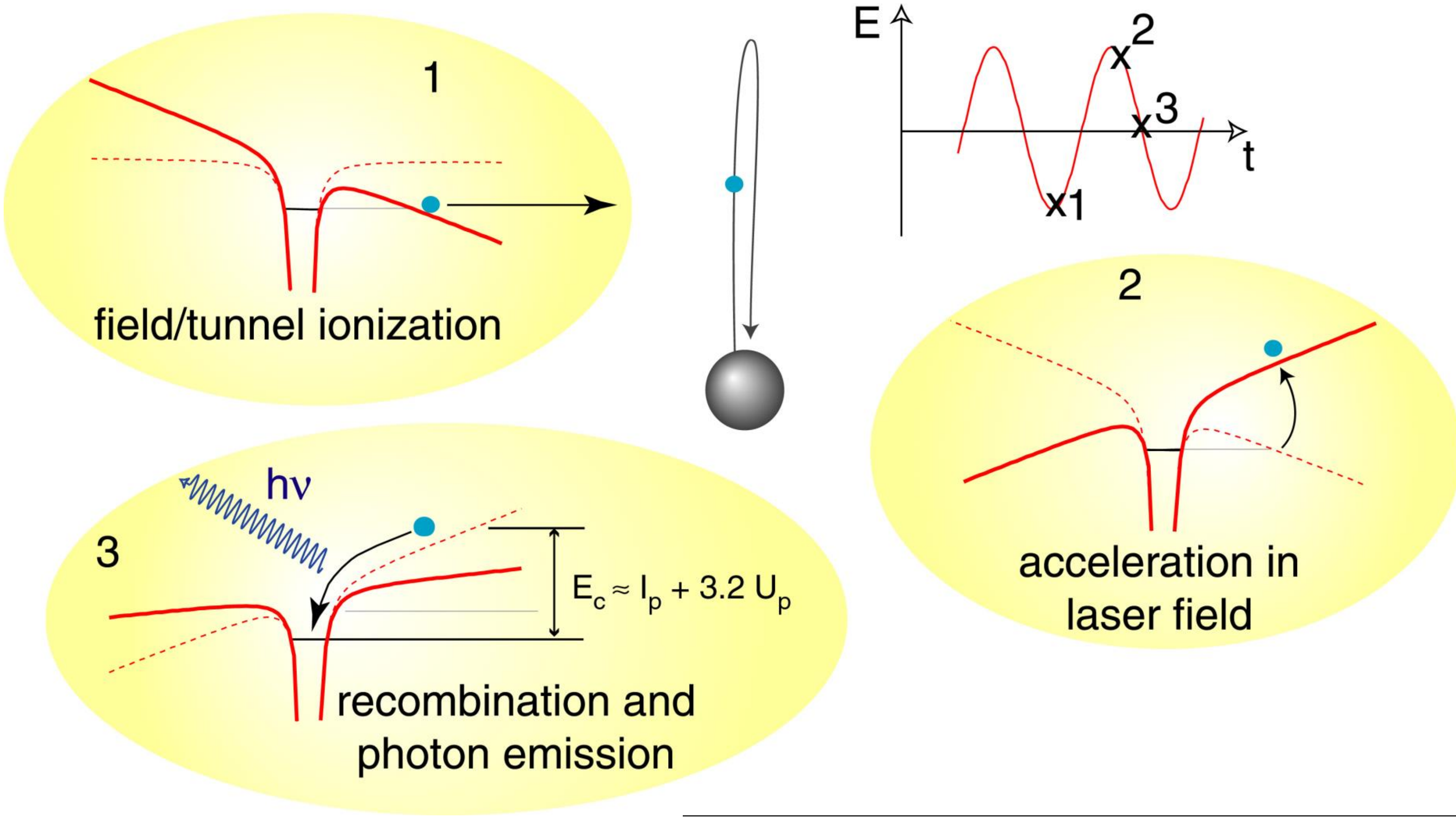

P. Corkum, Phys. Rev. Lett. **71**, 1994 (1993)

Harmonic generation geometry

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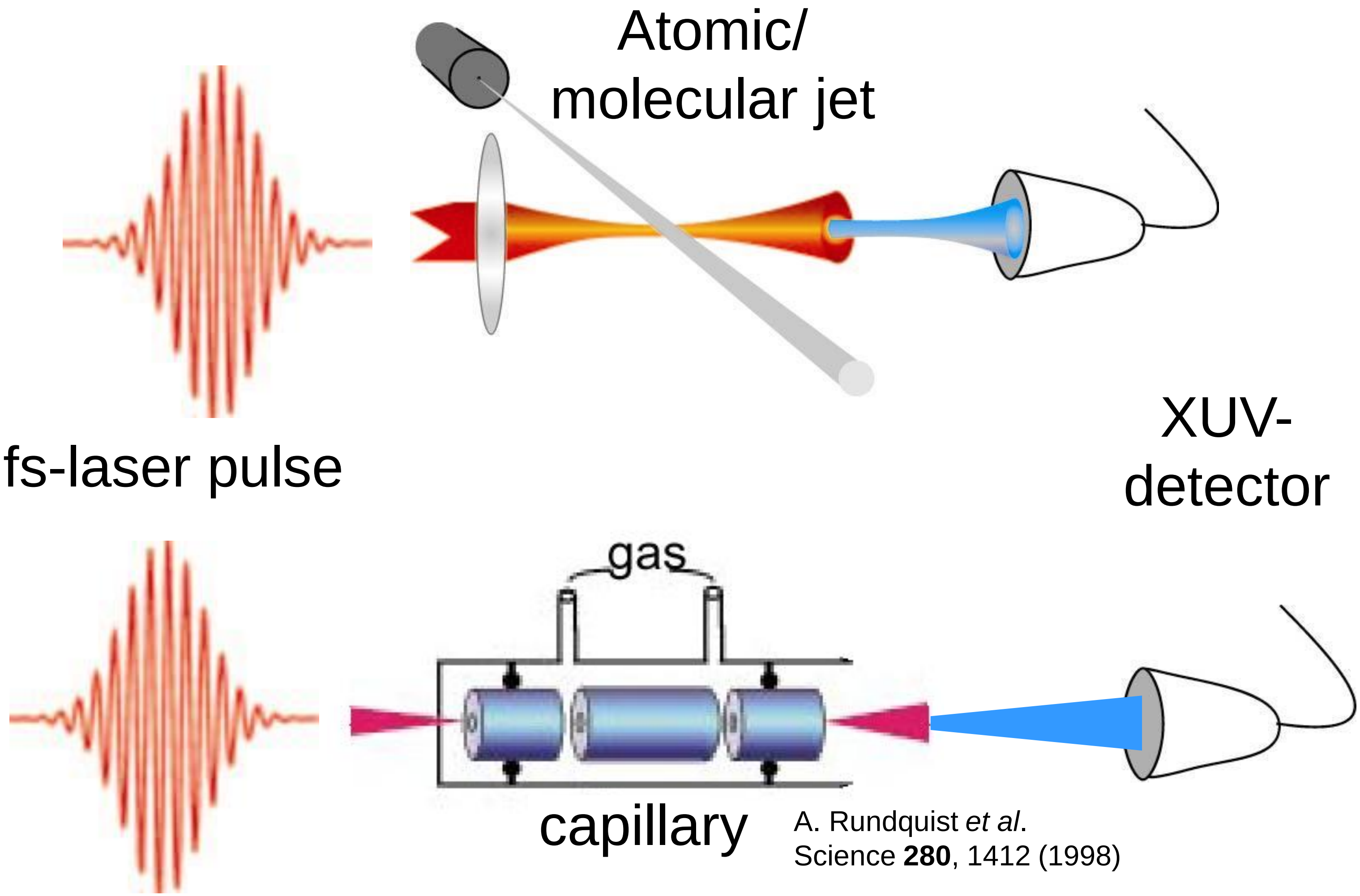

A. Rundquist *et al*.
Science **280**, 1412 (1998)

Experimental setup

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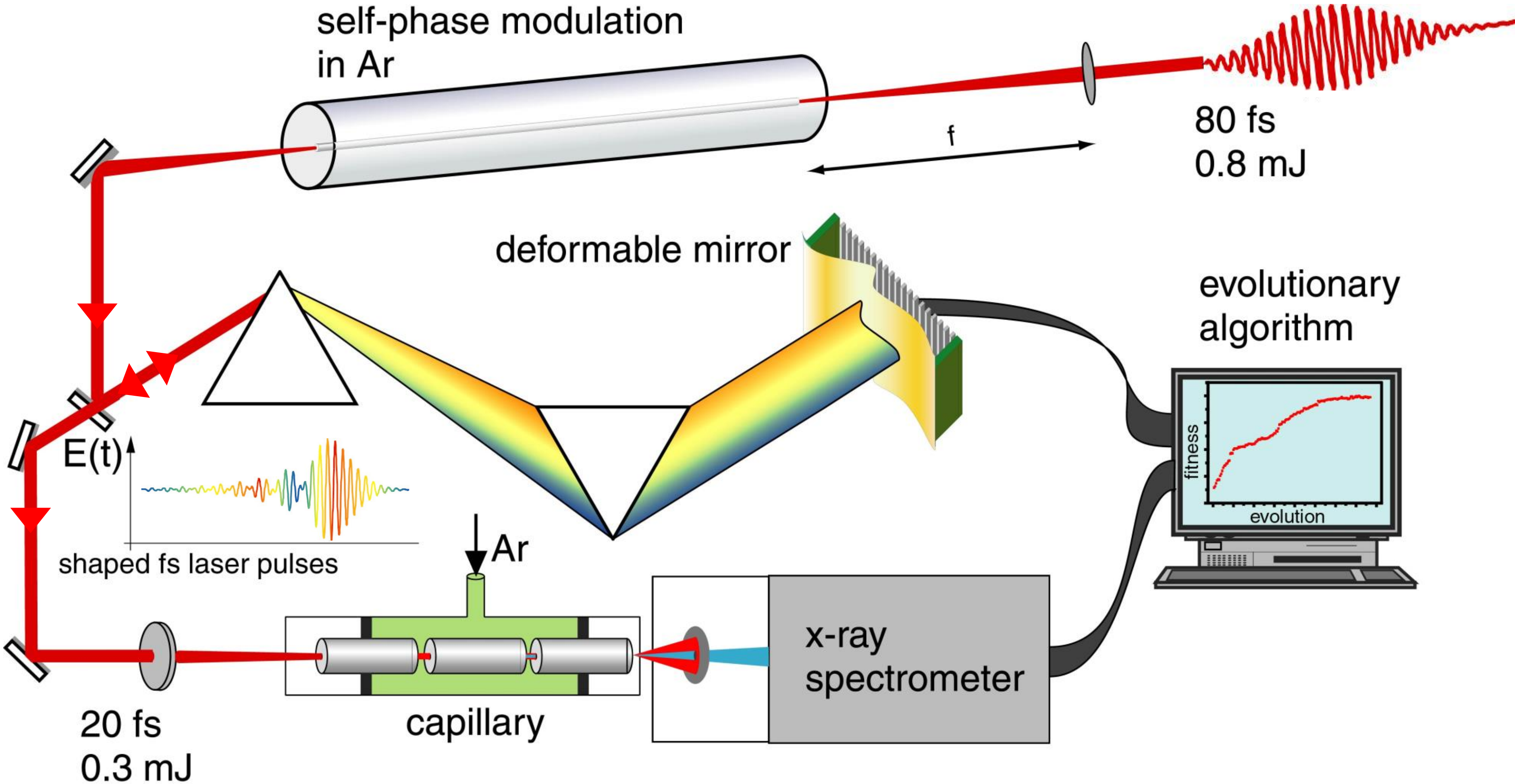

Harmonic enhancement

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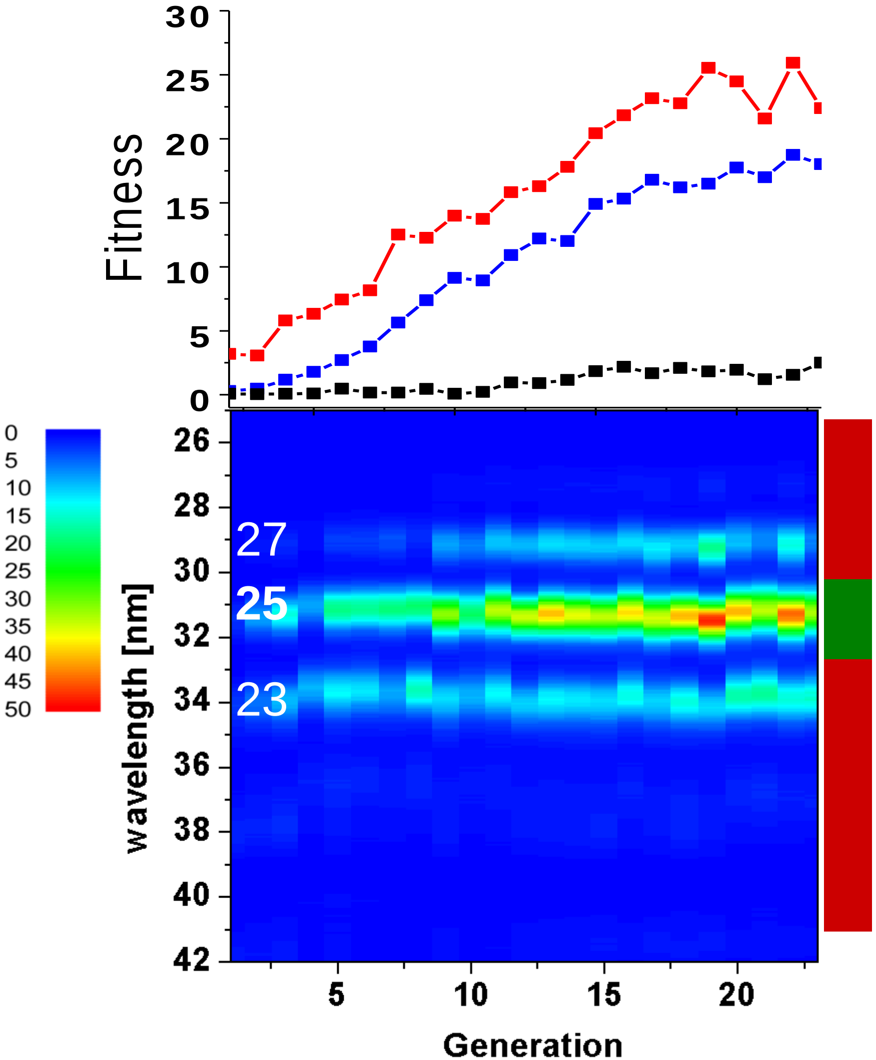


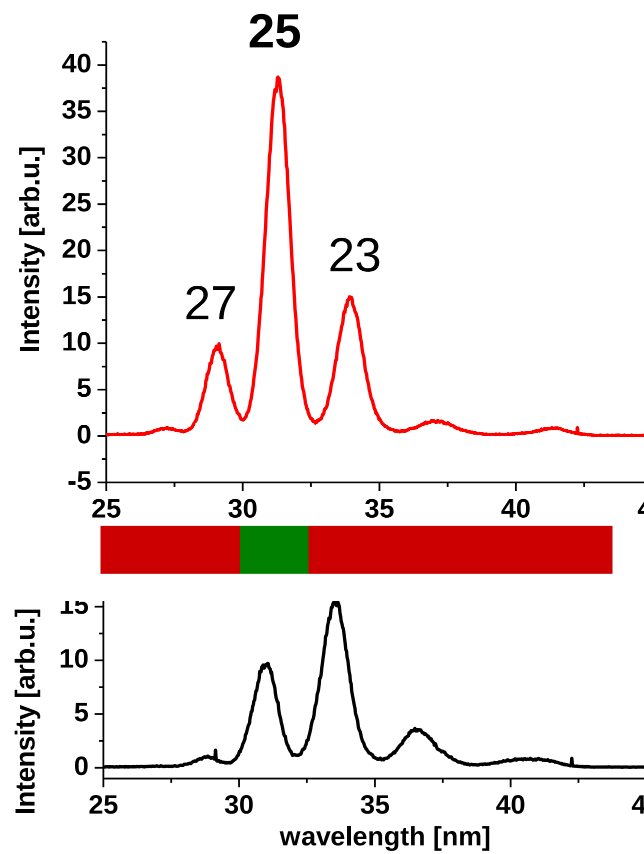
fittest pulse shape

average fitness

unshaped pulse / reference signal

fitness:

$$\frac{\text{green}^2}{\text{red}}$$



efficiency: ≈ 10^6 photons/pulse in a single harmonic!

selective enhancement of HHG

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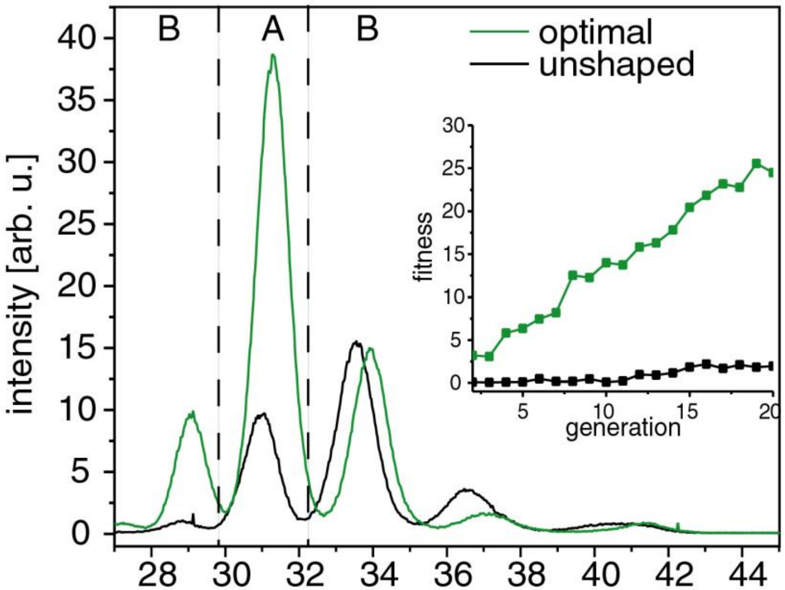

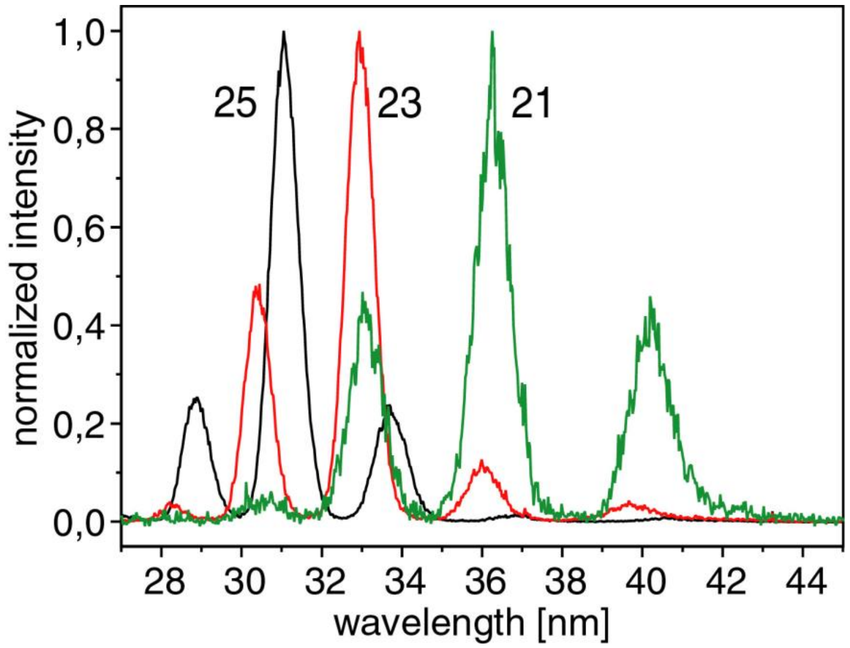

Phase-matching

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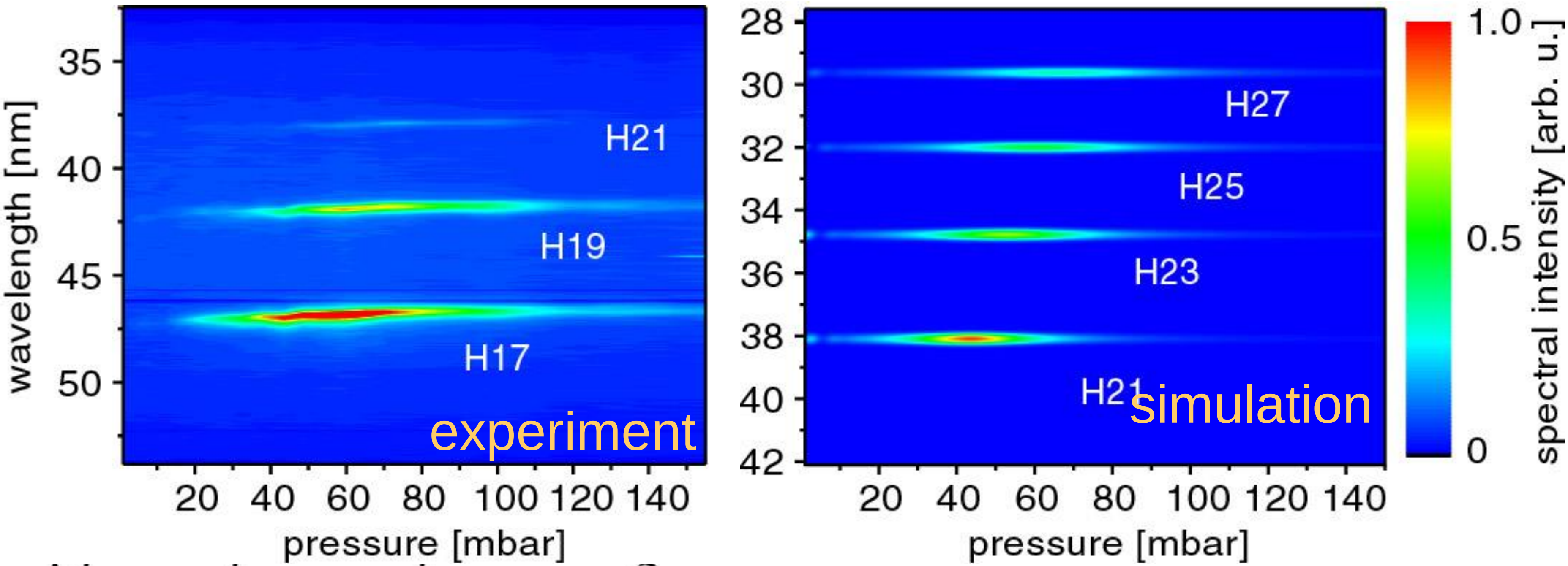

$$\Delta k = q k_{\mathrm{laser}} - k_{\mathrm{x\text{-}ray}} = 0$$

$$k \approx \frac{2\pi}{\lambda} + \frac{2\pi N_a \, \delta(\lambda)}{\lambda} - N_e r_e \lambda - \frac{u_{nm}^2 \lambda}{4\pi a^2}$$

vacuum propagation	material dispersion	plasma dispersion	waveguide dispersion

Selective Control of HHG

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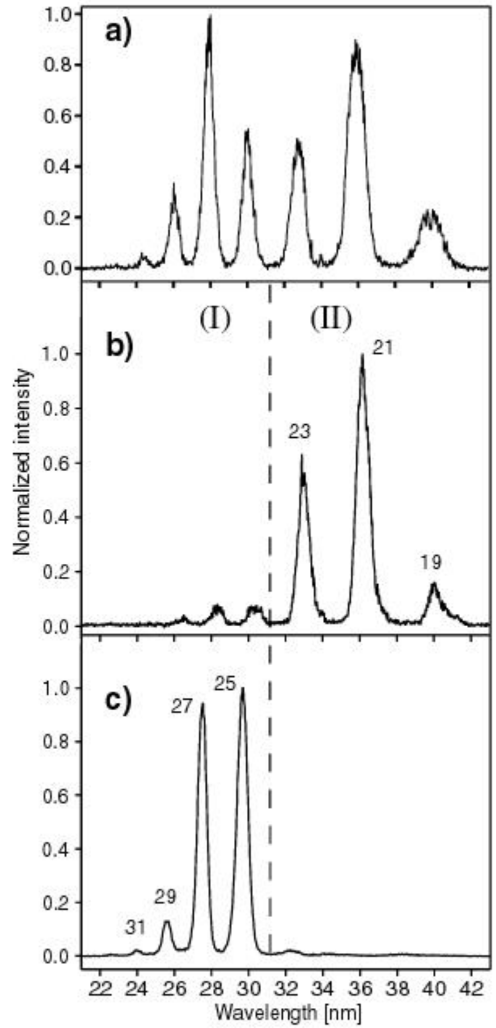

Suppression of Harmonics

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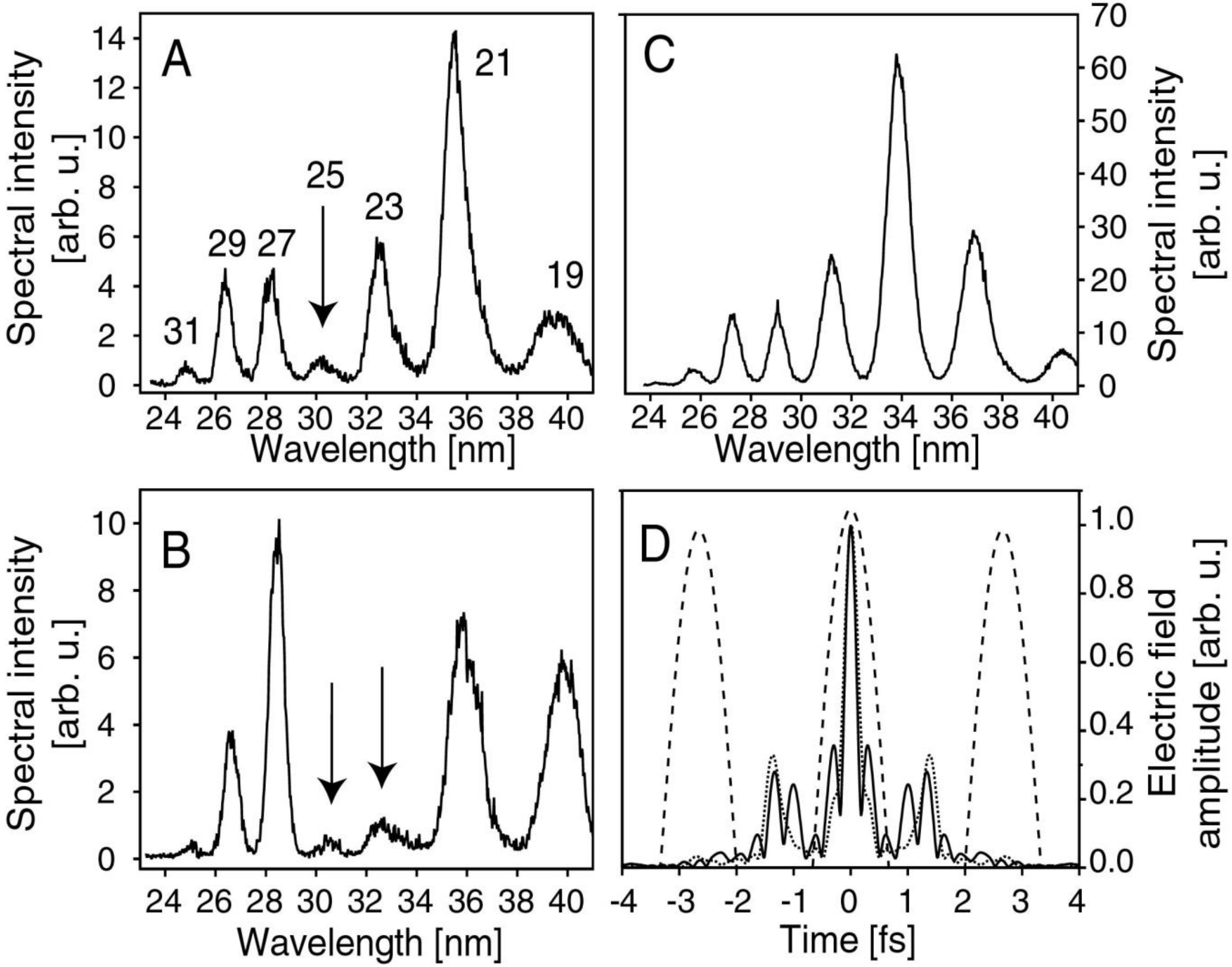

High-harmonic generation

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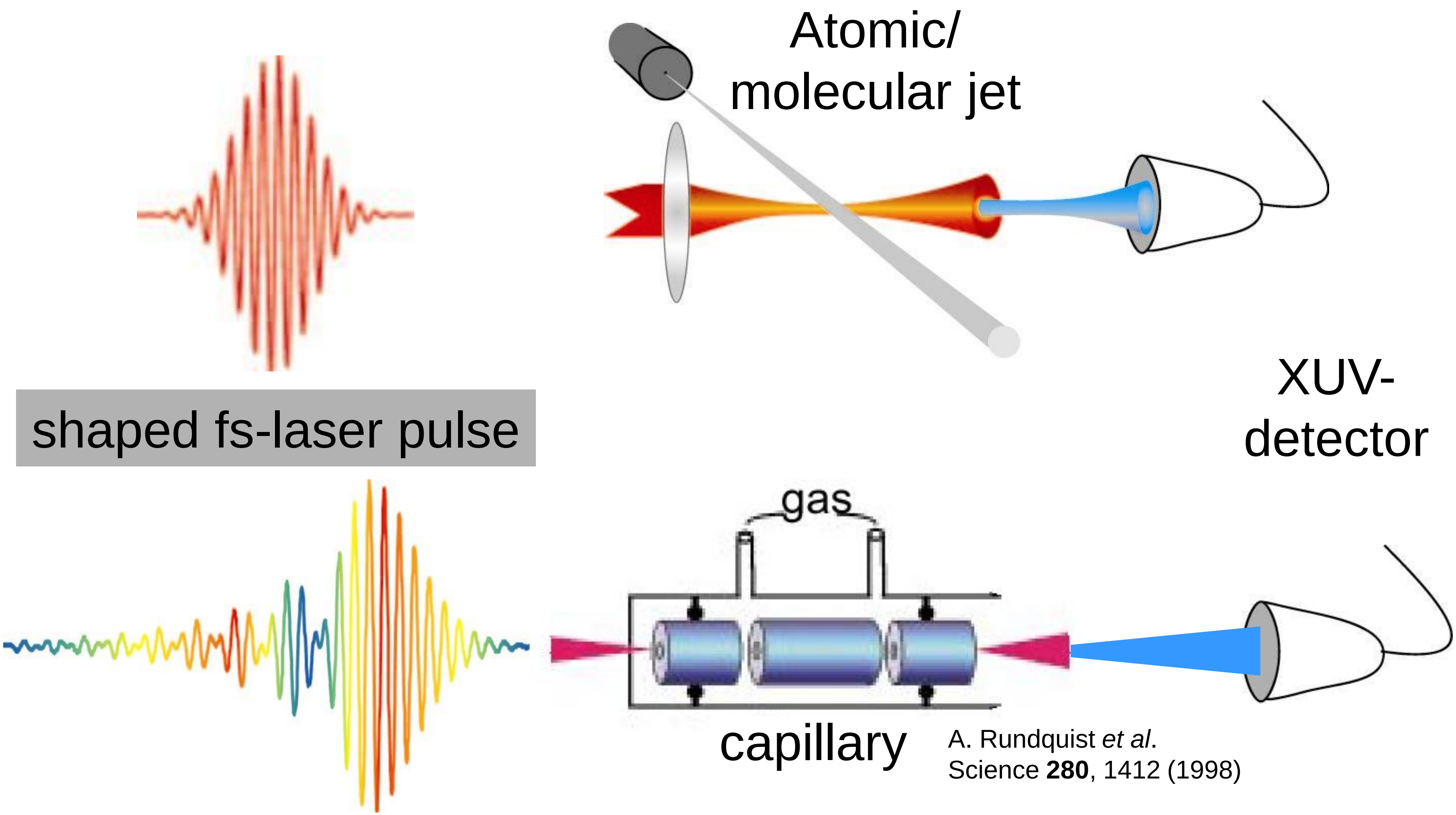

A. Rundquist *et al.*
Science **280**, 1412 (1998)

generation geometry

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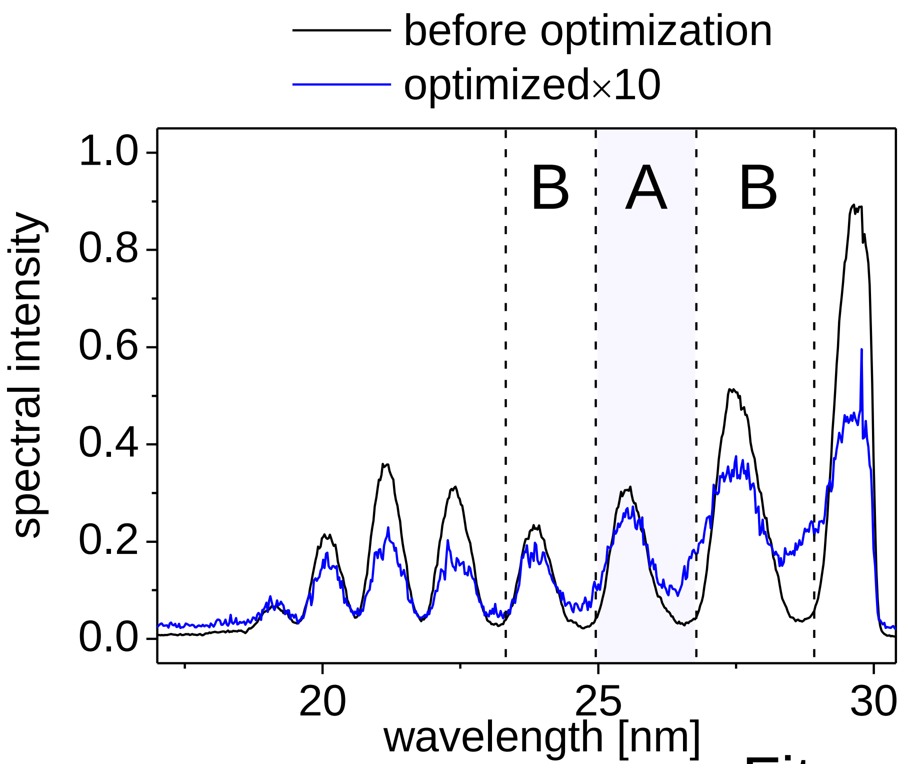
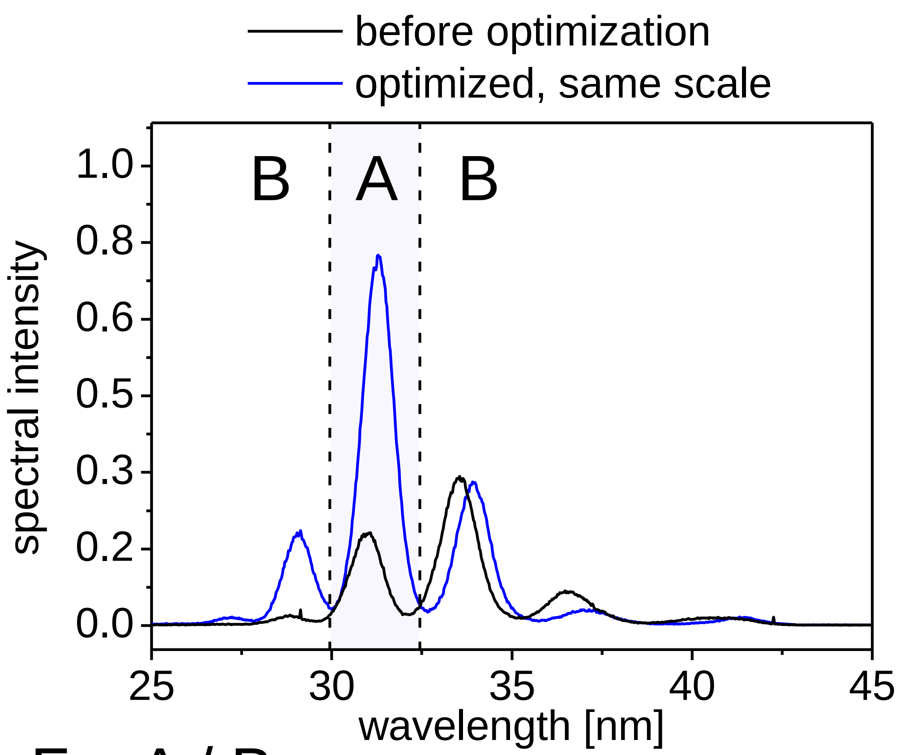
jet vs. capillary





Fitness: F = A / B

control not only governed by the single atom response

Summary

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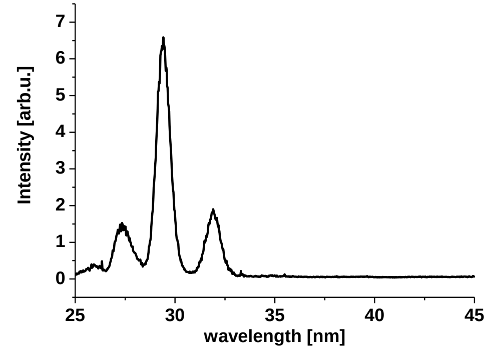
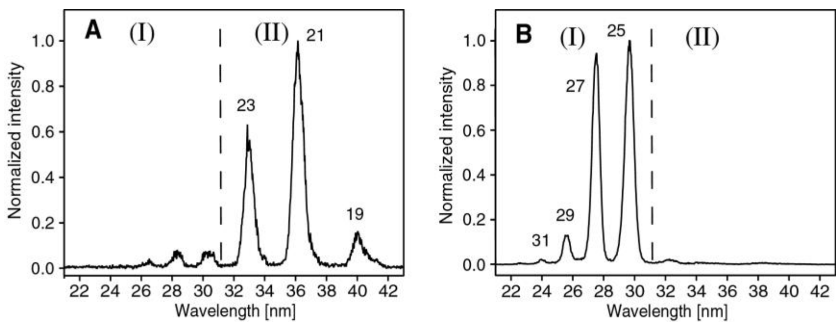
Department of Physics, University of Würzburg, Germany

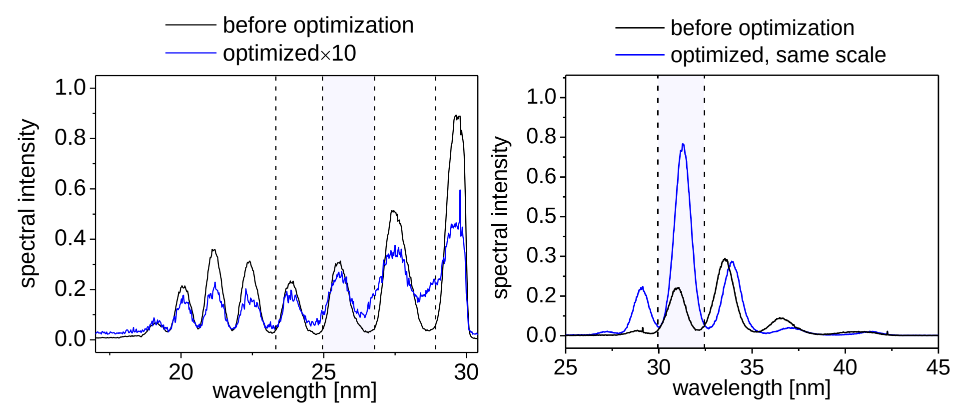
Selective Enhancement →



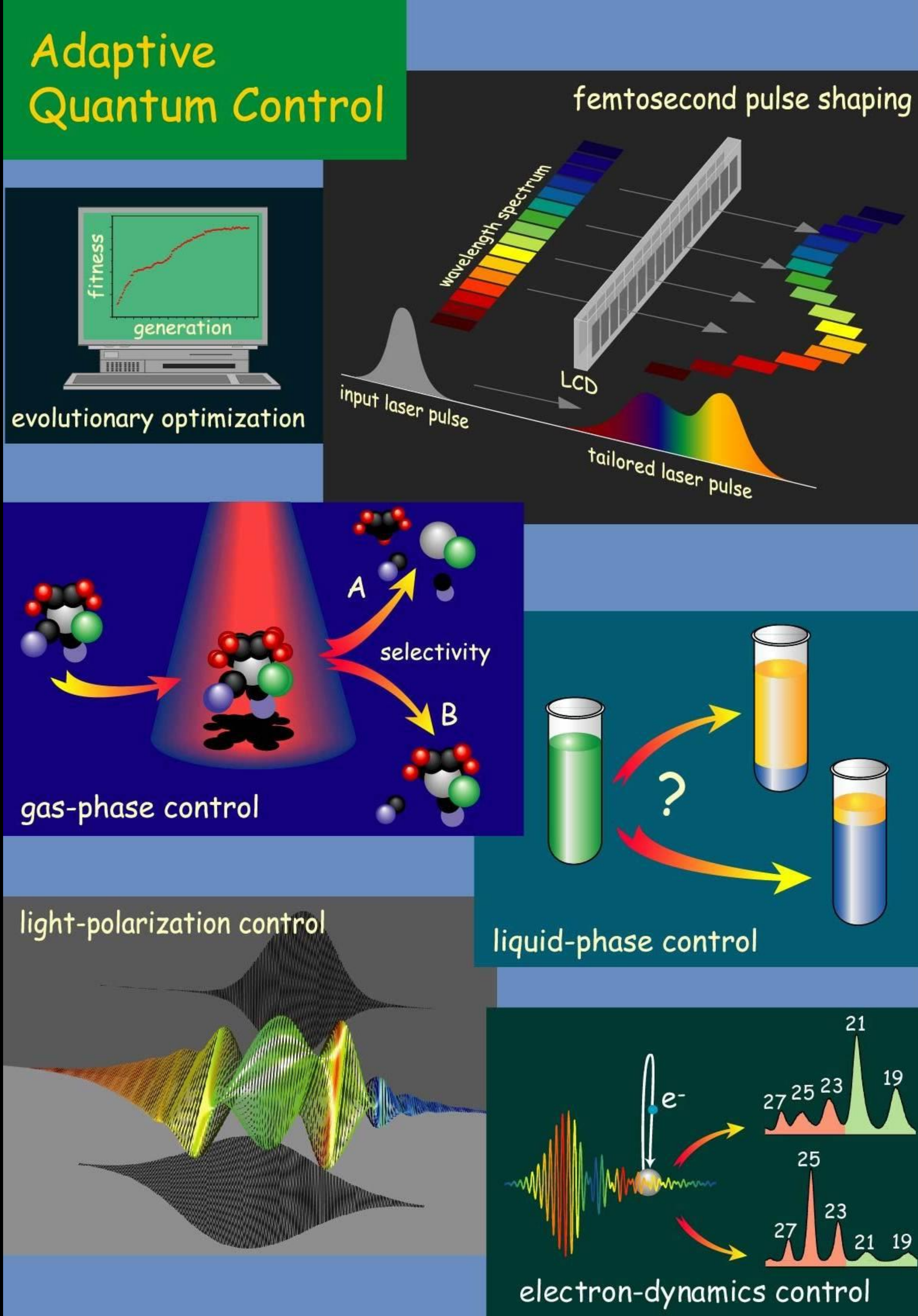


← Comprehensive Control

Control beyond the atomic dipole phase →



Attosecond Quantum Control


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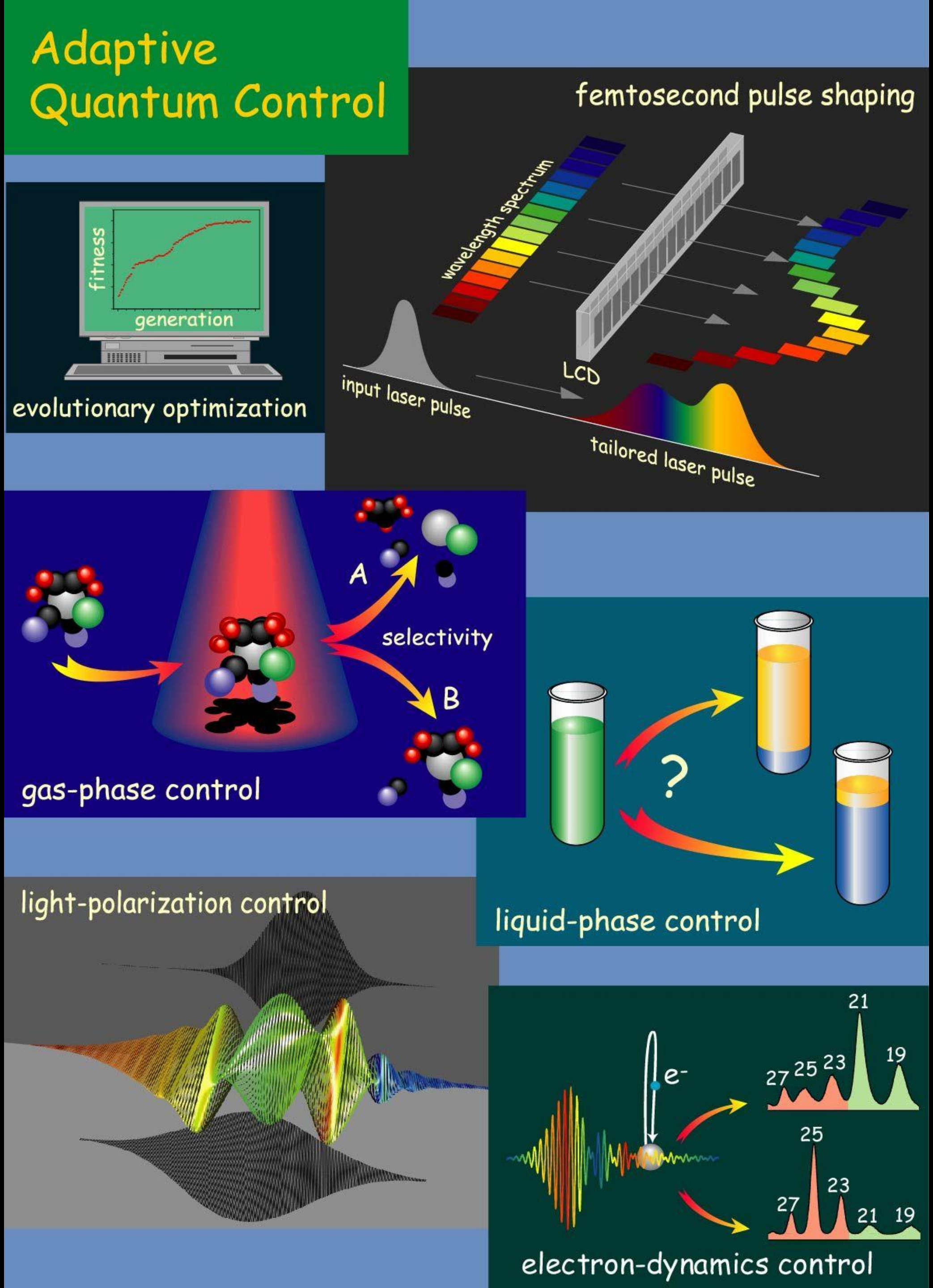
27 25 23
25
23
27
21 19
electron-dynamics control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