Laser-controlled Molecular Alignment and Orientation

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FOM Institute AMOLF

Summer School Cargese - Tuesday August 19th 2008

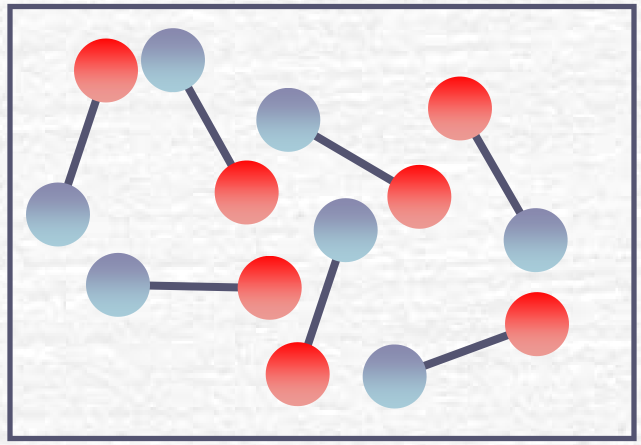
Contents

- What is molecular alignment resp. orientation, and why is it an interesting property?
- Laser-controlled molecular alignment (adiabatic vs. impulsive, 2D vs. 3D)
- Laser-controlled molecular orientation
- Optimization of alignment and orientation

What is molecular alignment resp. orientation, and why is it an interesting property?

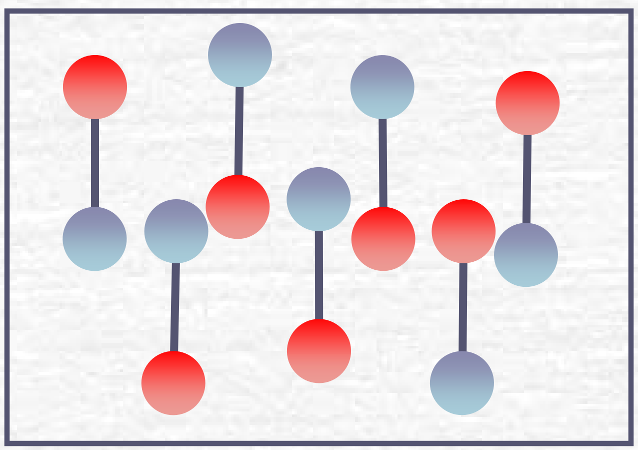
Alignment: $\langle\cos^2\theta\rangle$

Orientation: $\langle\cos\theta\rangle$



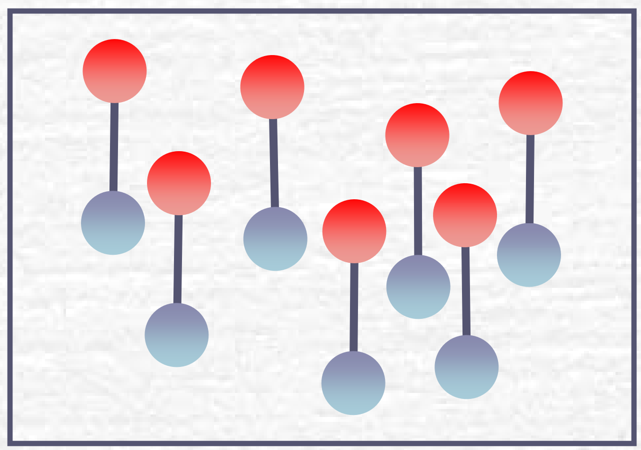
$\langle\cos^2\theta\rangle = 1/3$
$\langle\cos\theta\rangle = 0$

“Isotropic”



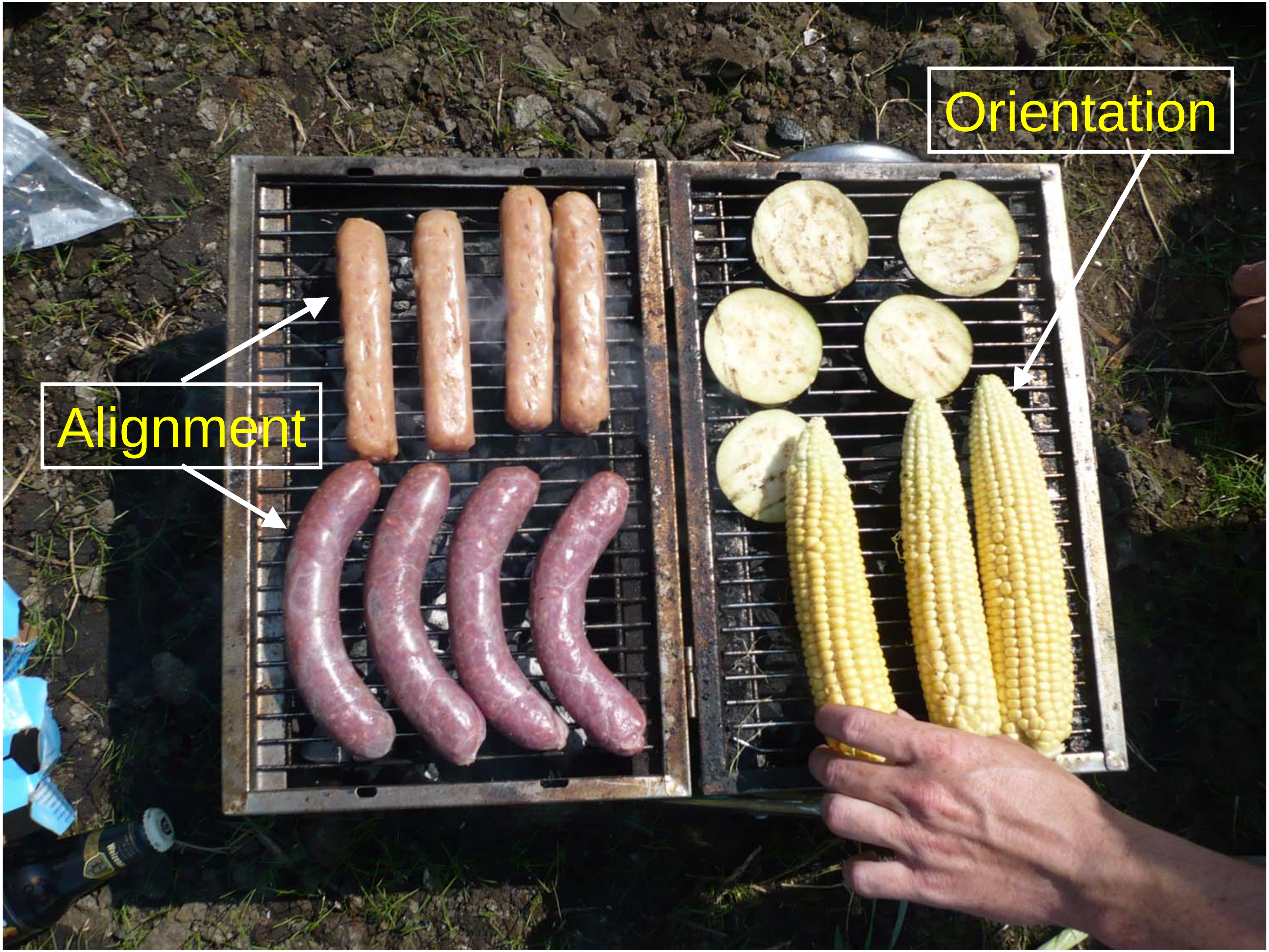
$\langle\cos^2\theta\rangle > 1/3$
$\langle\cos\theta\rangle = 0$

“Aligned”



$\langle\cos^2\theta\rangle > 1/3$
$\langle\cos\theta\rangle > 0$

“Oriented”


Orientation
Alignment

What is molecular alignment resp. orientation, and why is it an interesting property?

- Molecular alignment and orientation are suitable observables that allow us to assess our ability to exert strong-field control over molecular properties

- Molecular alignment and orientation provide the connection between **laboratory-frame** measurements and measurements in the **molecular-frame**

Laboratory frame Photofragmentation ←→ Molecular Frame Photofragmentation

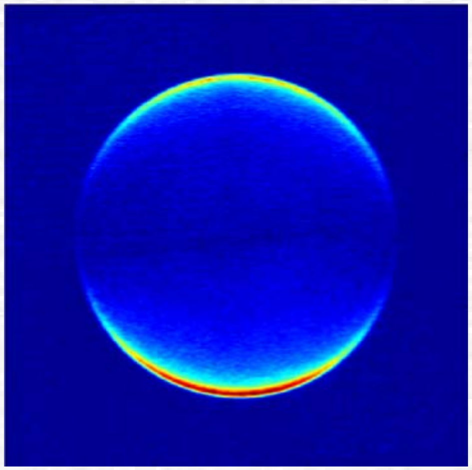
$P(\cos\theta) = 1 + \beta P_2(\cos\theta)$

$P(\cos\theta)$ ~ electron scattering or nuclear dynamics in the molecular frame

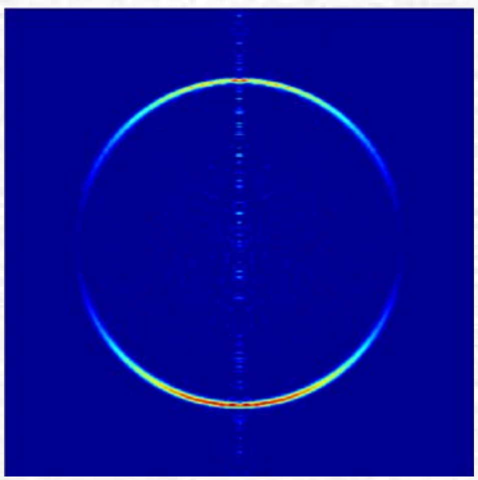
Example: Photoionization of H_2 at XUV wavelengths

Photoionization of H_2 at XUV wavelengths

Laboratory frame Photofragmentation ←→ Molecular Frame Photofragmentation



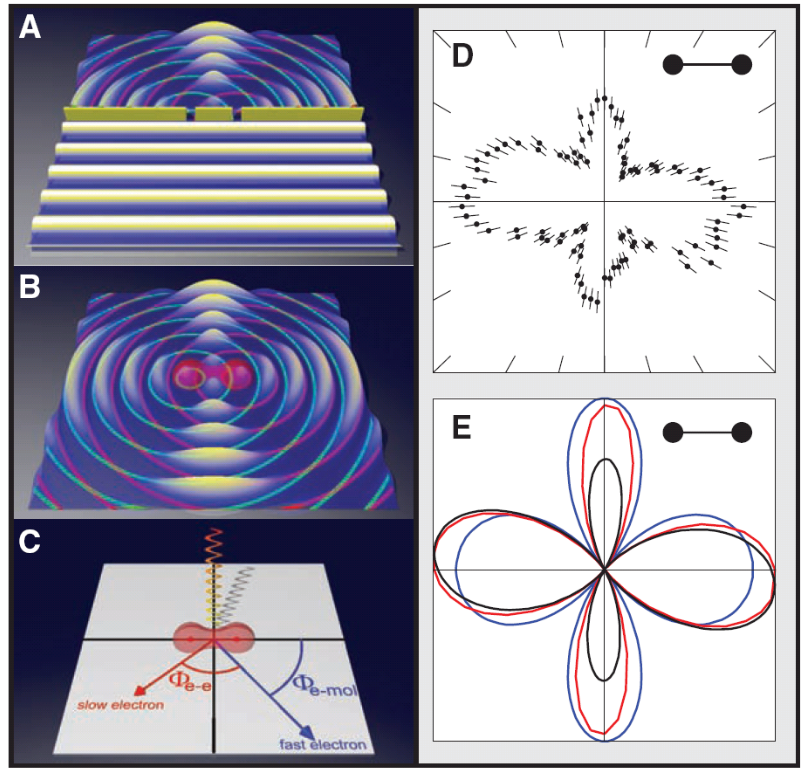
Raw velocity map image



Inverted velocity map image

46 eV photoionization of H_2 VMI

Johnsson et al., J. Mod. Optics (in press)

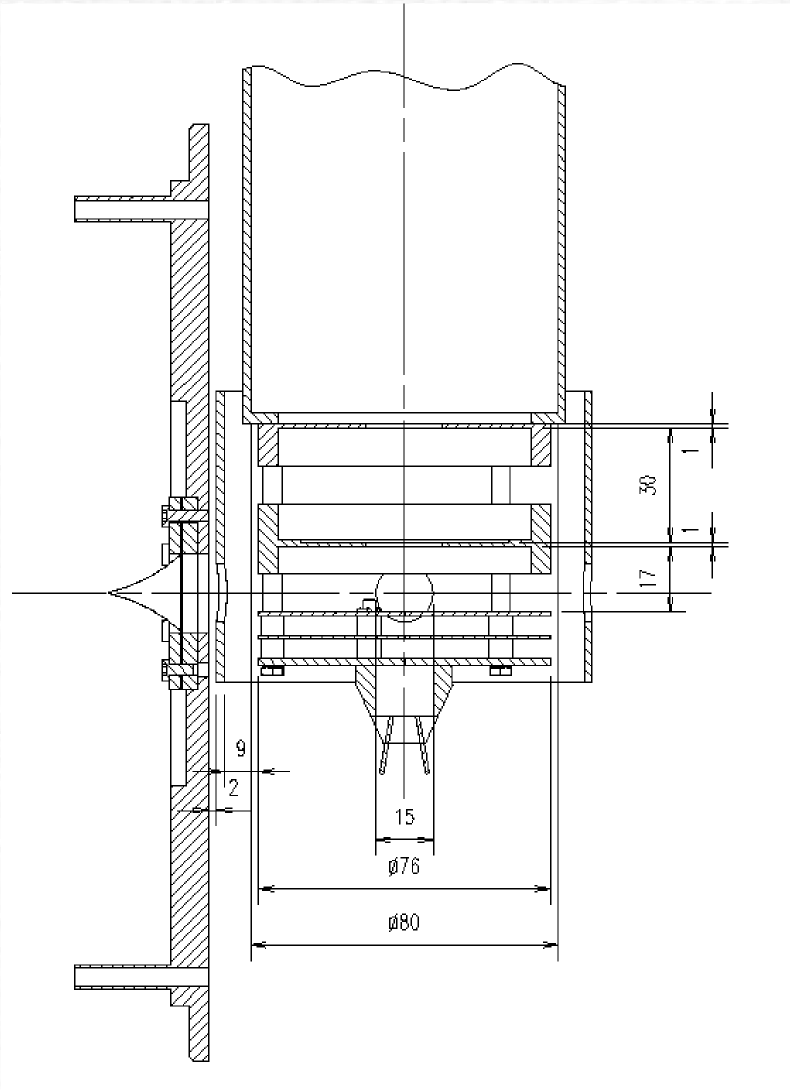


240 eV photoionization of H_2 COLTRIMS

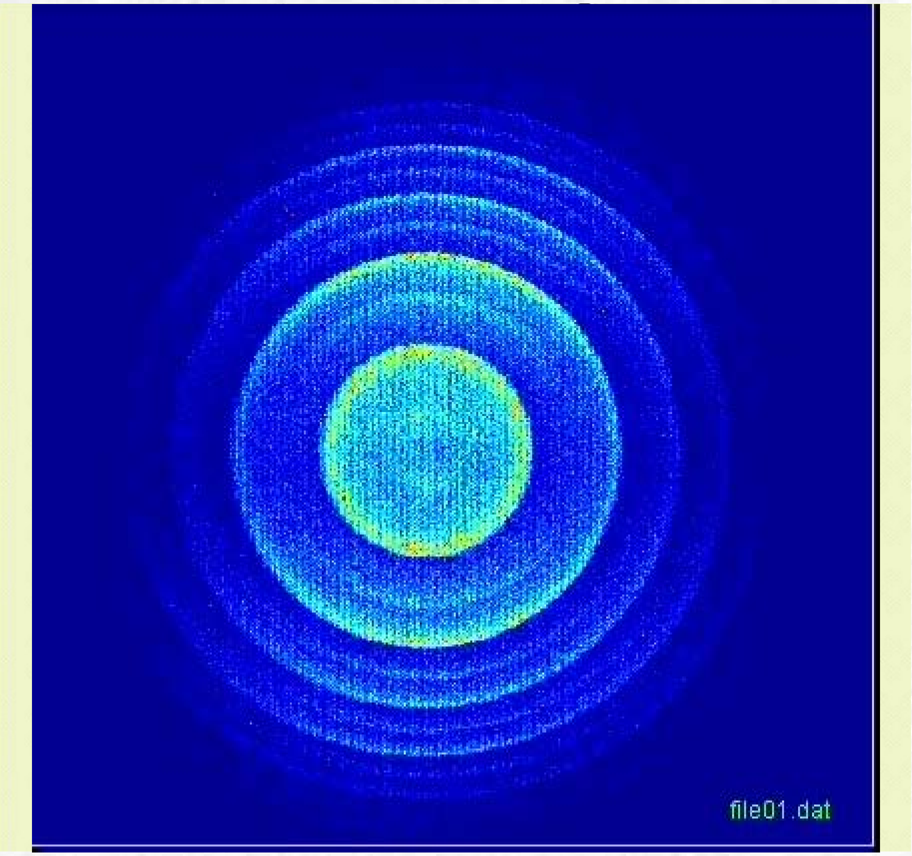
Akoury et al. Science 318, 949 (2007)

Velocity Map Imaging - 1

Experimental setup

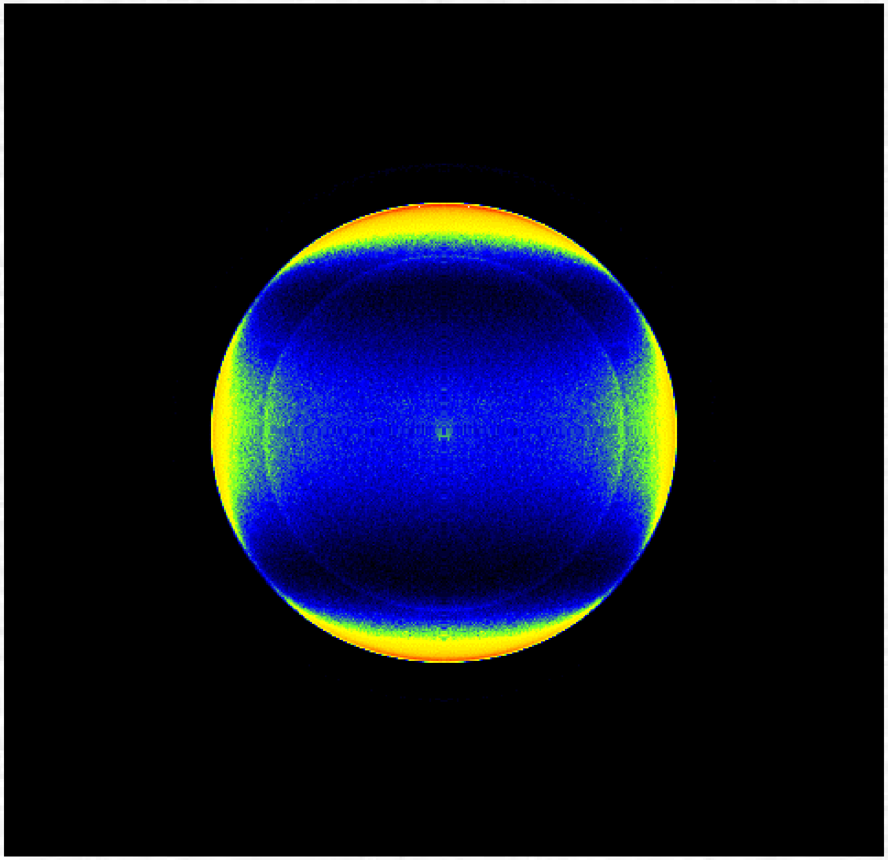


Characterization of an attosecond pulse train using RABBITT

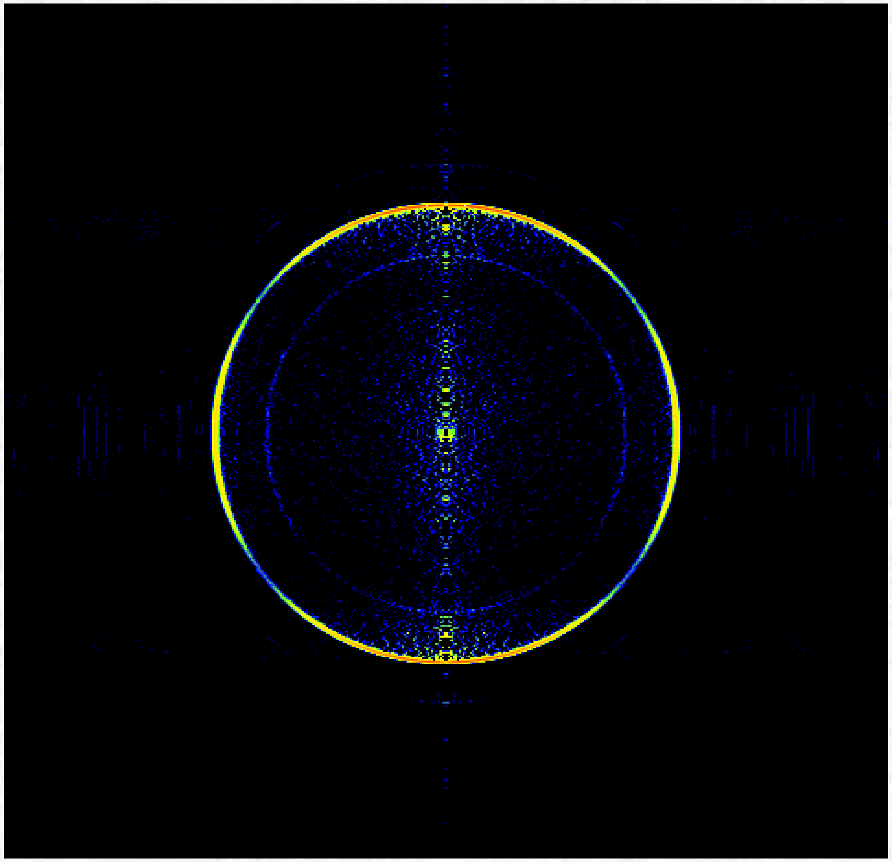


Aseyev et.al., Phys. Rev. Lett. 91, 223902 (2003)

Velocity Map Imaging - 2



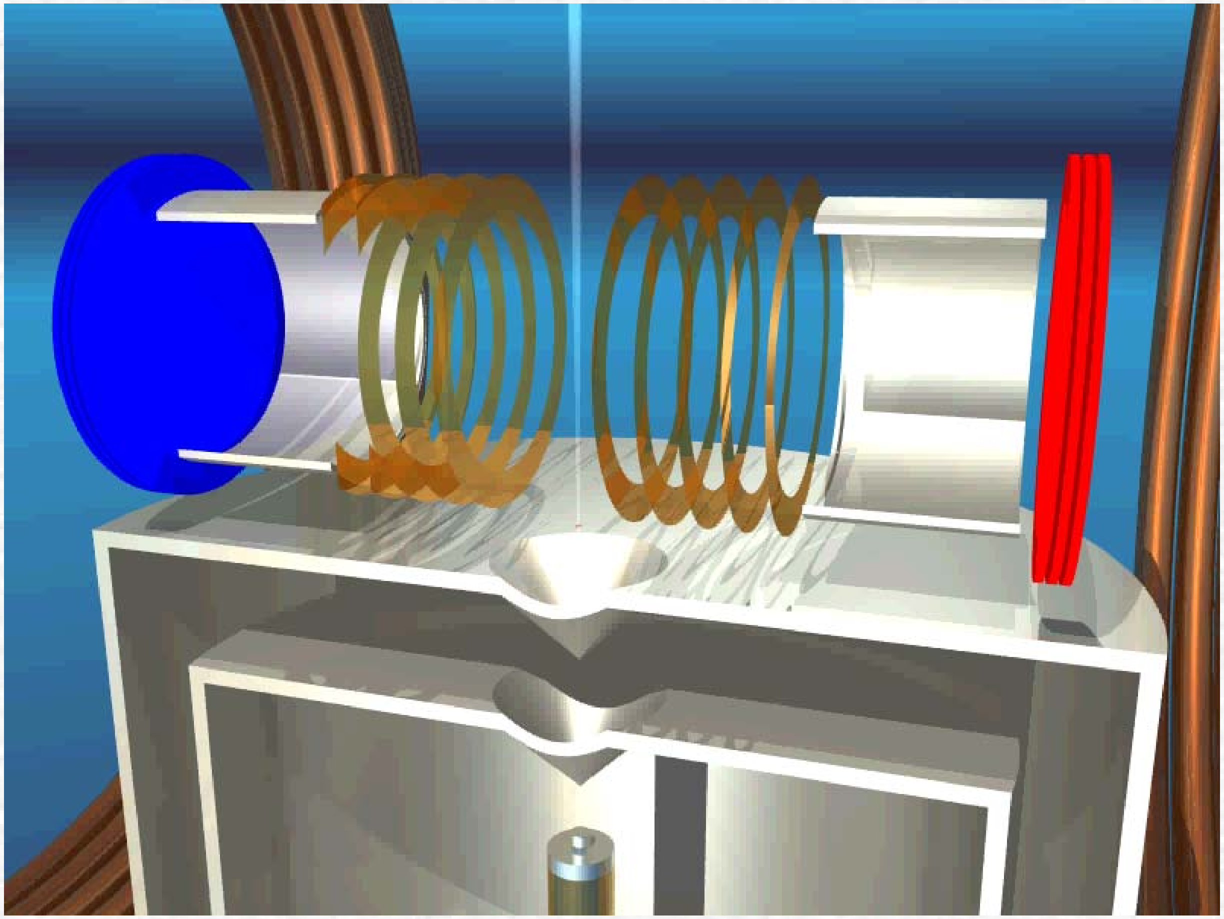
Raw image for 2-photon ionisation of Ar by 532 nm light



Slice through the 3D velocity distribution, obtained by Abel inversion of the image $\Delta v/v$ = 1% (N.B. also use iterative technique)

COLTRIMS

(Cold Target Recoil Ion Momentum Spectroscopy)



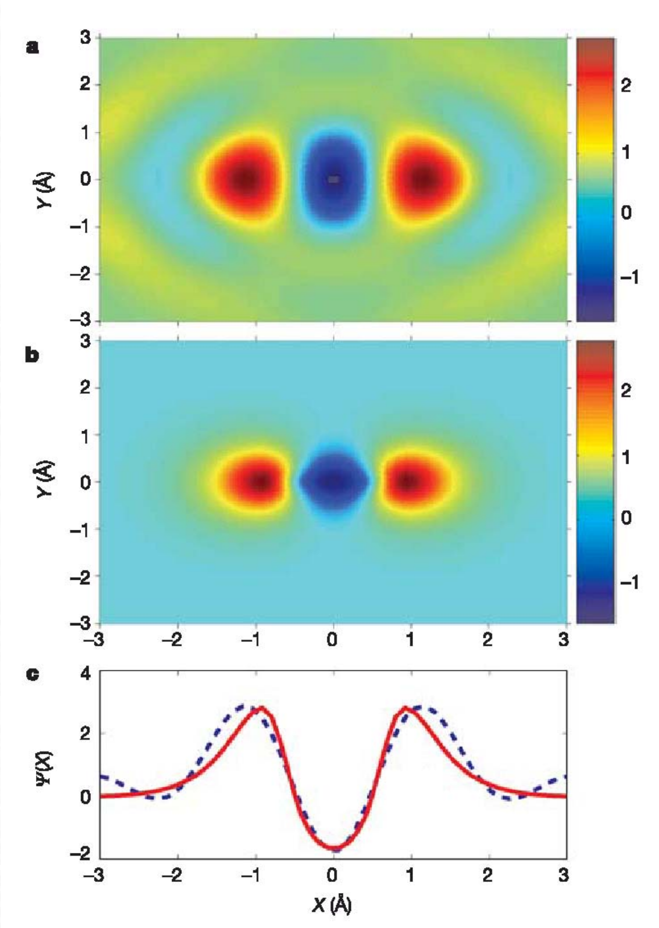
R. Dörner (Frankfurt)

Using COLTRIMS an experiment can be performed where the alignment and orientation can be read out **afterwards**, provided that the molecule dissociates

Challenge: coincidence measurement → one can study only one molecule per laser shot

When we cannot use only one molecule….

N_2 ground state orbitals determined by molecular tomography (= HHG)



D.M. Villeneuve et al., Nature 432, 867 (2004).

Pump-probe spectroscopy at emerging XUV and x-ray FELs

Aerial view of the FLASH Free Electron Laser in Hamburg

→ **Let's try to align/orient all molecules in our sample beforehand**

Interaction of a molecule with a DC field and an intense laser field

$$H = J^2 + V_\mu(\omega,\theta_s) + V_\alpha(\omega_{par},\omega_{perp},\vartheta_L)$$

Interaction with a DC field

$$V_\mu(\omega,\theta_s) = -\omega \cos\vartheta_s \qquad \omega = \frac{\mu\varepsilon_s}{B}$$

Interaction with an intense laser field

$$V_\alpha(\omega_{par},\omega_{perp},\vartheta_L) = -(\Delta\omega \cos^2\theta_L + \omega_L)$$

$$\Delta\omega = \omega_{par} - \omega_{perp} \qquad \omega_{par,perp} = \frac{\alpha_{par,perp} I_L}{2B}$$

B. Friedrich and D. Herschbach, J. Chem. Phys. 111, 6157 (1999)

Alignment/orientation with a DC field

1965: Hexapole state-selection and orientation of polar molecules (Bernstein)

J. Chem. Phys. 42, 767 (1965)

1991: “Brute-force” orientation (Loesch)

J. Chem. Phys. 93, 4779 (1990)

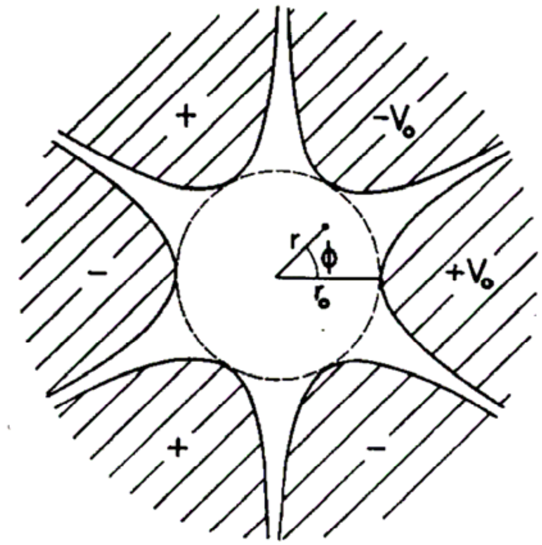


FIG. 1. The six-pole field.

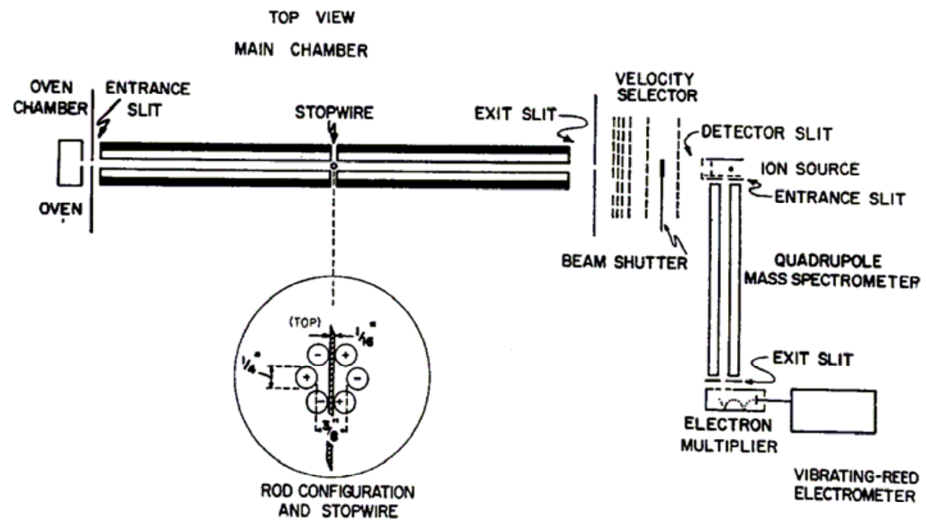


FIG. 2. Sketch of the apparatus. The cross section of the six-pole field is shown in the circular insert.

Alignment/orientation with intense laser fields - overture

1991: Ion TOF distributions in Multi-Electron Dissociative Ionization

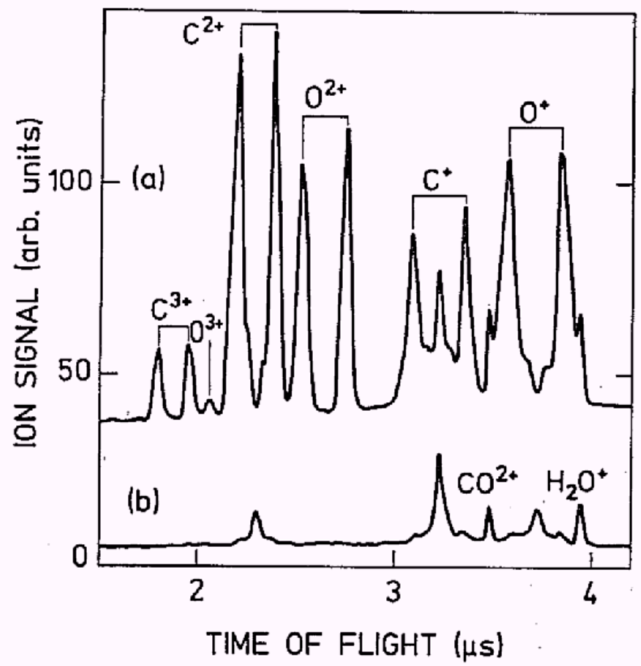
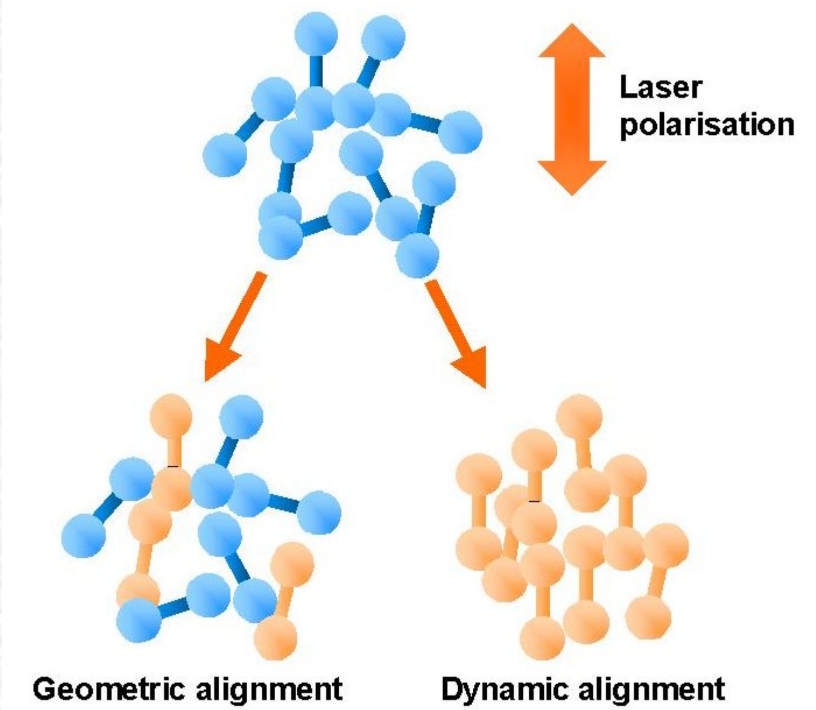


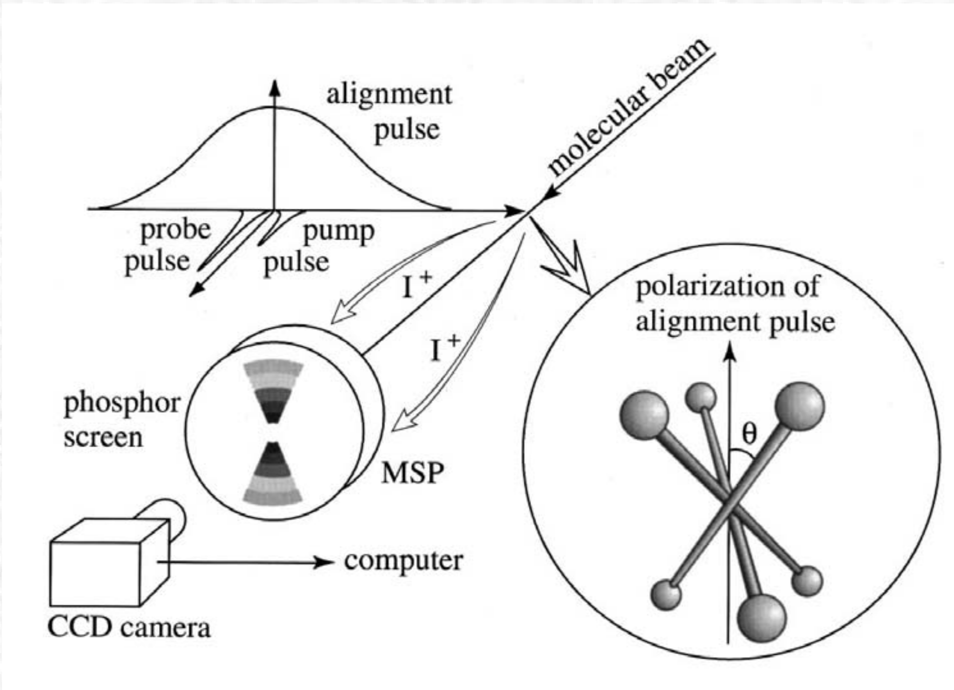
FIG. 2. TOF ion mass spectra of CO with the laser polarization (a) parallel to the drift tube axis and (b) perpendicular to the drift tube axis. The scale for the ion signals is the same for both spectra.

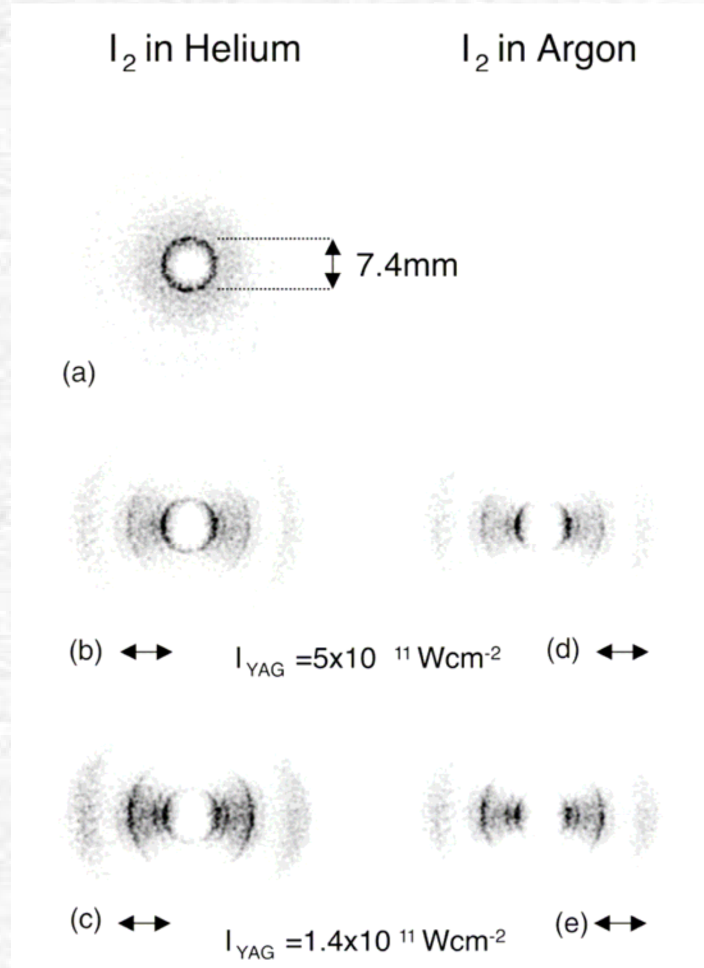


C. Cornaggia et.al., Phys. Rev. A 44, 4499 (1991).

Alignment/orientation with intense laser fields - 1

1998: Adiabatic molecular alignment (Sakai & Stapelfeldt)



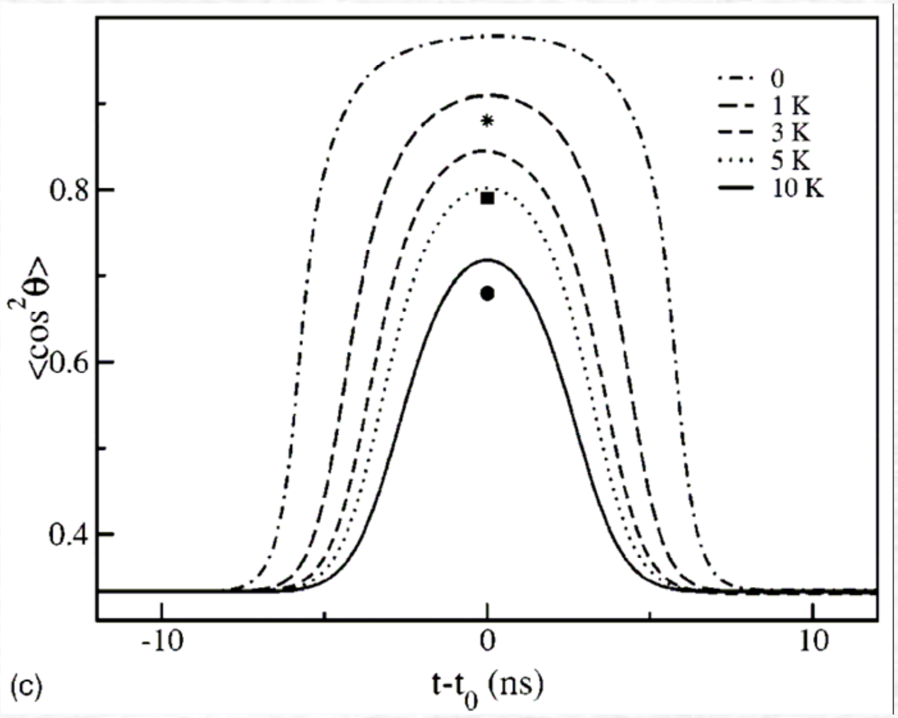


$I_2 \rightarrow I_{2,aligned} \rightarrow I{+}I \rightarrow I^{+}{+}I$

YAG **Pump** **Probe**

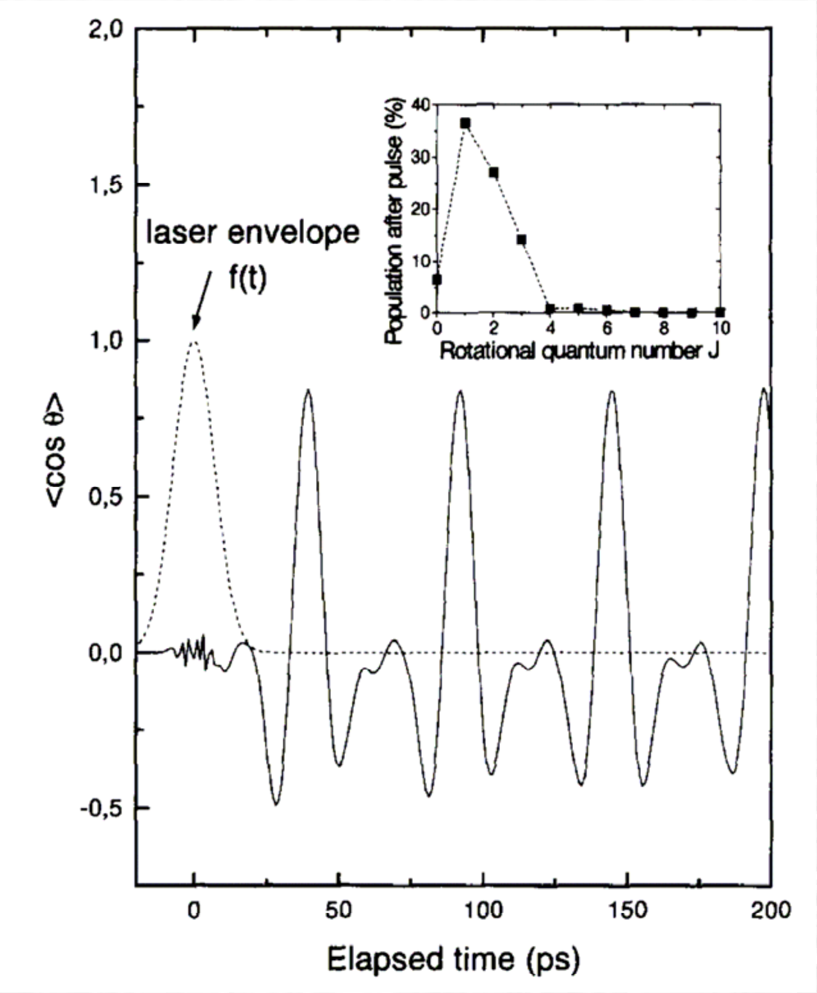
J. Chem. Phys. 110, 10235 (1998)

Adiabatic vs. diabatic alignment



Alignment of I_2 under adiabatic conditions

Stapelfeldt and Seideman
Rev. Mod. Phys. 75, 543 (2003)

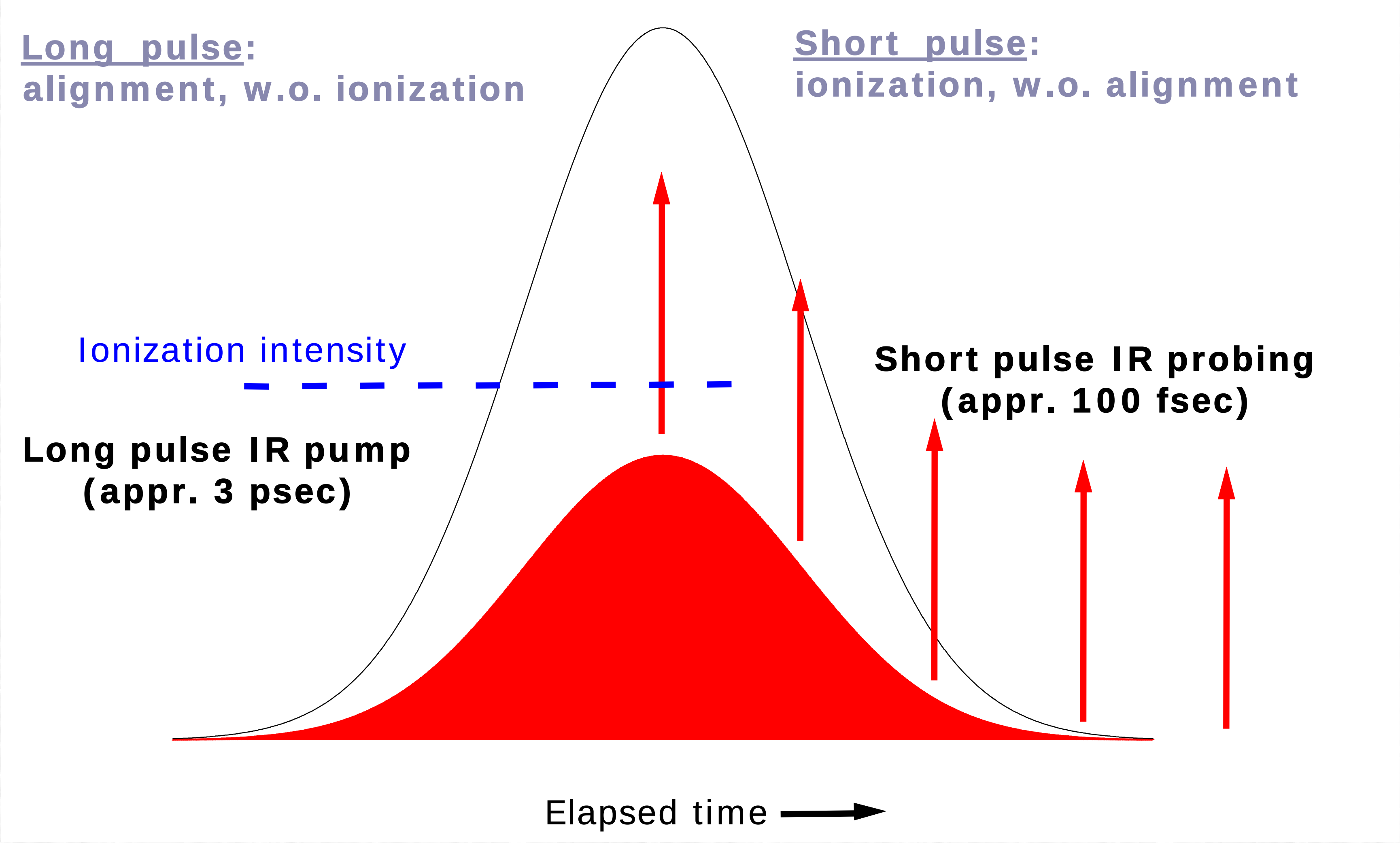


Orientation (and alignment) under diabatic (impulsive) conditions

Vrakking and Stolte
Chem. Phys. Lett. 271, 209 (1997)

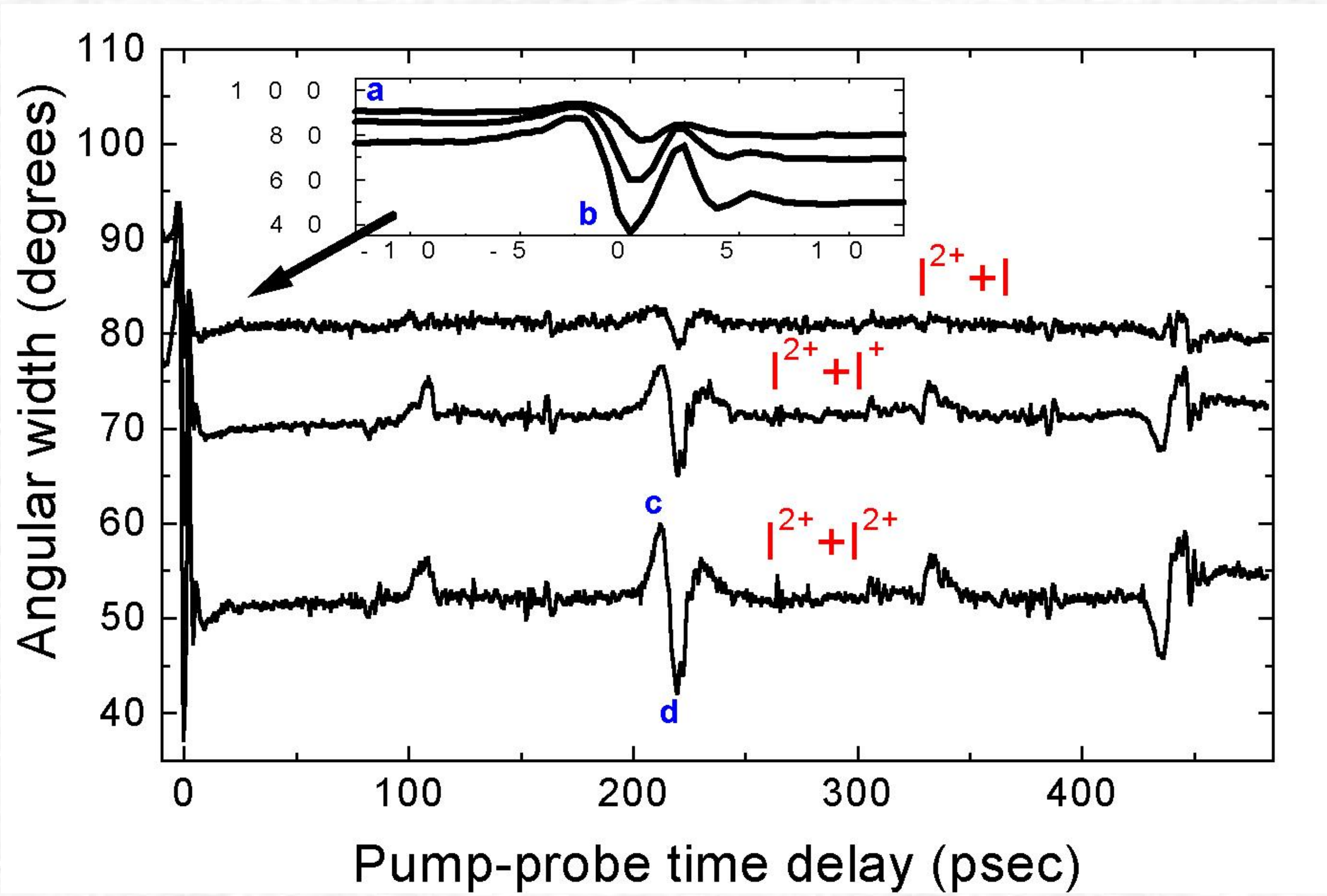
Probing alignment in real time:

Long pulse IR + Short pulse IR Pump-probe experiments

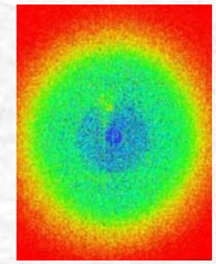


Alignment/orientation with intense laser fields - 2

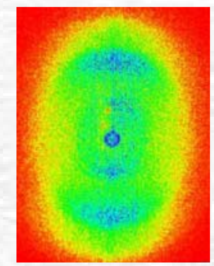
2001: Impulsive molecular alignment (Rosca-Pruna and Vrakking)



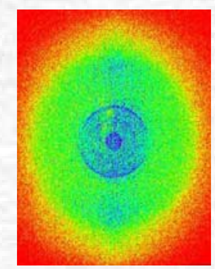
a)



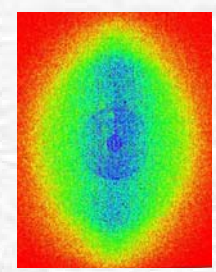
b)



c)



d)



Phys. Rev. Lett. 87, 153902 (2001)

Popular activities since these earliest demonstrations of laser-induced alignment

- From diatomic to complexer, polyatomic molecules
- From 2D to 3D dynamic alignment
- Schemes to optimize dynamic alignment
- Alternative probes of molecular alignment
- From molecular alignment to molecular orientation

Stapelfeldt and Seideman, Rev. Mod. Phys. 75, 543 (2003)

VOLUME 85, NUMBER 12 PHYSICAL REVIEW LETTERS 18 SEPTEMBER 2000

Three Dimensional Alignment of Molecules Using Elliptically Polarized Laser Fields

Jakob Juul Larsen,[1] Kasper Hald,[2] Nis Bjerre,[1] and Henrik Stapelfeldt[2]
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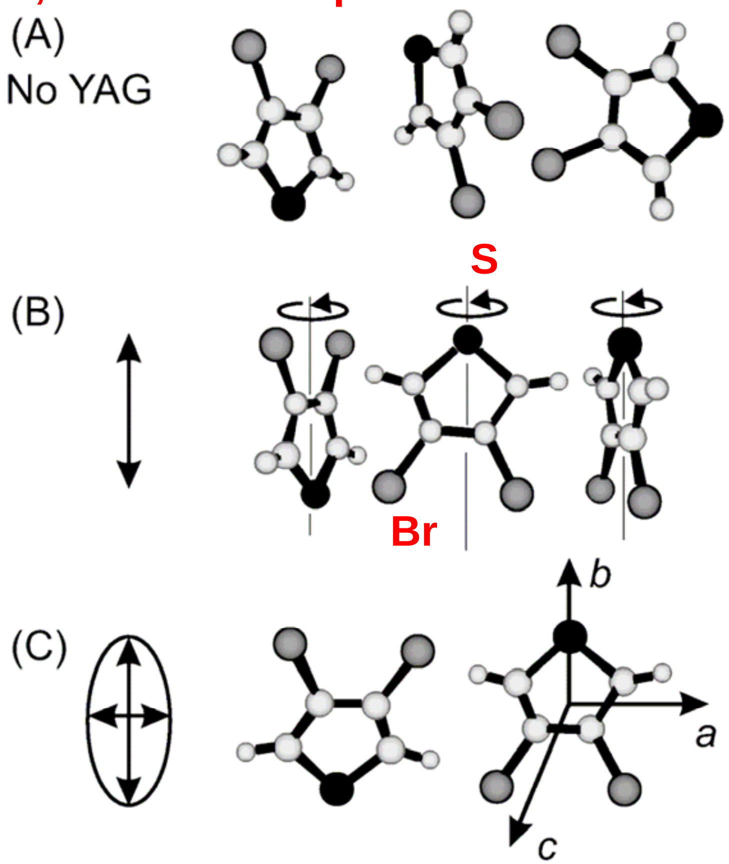
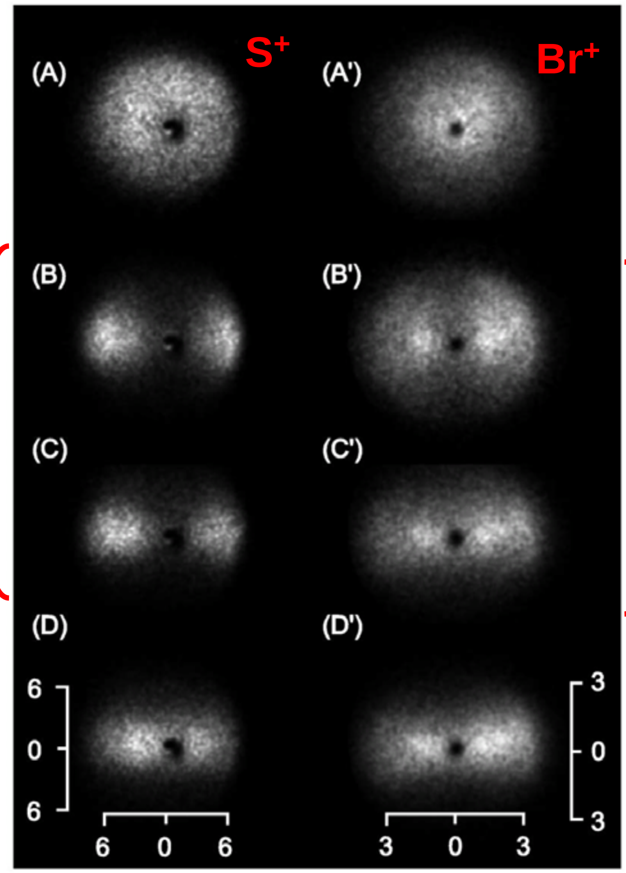
Tamar Seideman
Steacie Institute for Molecular Science, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR6
(Received 9 May 2000)

3,4-dibromothiophene



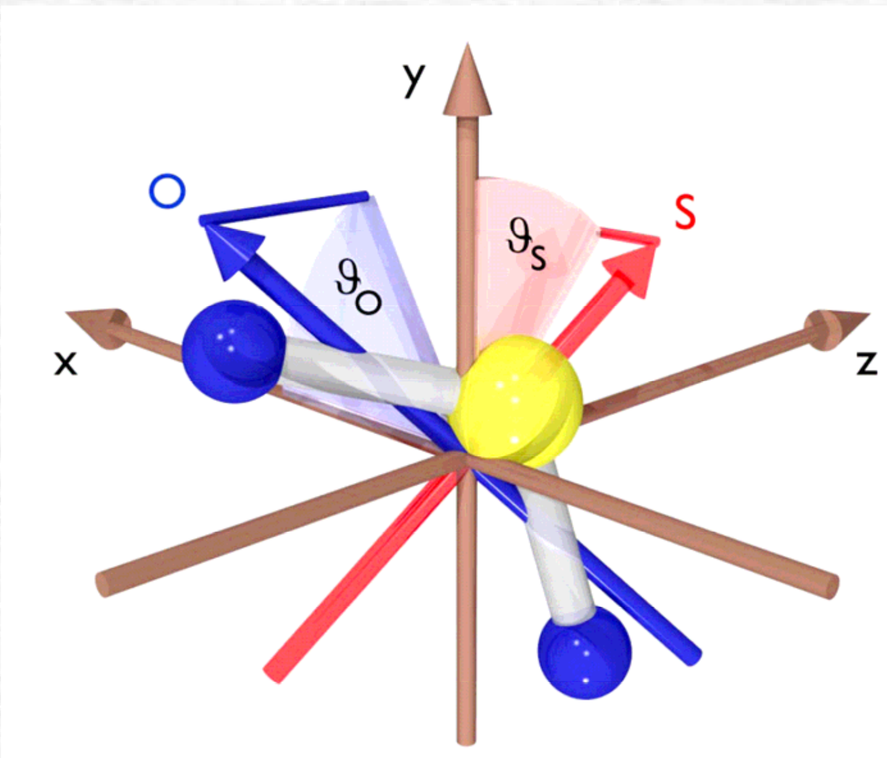


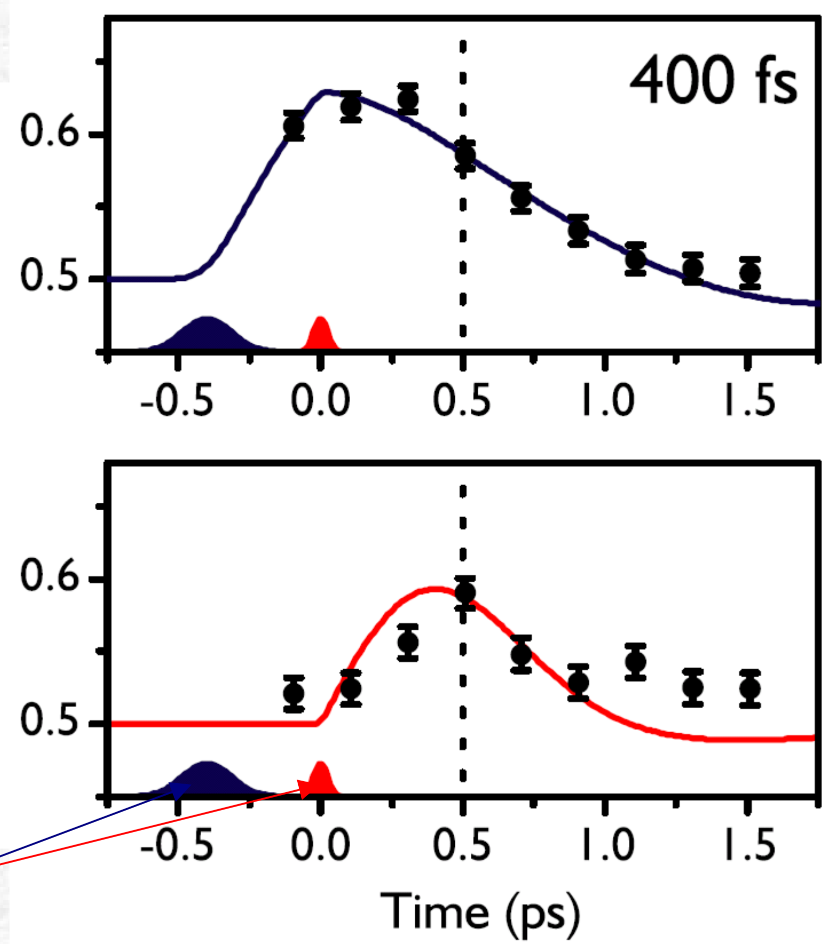
Both linear and elliptical polarization lead to alignment

Confine-ment of the Br-cone for elliptical polarization

Field-Free Three-Dimensional Alignment of Polyatomic Molecules

Kevin F. Lee,[1,2] D. M. Villeneuve,[1] P. B. Corkum,[1,2] Albert Stolow,[1] and Jonathan G. Underwood[3,*]
[1]Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, K1A 0R6, Canada
[2]Department of Physics and Astronomy, McMaster University, 1280 Main Street West, Hamilton, Ontario, L8S 4M1, Canada
[3]Department of Physics and Astronomy, The Open University, Walton Hall, Milton Keynes, MK7 6AA, United Kingdom
(Received 28 June 2006; published 26 October 2006)





Cross-polarized impulsive alignment pulses

Holding and Spinning Molecules in Space

Simon S. Viftrup,[1] Vinod Kumarappan,[2] Sebastian Trippel,[3] and Henrik Stapelfeldt[2,4]
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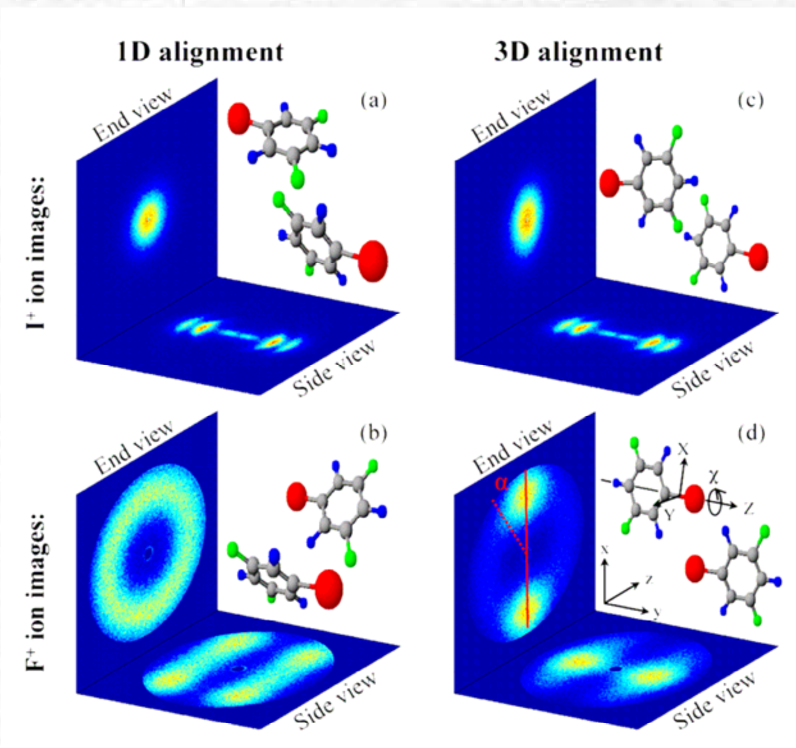
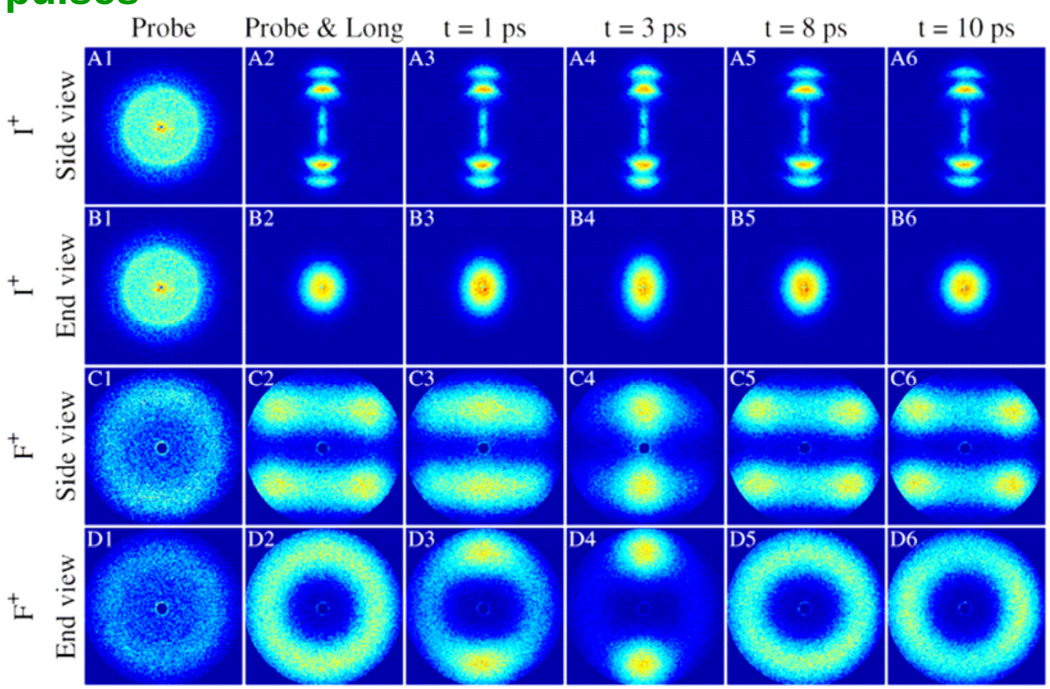
(Received 9 May 2007; published 5 October 2007)



Cross-polarized adiabatic and impulsive alignment pulses



VOLUME 87, NUMBER 16 PHYSICAL REVIEW LETTERS 15 OCTOBER 2001

Angular Focusing, Squeezing, and Rainbow Formation in a Strongly Driven Quantum Rotor

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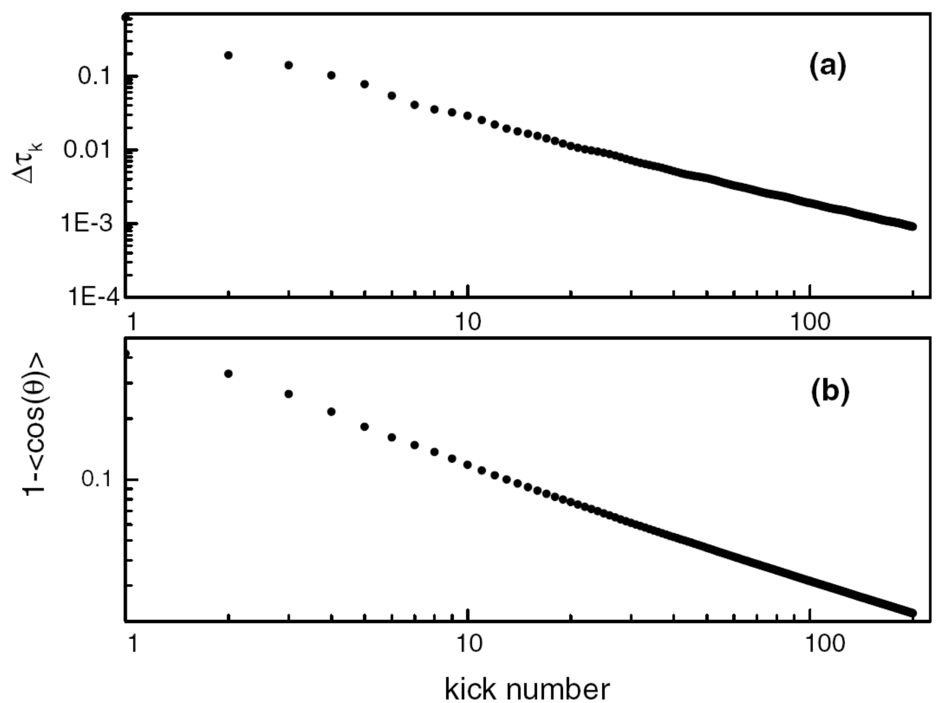
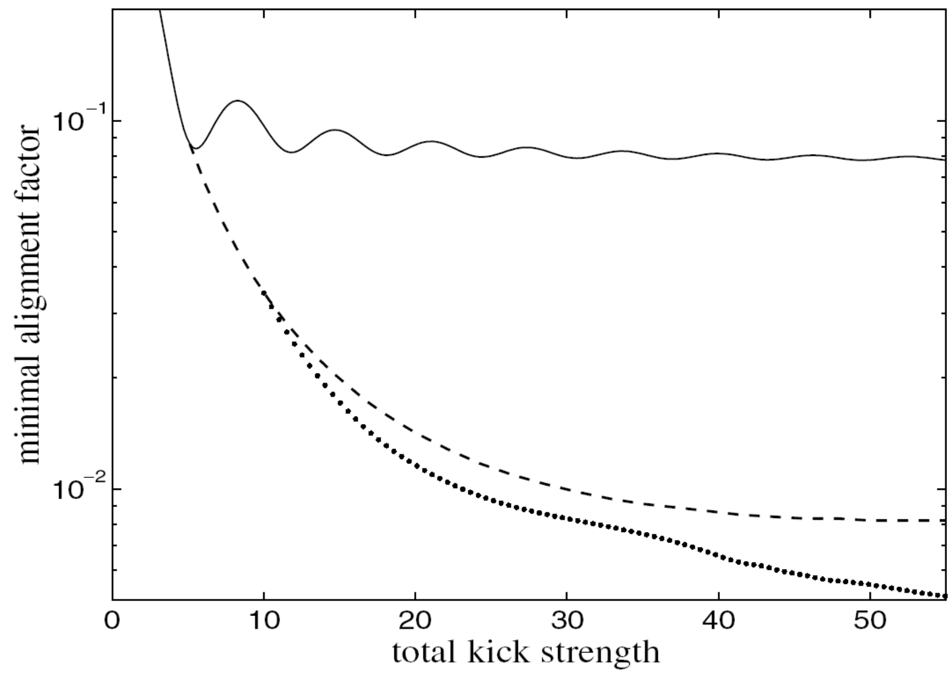
[1]Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel
[2]Institut des Sciences Nucléaires, F 38026 Grenoble Cedex, France
(Received 6 December 2000; published 28 September 2001)



QM follow-up (w. Rabitz)
Phys. Rev. Lett. 90, 213001 (2003)



A classical rotor can be focussed to angular distribution that is arbitrarily narrow, using a sequence of properly timed pulses

Experimental verification (Stapelfeldt)
Phys. Rev. Lett. 92, 173004 (2004)

VOLUME 90, NUMBER 22 PHYSICAL REVIEW LETTERS week ending 6 JUNE 2003

Switched Wave Packets: A Route to Nonperturbative Quantum Control

Jonathan G. Underwood,[1] Michael Spanner,[1,2] Misha Yu. Ivanov,[1] Jeff Mottershead,[1] Benjamin J. Sussman,[1,3] and Albert Stolow[1,3,*]

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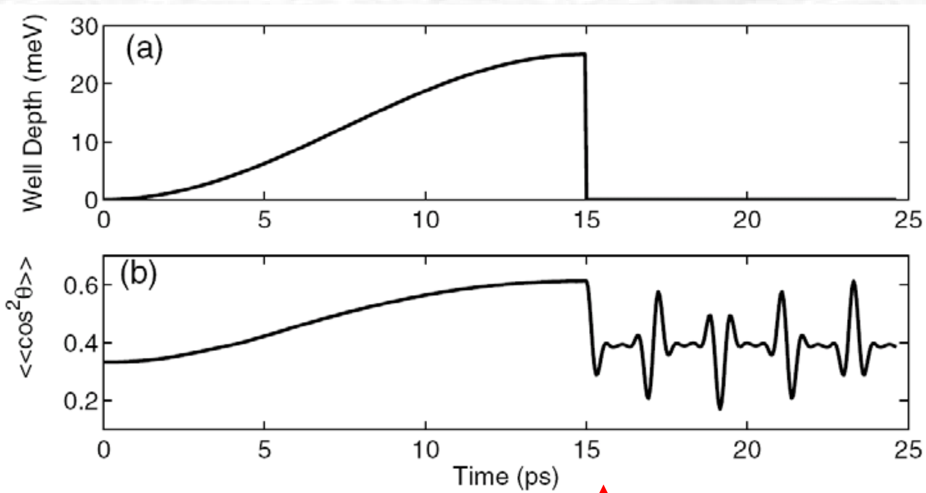
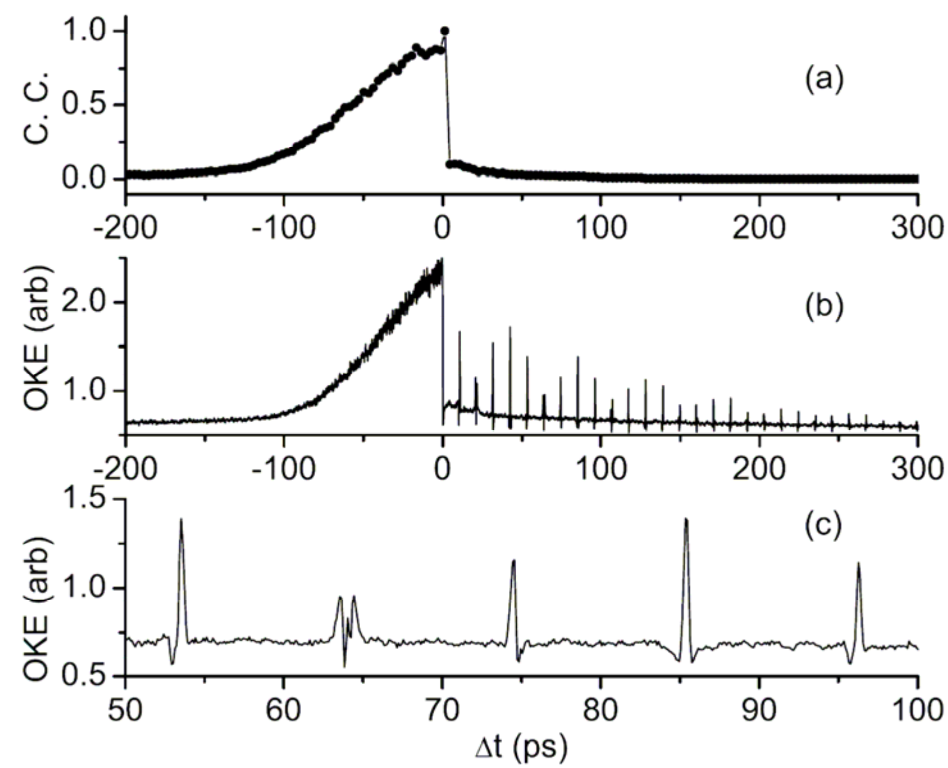
(Received 19 February 2003; published 4 June 2003)





Theory

Experiment (OKE method)

PHYSICAL REVIEW A **77**, 041404(R) (2008)

Ultimate field-free molecular alignment by combined adiabatic-impulsive field design

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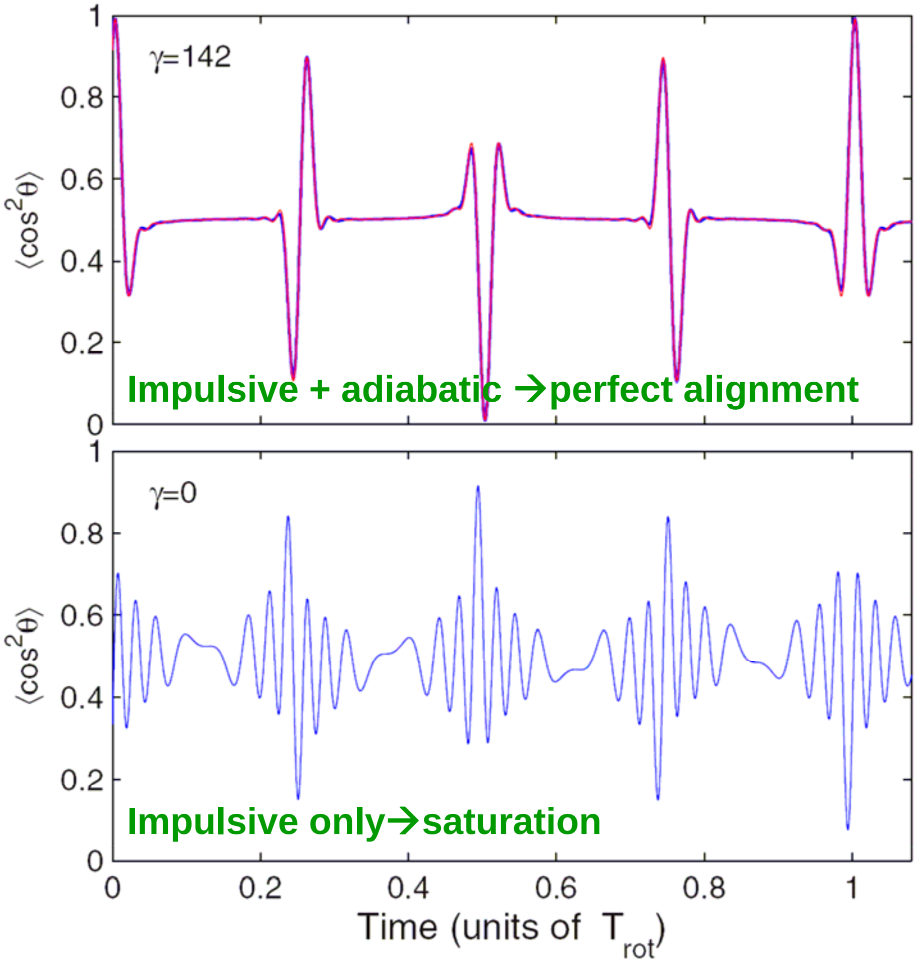
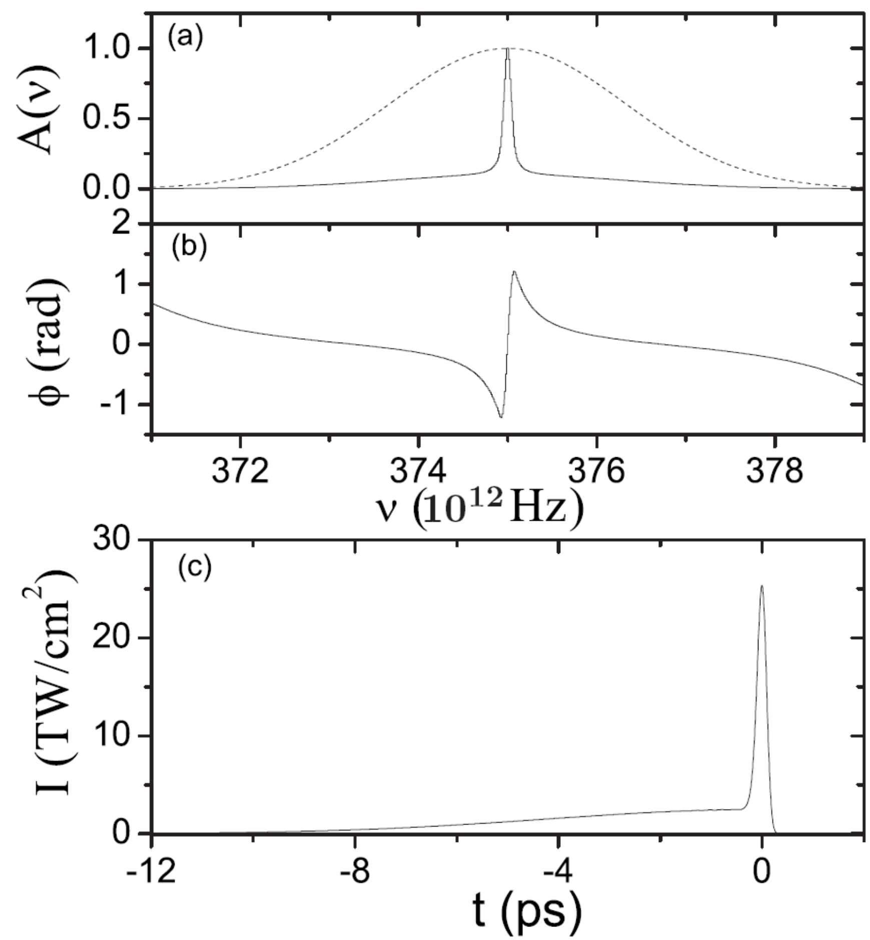
(Received 14 November 2007; revised manuscript received 8 February 2008; published 23 April 2008)



Realization: phase-jump



Intermezzo

IOP PUBLISHING JOURNAL OF PHYSICS B: ATOMIC, MOLECULAR AND OPTICAL PHYSICS

J. Phys. B: At. Mol. Opt. Phys. **41** (2008) 074021 (11pp) doi:10.1088/0953-4075/41/7/074021

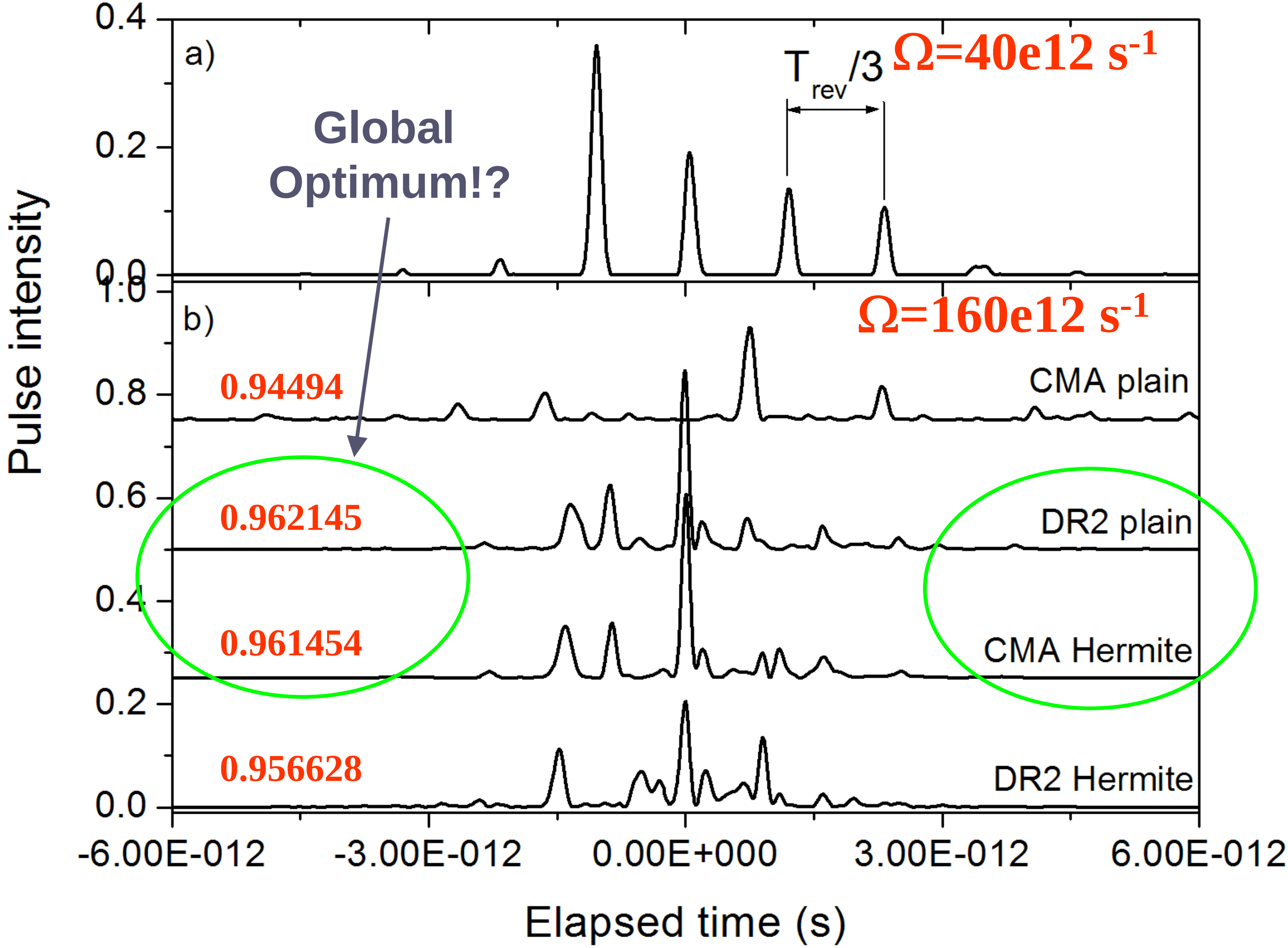
On the diversity of multiple optimal controls for quantum systems

O M Shir[1], V Beltrani[2], Th Bäck[1], H Rabitz[2] and M J J Vrakking[3]

Application of advanced evolutionary algorithms towards the optimization of dynamical alignment (starting from J=0) and towards rotational ladder climbing

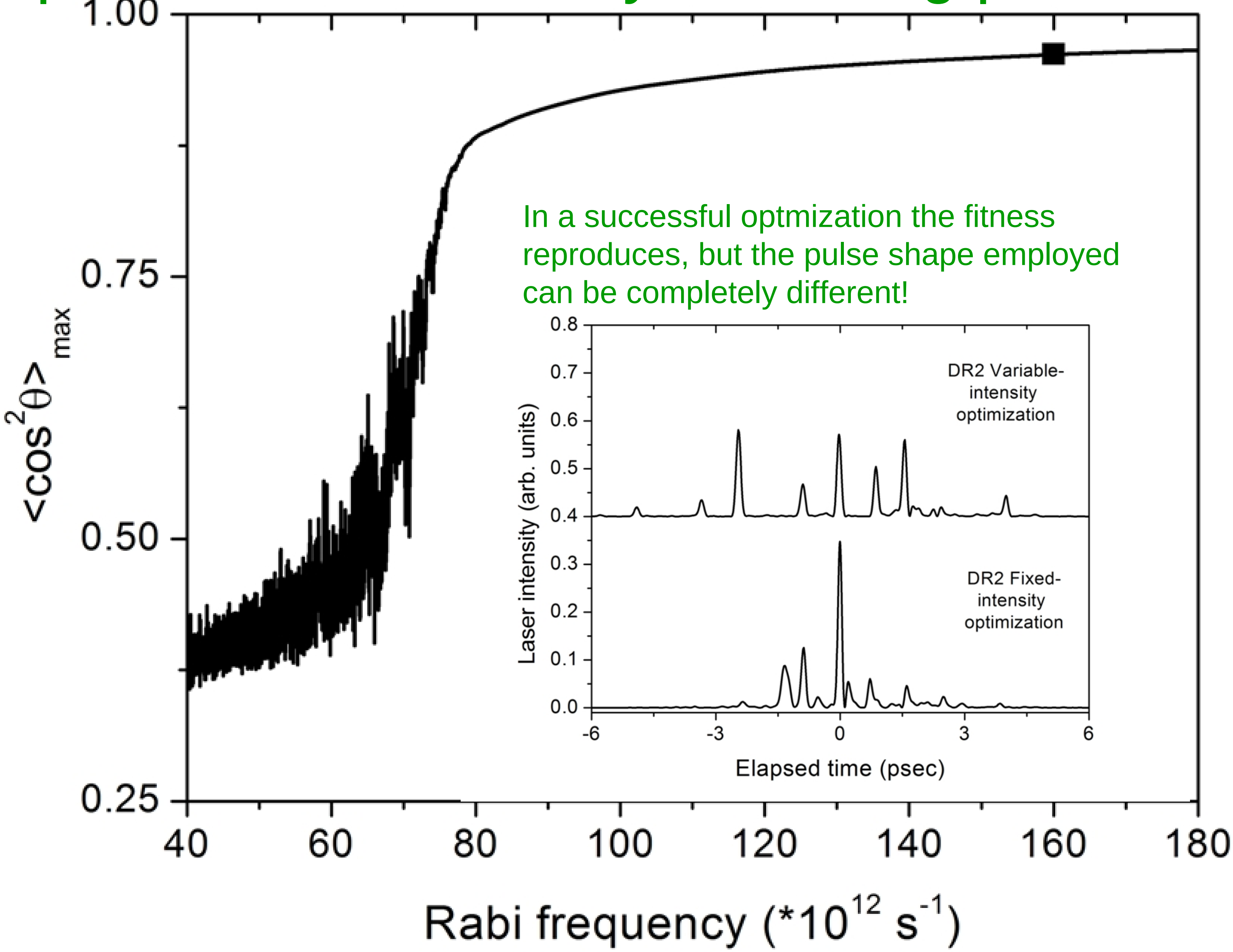
- Perform series of calculations (20 each) for DR2 and CMA algorithms combined with simple/Hermite phase parameterization

- Define the fitness as $\langle\cos^2\theta\rangle$ in the dynamical alignment problem, or as the population in a target state in the ladder climbing problem



Pulse intensity
Elapsed time (s)
a)
b)
T rev/3
Ω=40e12 s-1
Ω=160e12 s-1
Global
Optimum!?
0.94494
0.962145
0.961454
0.956628
CMA plain
DR2 plain
CMA Hermite
DR2 Hermite
0.4
0.2
0.0
1.0
0.8
0.6
0.4
0.2
0.0
-6.00E-012
-3.00E-012
0.00E+000
3.00E-012
6.00E-012

Optimizaton with slowly increasing pulse energy



In a successful optmization the fitness reproduces, but the pulse shape employed can be completely different!

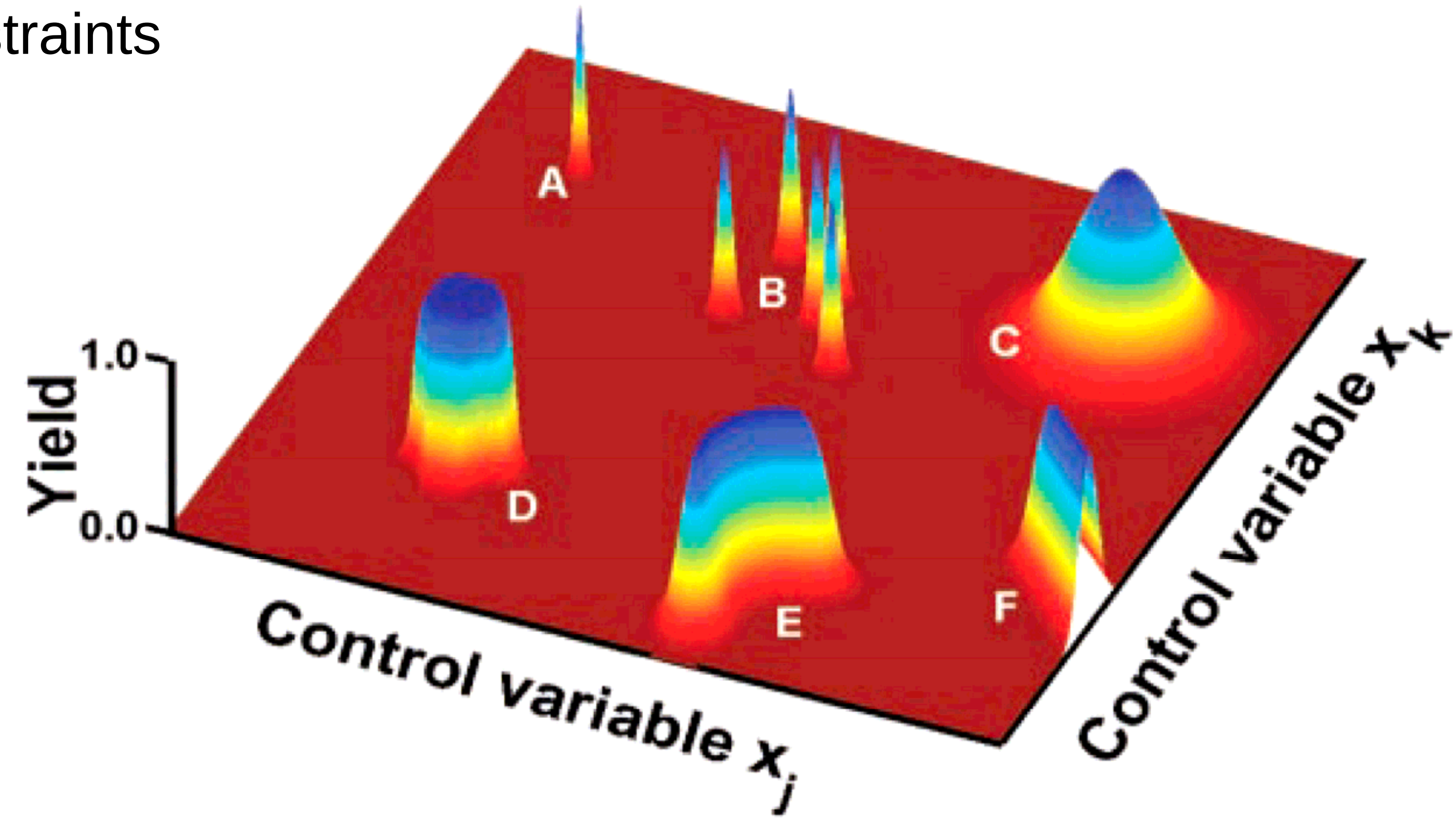
Quantum Optimally Controlled Transition Landscapes

Herschel A. Rabitz,[1*] Michael M. Hsieh,[1] Carey M. Rosenthal[2]

A large number of experimental studies and simulations show that it is surprisingly easy to find excellent quality control over broad classes of quantum systems. We now prove that for controllable quantum systems with no constraints placed on the controls, the only allowed extrema of the transition probability landscape correspond to perfect control or no control. Under these conditions, no suboptimal local extrema exist as traps that would impede the search for an optimal control. The identified landscape structure is universal for all controllable quantum systems of the same dimension when seeking to maximize the same transition probability, regardless of the detailed nature of the system Hamiltonian. The presence of weak control field noise or environmental decoherence is shown to preserve the general structure of the control landscape, but at lower resolution.

26 MARCH 2004 VOL 303 SCIENCE

Optimal control works perfectly (or not at all) if there are no constraints



Existing constraints (bandwidth, phase parametrization, etc.) limit the achievable control

The achievable control is unique, the solution that leads to this control is not → convergence of a solution is **not** the right way to perform an optimal control experiment

Controlling the Orientation of Polar Molecules with Combined Electrostatic and Pulsed, Nonresonant Laser Fields

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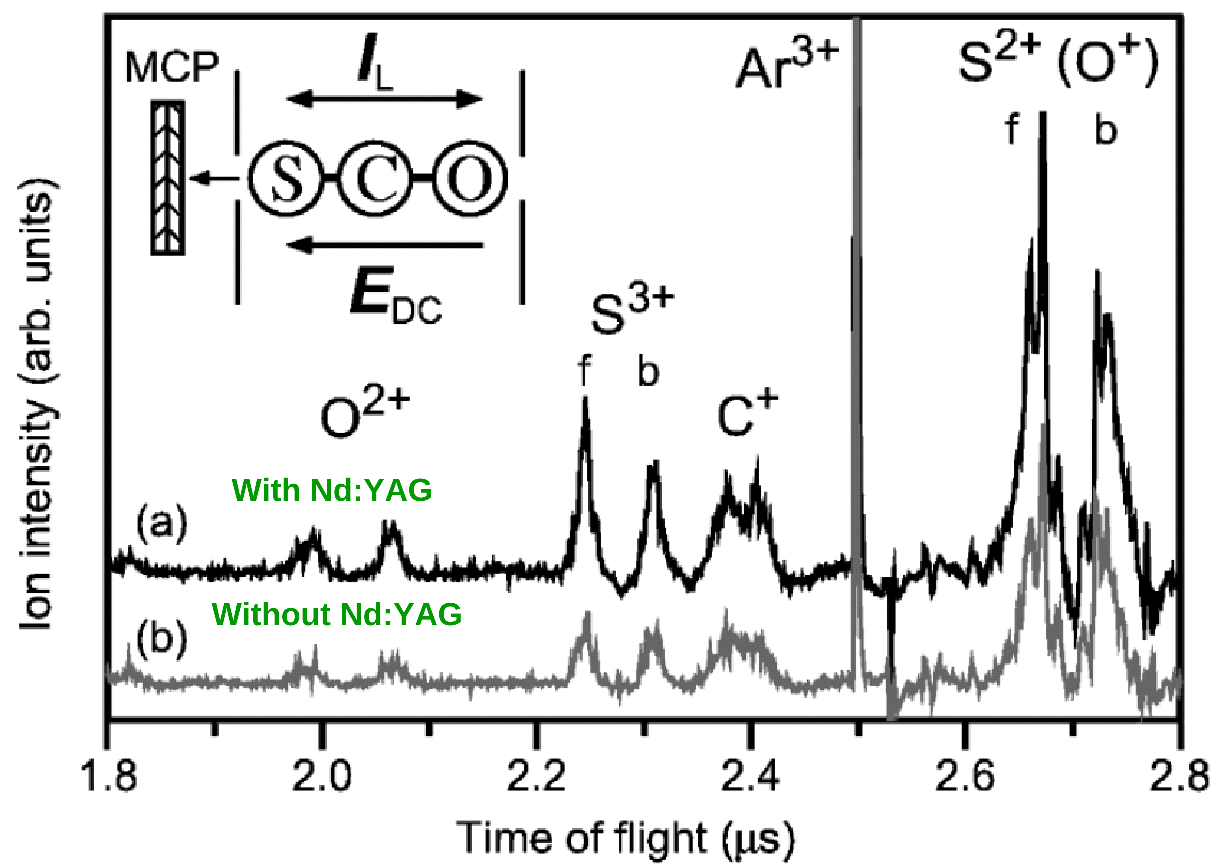
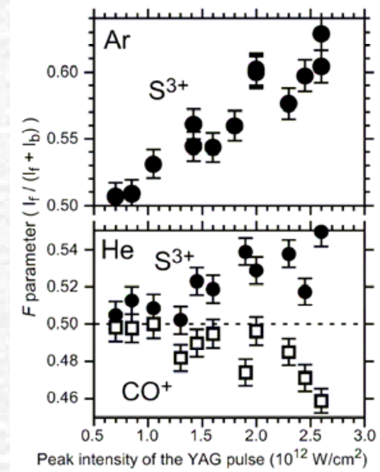
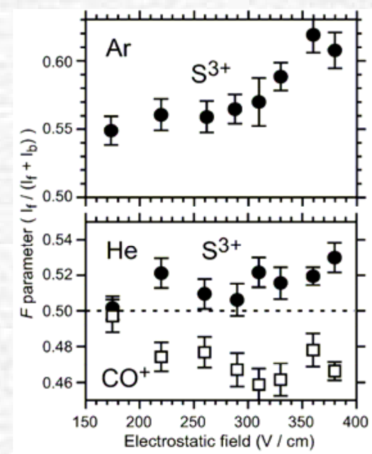
(Received 16 June 2002; revised manuscript received 19 August 2002; published 25 February 2003)







PRL 101, 013001 (2008) PHYSICAL REVIEW LETTERS week ending 4 JULY 2008

Laser-Field-Free Molecular Orientation

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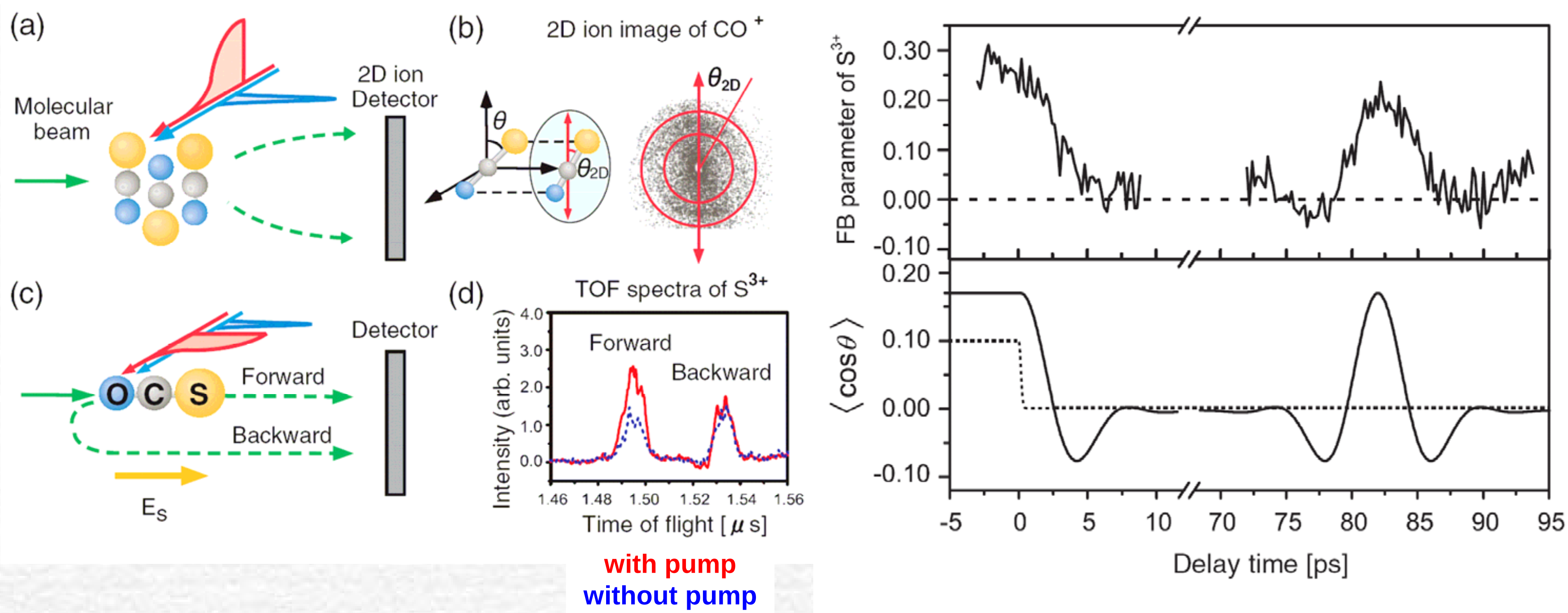
(Received 4 April 2008; published 30 June 2008)



Laser-induced orientation demonstrated, but not yet better than convention DC techniques

Impulsive Orientation and Alignment of Quantum State-selected NO Molecules

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Reach a very high degree of impulsive orientation by combining:

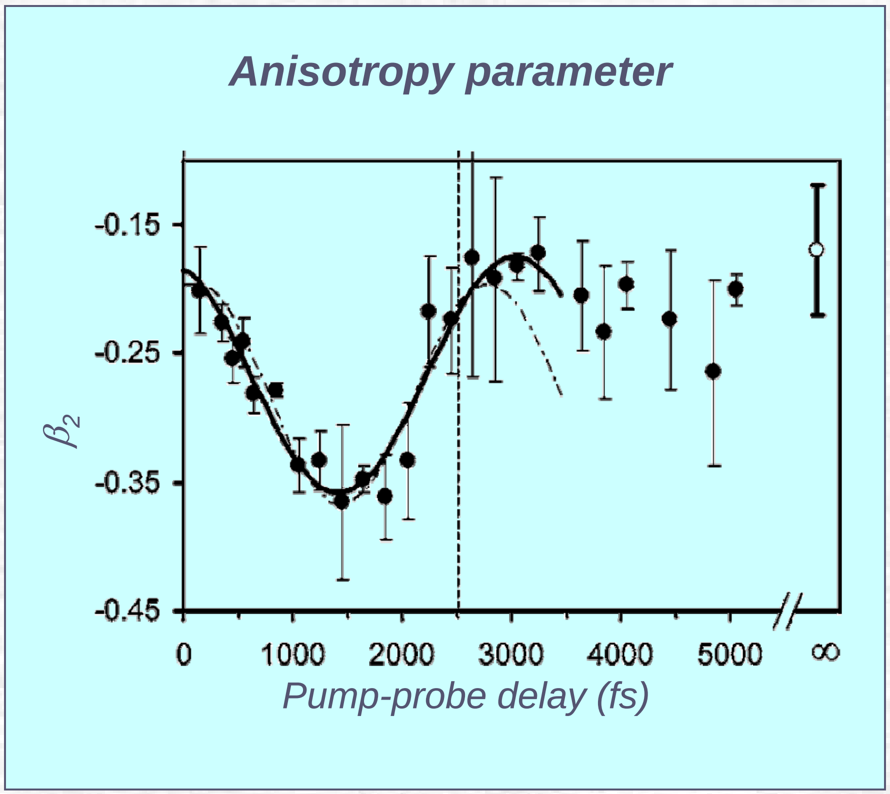
- ❖Hexapole state-selection
  - ❖A dc electric field
    - ❖Femtosecond laser excitation
      - ❖Laser pulse shaping

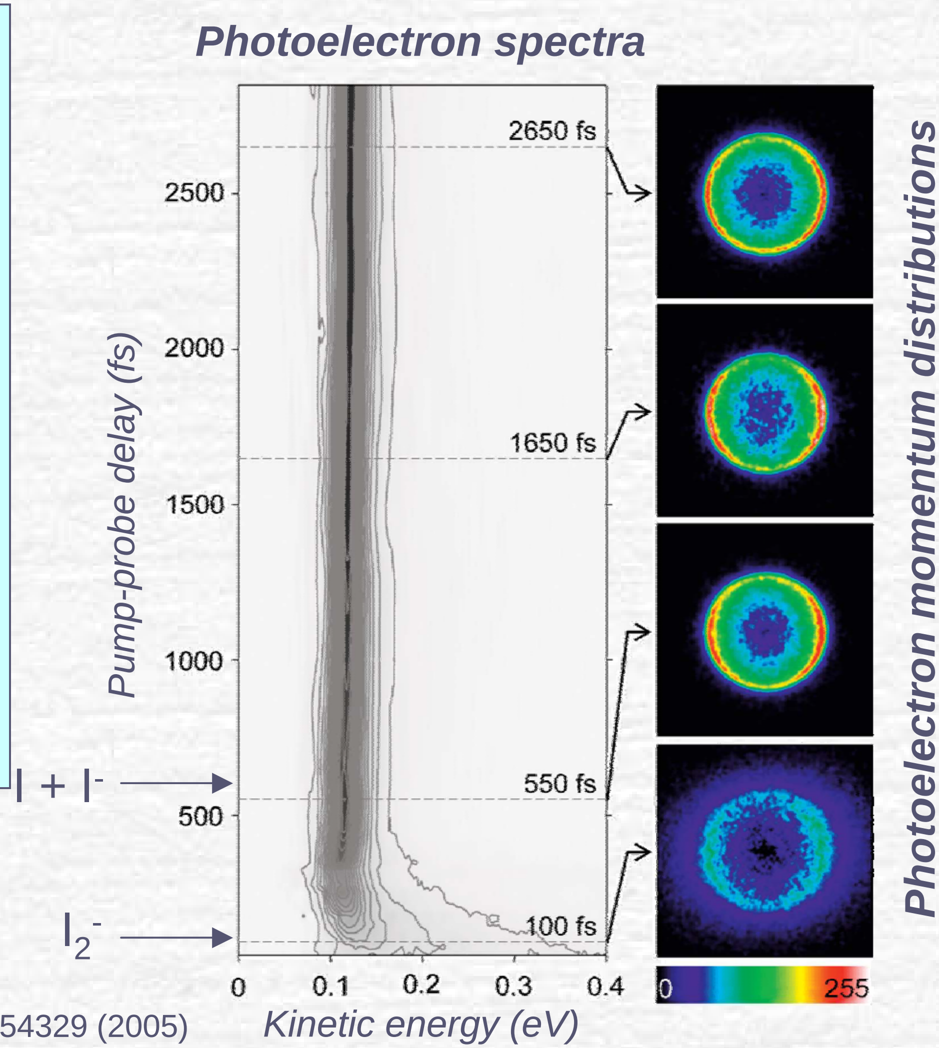
So what are we doing this for?

Pump-probe spectroscopy at emerging XUV and x-ray FELs

From 2014: XFEL in Hamburg

Ambition: molecular interferometer

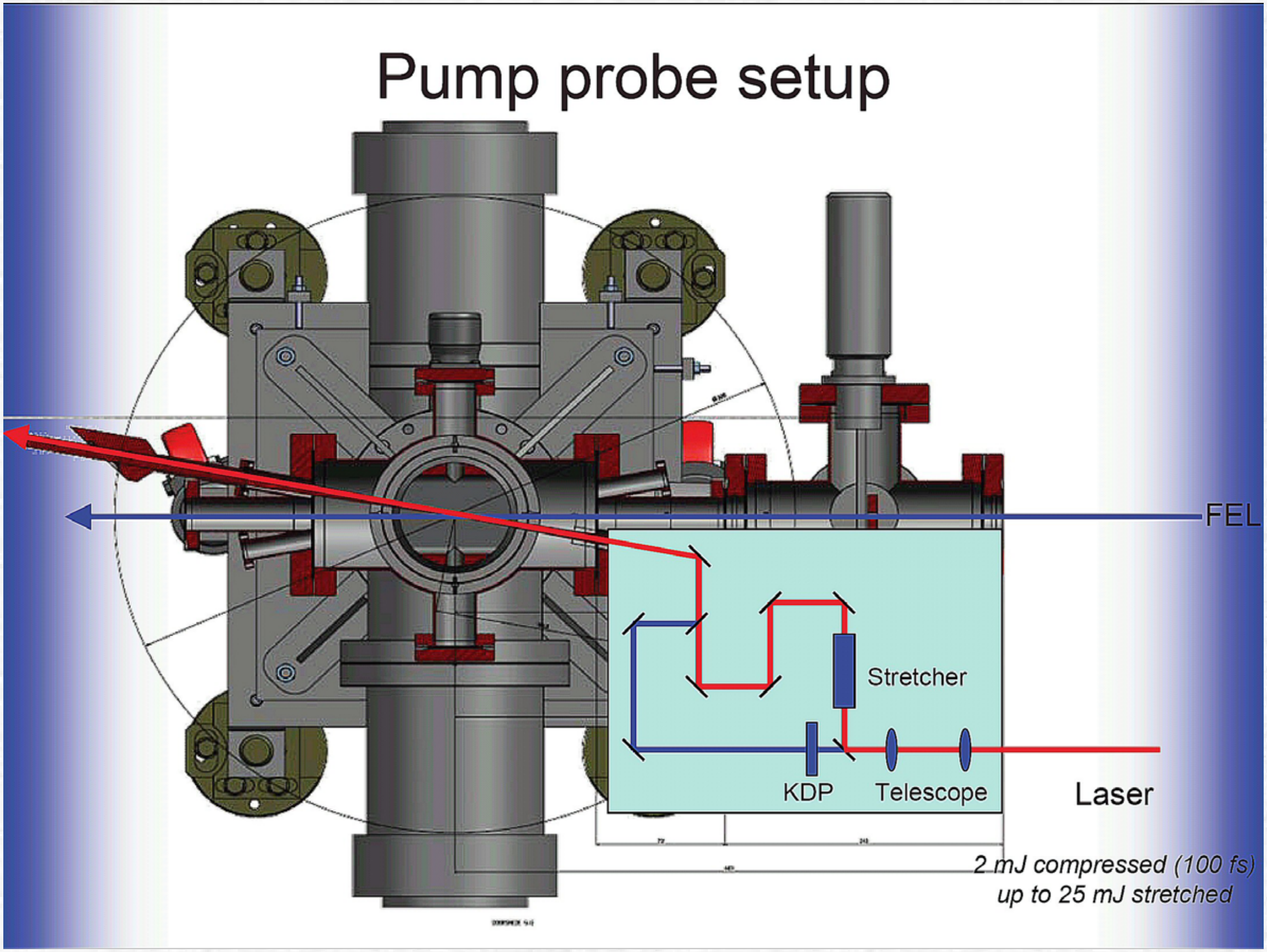




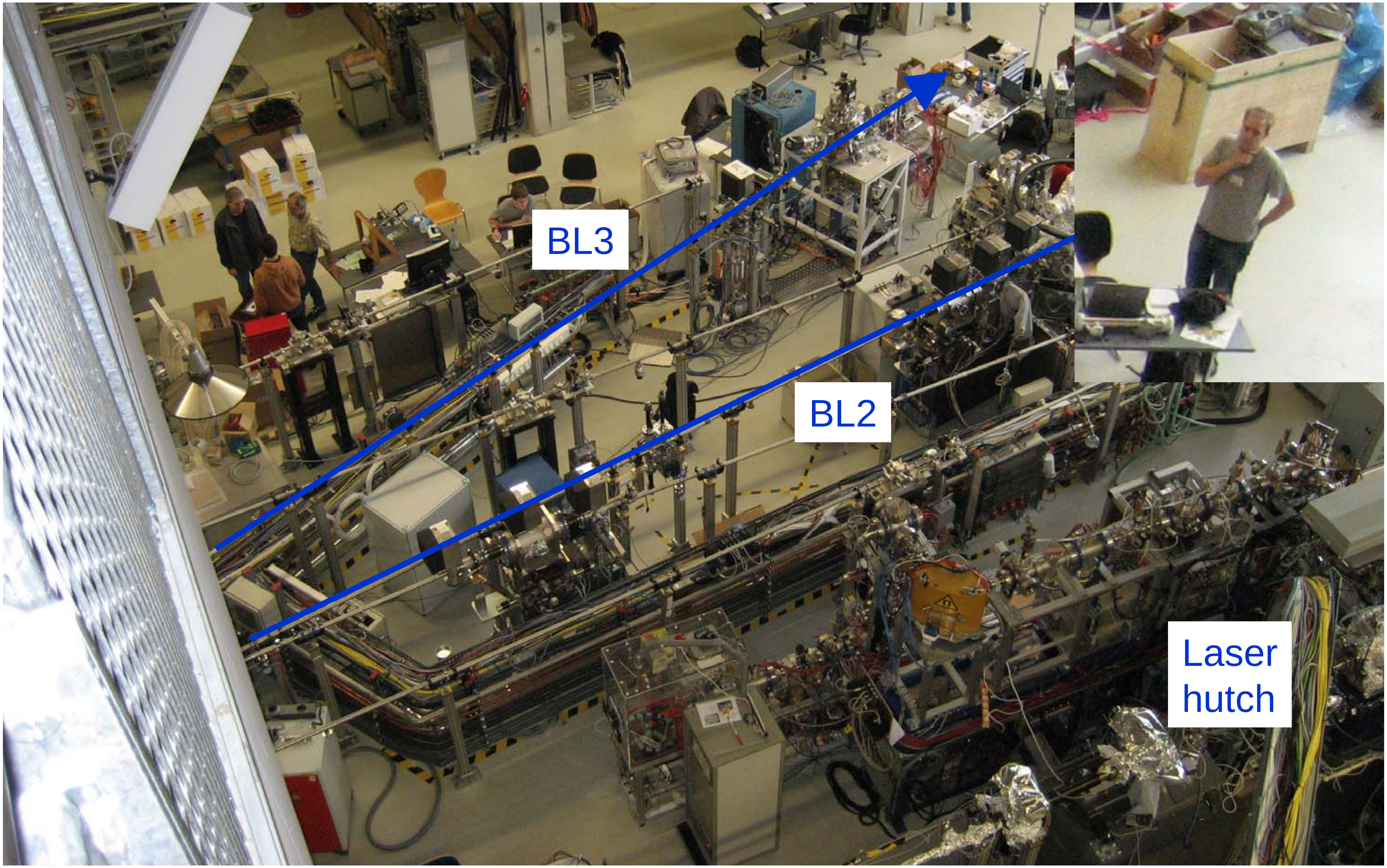
Aerial view of the FLASH Free Electron Laser in Hamburg

Mabbs *et al*, J. Chem. Phys. **123**, 054329 (2005)

Pump-probe experiment on CO_2 alignment (FLASH Campaign 2008)



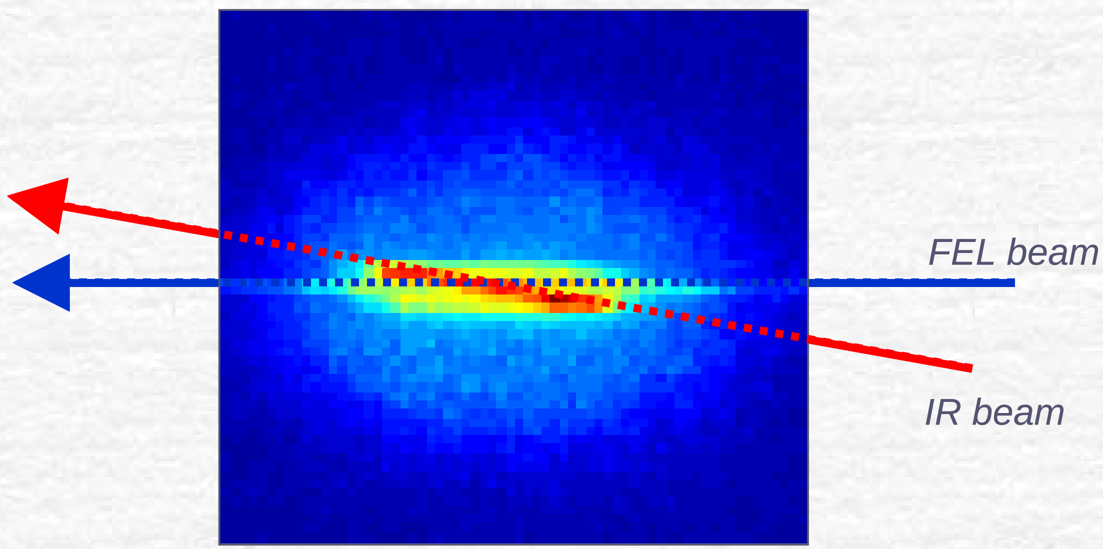
The experimental hall at the FLASH FEL in Hamburg

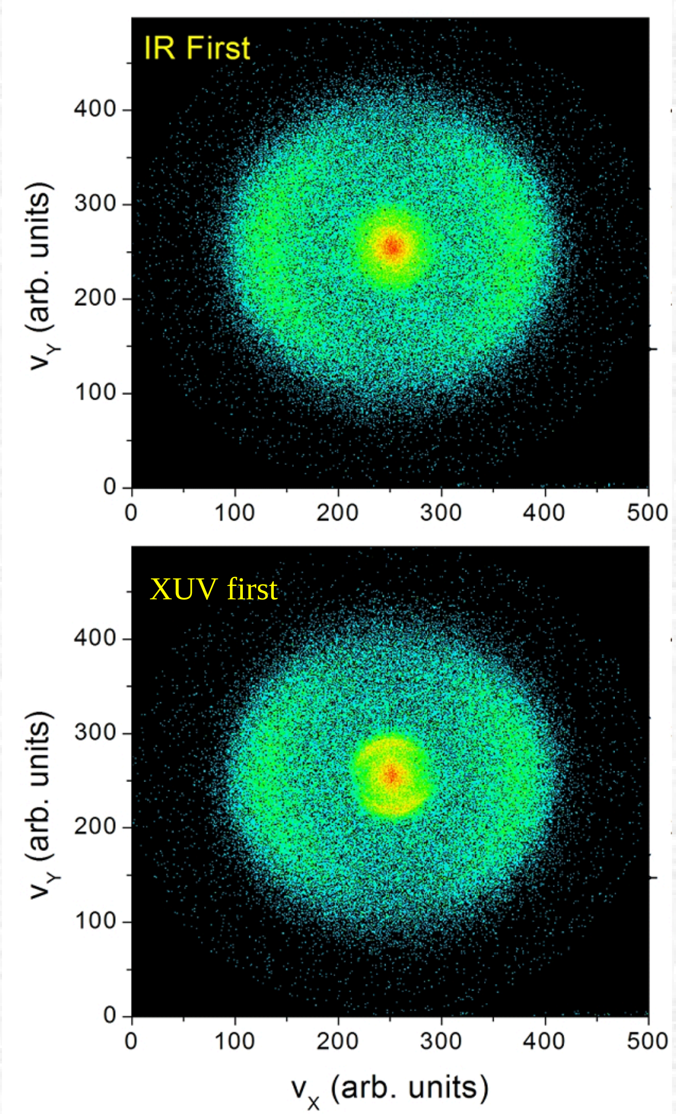


Pump-probe experiment on CO_2 alignment (FLASH Campaign 2008)

Finding the two-color overlap

- Use bond-softening in H_2
- XUV-production of H_2^+
- IR-dissociation into H^+ + H
- Velocity and angle-resolved detection of H^+

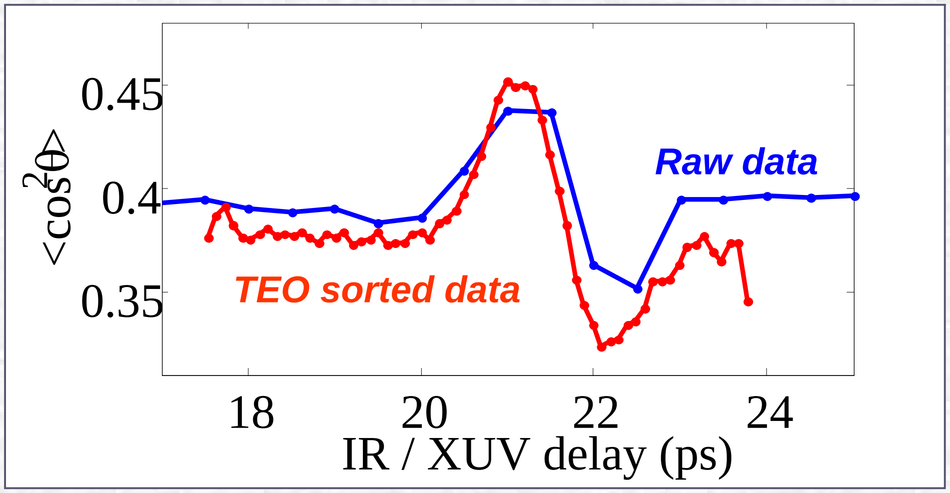


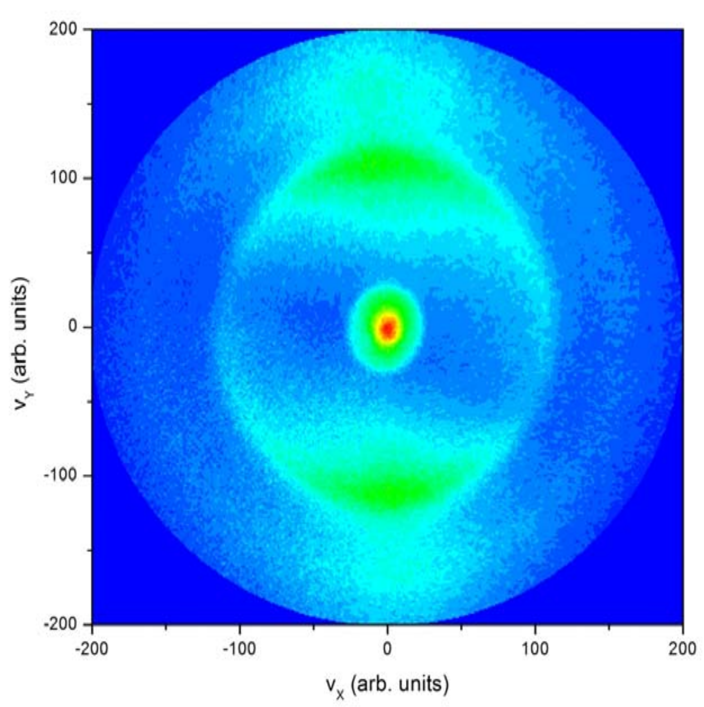


Pump-probe experiment on CO_2 alignment (FLASH Campaign 2008)

Time-dependent alignment of CO_2

- Use IR to align the molecule
- Use FLASH FEL to dissociatively ionize
- Velocity and angle-resolved detection of O^+
- Step towards molecular frame dynamics (fragmentionation, imaging)





Next step: photodissociation of Br_2 (spring 2009)