Novel methods for studying time-resolved structural and electronic dynamics in molecules

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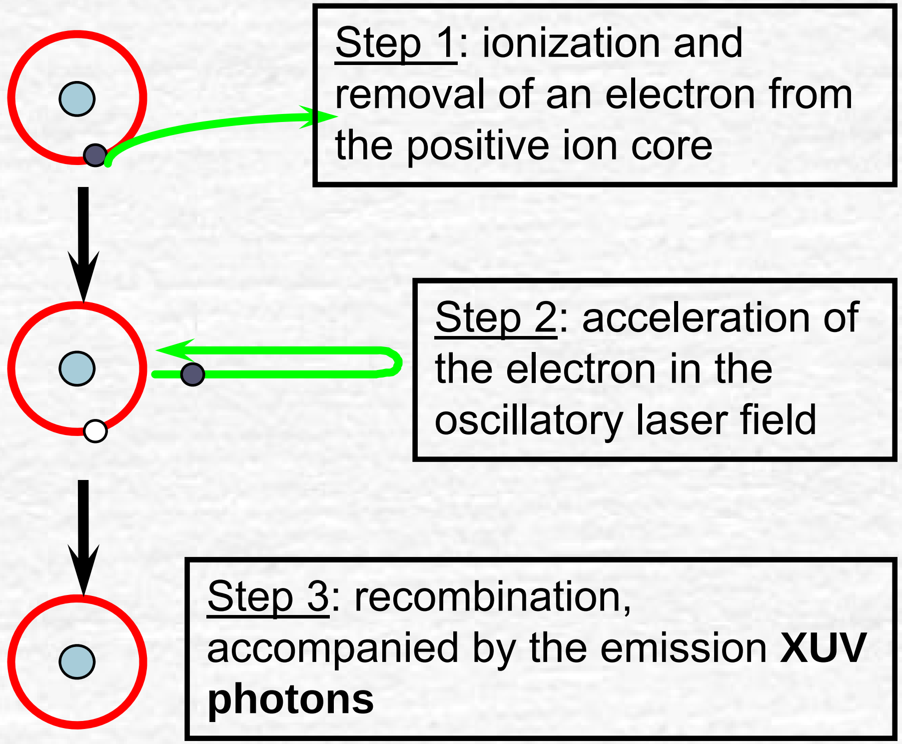
Several novel schemes for studying structural and electronic dynamics in atomic and molecular systems:

- *Novel pump-probe spectroscopy schemes, in particular using XUV/X-ray light*
- *Various schemes involving strong-field ionization at THz to XUV/X-ray wavelengths*

Novel XUV/x-ray sources (HHG and FELs)	Near-IR/Mid-IR strong field ionization	
Electron dynamics *Example:* *Attosecond time-resolved pump-probe spectroscopy*	*Example:* *Observations of the breakdown of the single-active electron approximation in ATI*	**Mostly lab-based lightsources**
Nuclear dynamics *Example:* *Molecular frame XUV/X-ray photo-emission*	*Example:* *Strong field photoelectron holography*	**Lab-based lightsources and FELs**

Two ways to use re-collision physics

High-harmonic Generation



Generation of ultrashort (attosecond) XUV pulses that can be used in experiments that relate to experiments at **XUV/X-ray FELs**

M. Ivanov and F. Krausz, Rev. Mod. Phys. 81, 163 (2009)

High-harmonic Imaging

(and related techniques)

The (time-dependent) electronic and nuclear structure leave signatures in the HHG and strong-field ionization process itself:

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

- Multi-centre interference
  H. Sakai et al., Nature 435, 470 (2005).

- High-harmonic interferometry
  O. Smirnova et al., Nature 460, 7258 (2009)

- Strong-field photoelectron holography
  Y. Huismans et al., Science 331, 61 (2011)

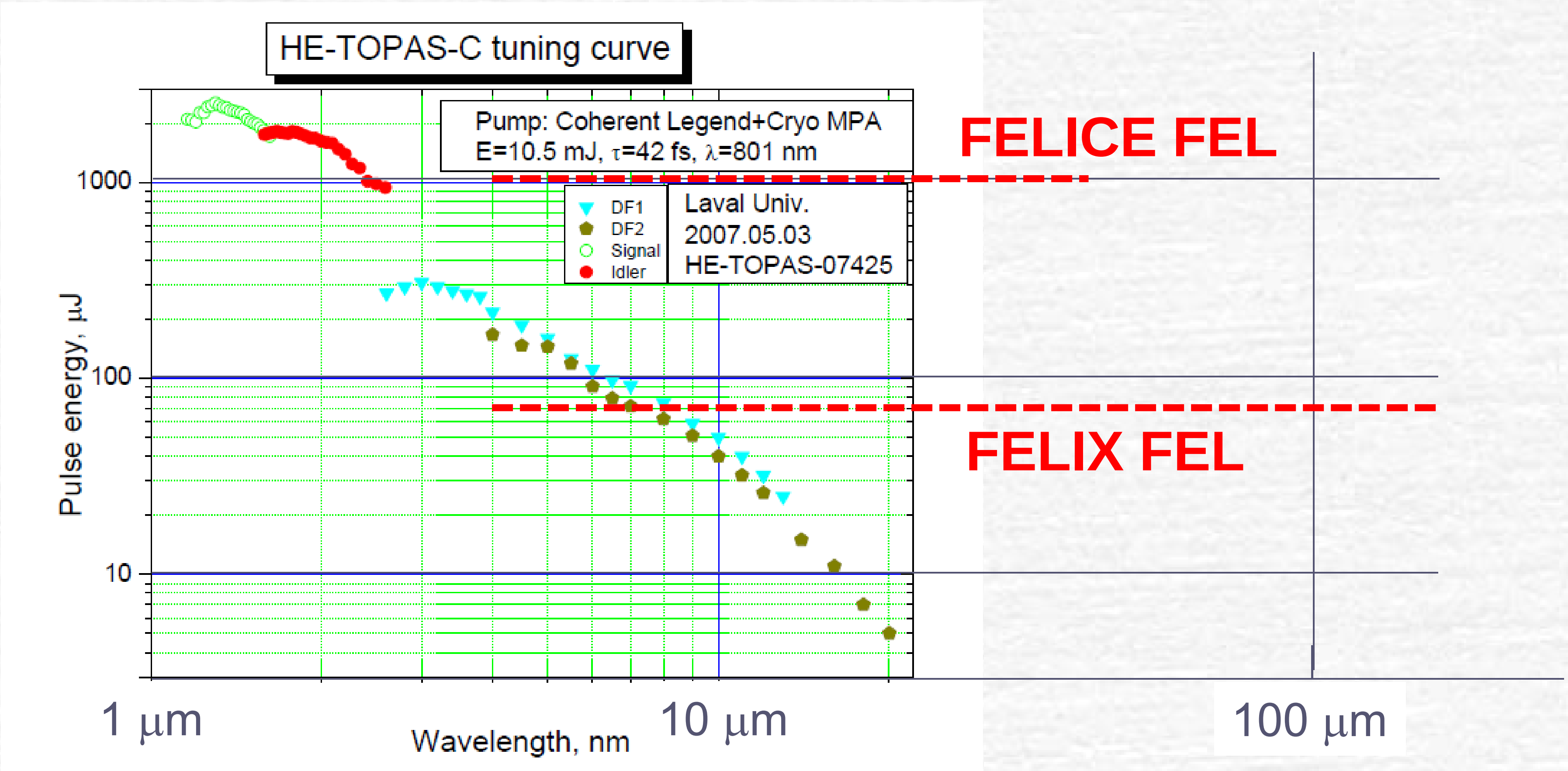
Many of these measurements favor the use of mid-infrared light → relate to experiments at **mid-infrared/THz FELs**

Comparison: XUV/X-ray FELs vs HHG

XUV/X-ray generation by HHG (ELI-HU Projections)	FEL source that can provide comparison	Approximate FEL XUV/X-ray specification (rough guesses)
12-300 nm, 4-100eV / 100-10nJ	FLASH	~10 μJ
3-12nm,100-400eV / >1nJ	FLASH	~100 μJ
12-120nm / 100-1μJ	FLASH	~100 μJ
1.2-12nm / 1-0.1μJ	XFEL	>1 mJ
0.12-1.2nm / 100-1nJ	XFEL	8 mJ
0.12-1.2A / >1nJ	XFEL	2 mJ

In terms of pulse energy FELs outperform even the best HHG sources by typ. 3 orders of magnitude or more.
Additional criteria for the selection between HHG and FEL sources are pulse duration, synchronization, repetition rate, accessibility, etc.

Comparison: THz FELs vs OPAs

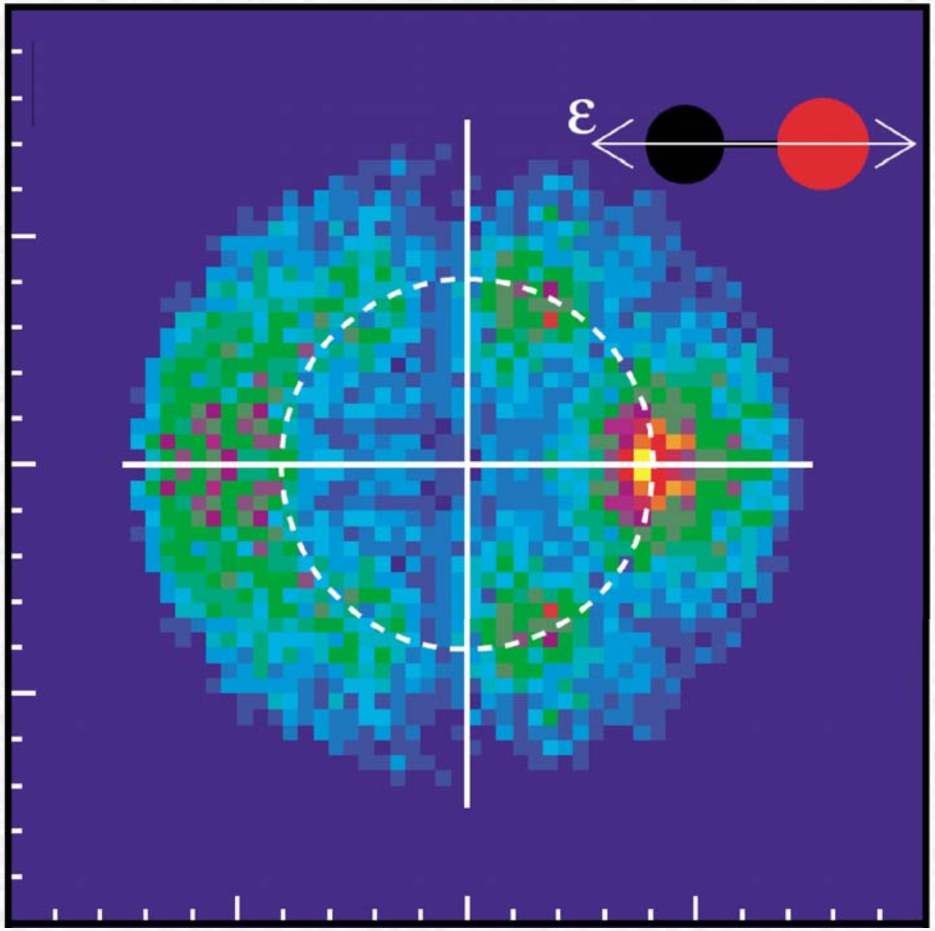


In terms of pulse energy FELs are better beyond 10 µm, while OPAs can reach higher energies below 10 µm.
Additional criteria for the selection between HHG and FEL sources are pulse duration, synchronization, repetition rate, accessibility, etc.

Studying Time-Resolved Molecular Dynamics using XUV/X-ray Photo-emission

Novel XUV/x-ray sources (HHG and FELs)	**Near-IR/Mid-IR strong field ionization**
Electron dynamics *Example:* *Attosecond time-resolved pump-probe spectroscopy*	*Example:* *Observations of the breakdown of the single-active electron approximation in ATI*
Nuclear dynamics *Example:* *Molecular frame XUV/X-ray photo-emission*	*Example:* *Strong field photoelectron holography*

Indications of structuring encoding in XUV/X-ray photoemission experiments



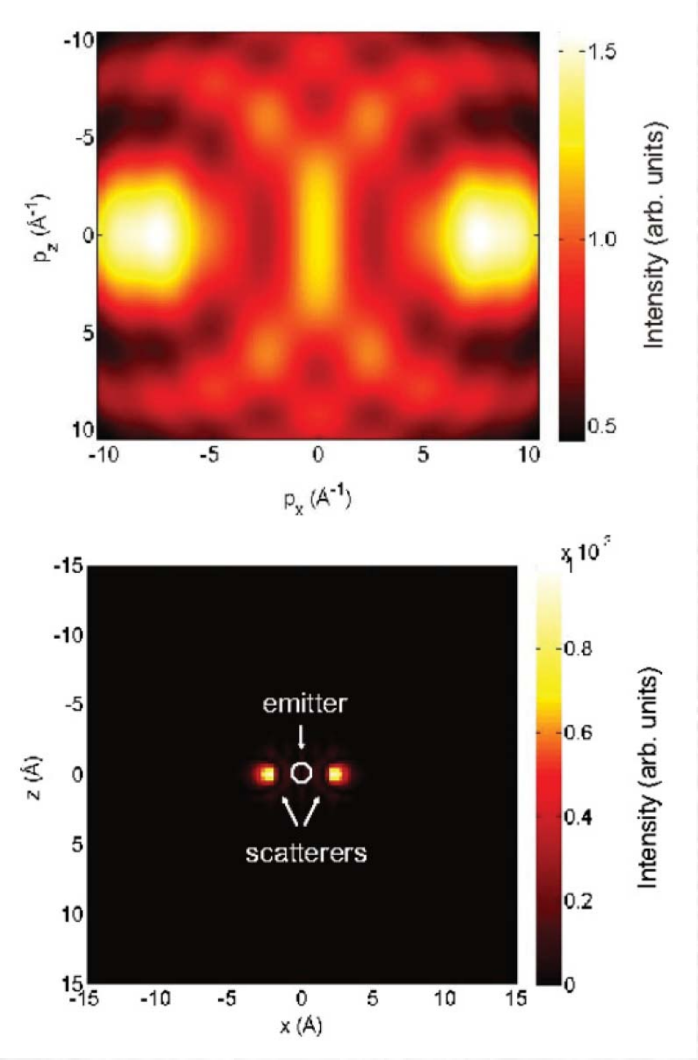
C(1s) core-shell photo-emission from CO using 294 to 326 eV radiation.

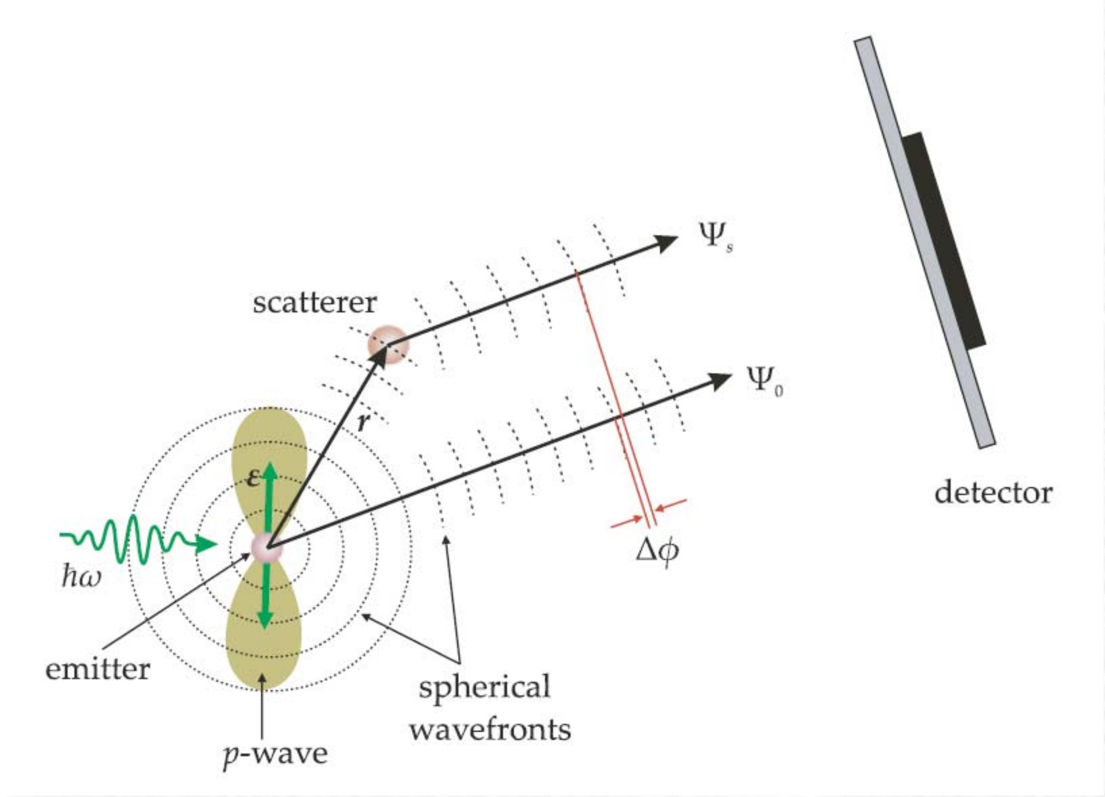
Away from the Carbon atom (black) the angular distribution is relatively unstructured.

In the direction of the Oxygen atom (red) a diffraction structure is observed.

Landers *et al*, Phys. Rev. Lett. 87, 013002 (2001)

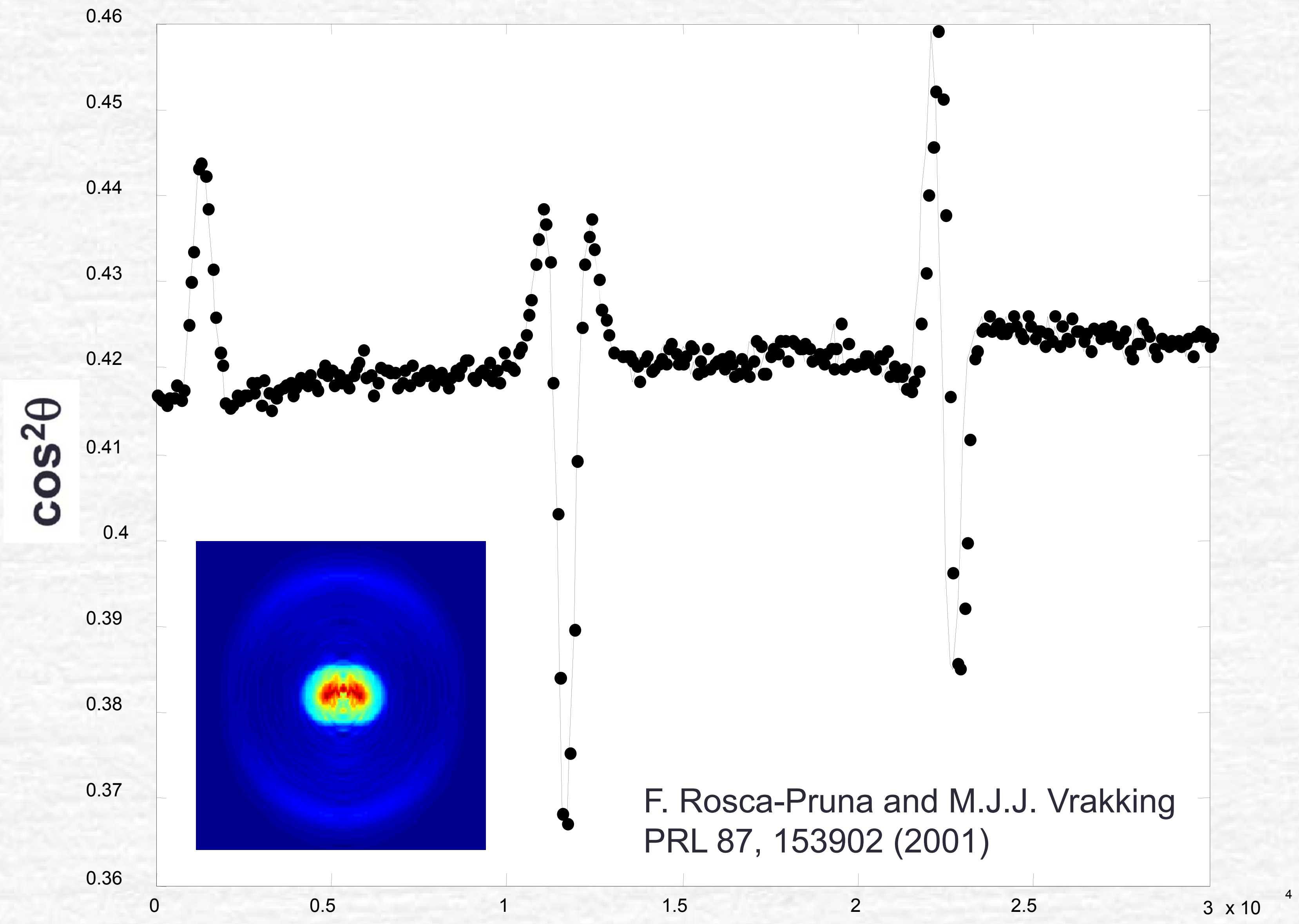
Using intra-molecular electron diffraction and interference to measure (time-resolved) molecular structure



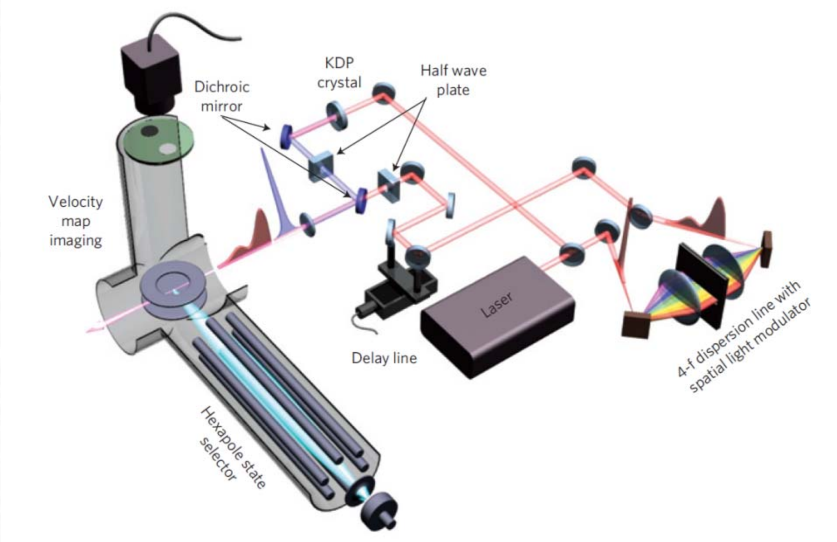


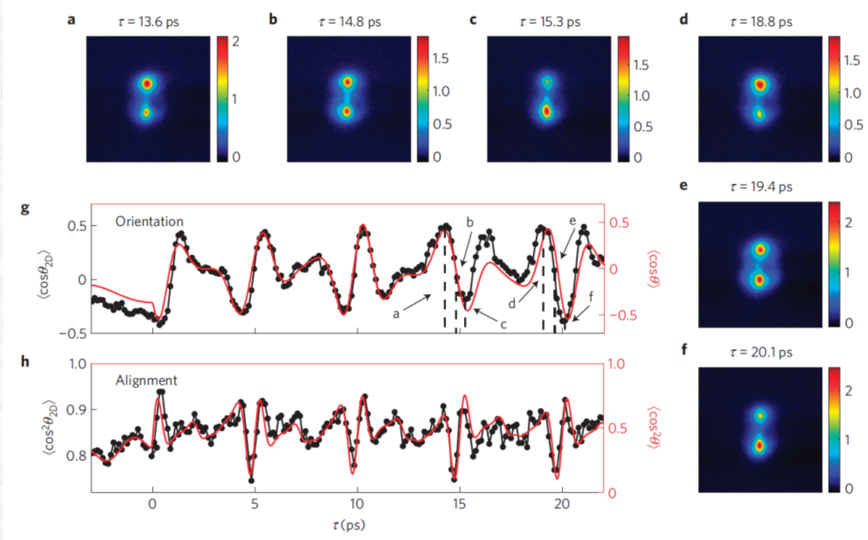
F. Krasniqi et al., Phys Rev. A 81, 033411 (2010)

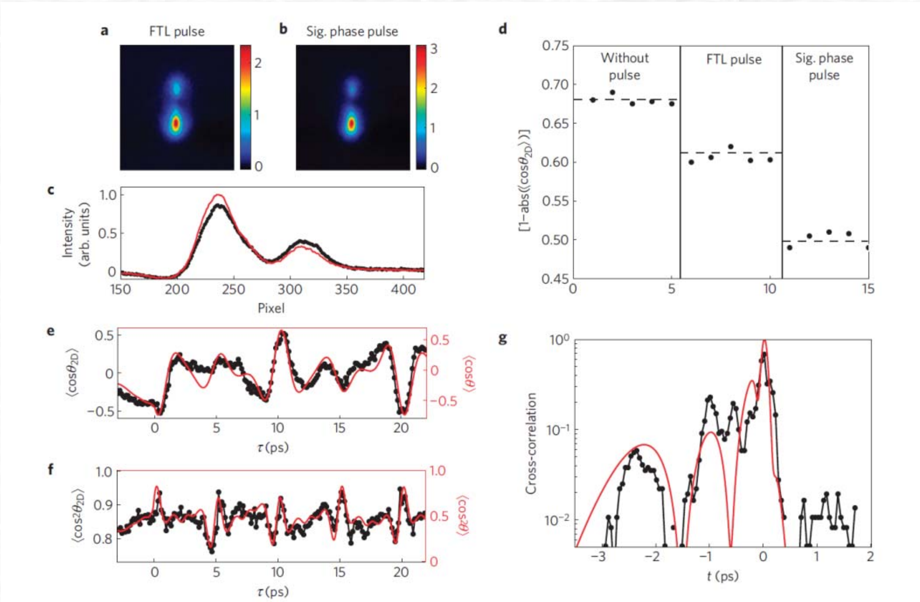
Dynamic Molecular Alignment of CO_2



Dynamic Molecular Orientation of NO

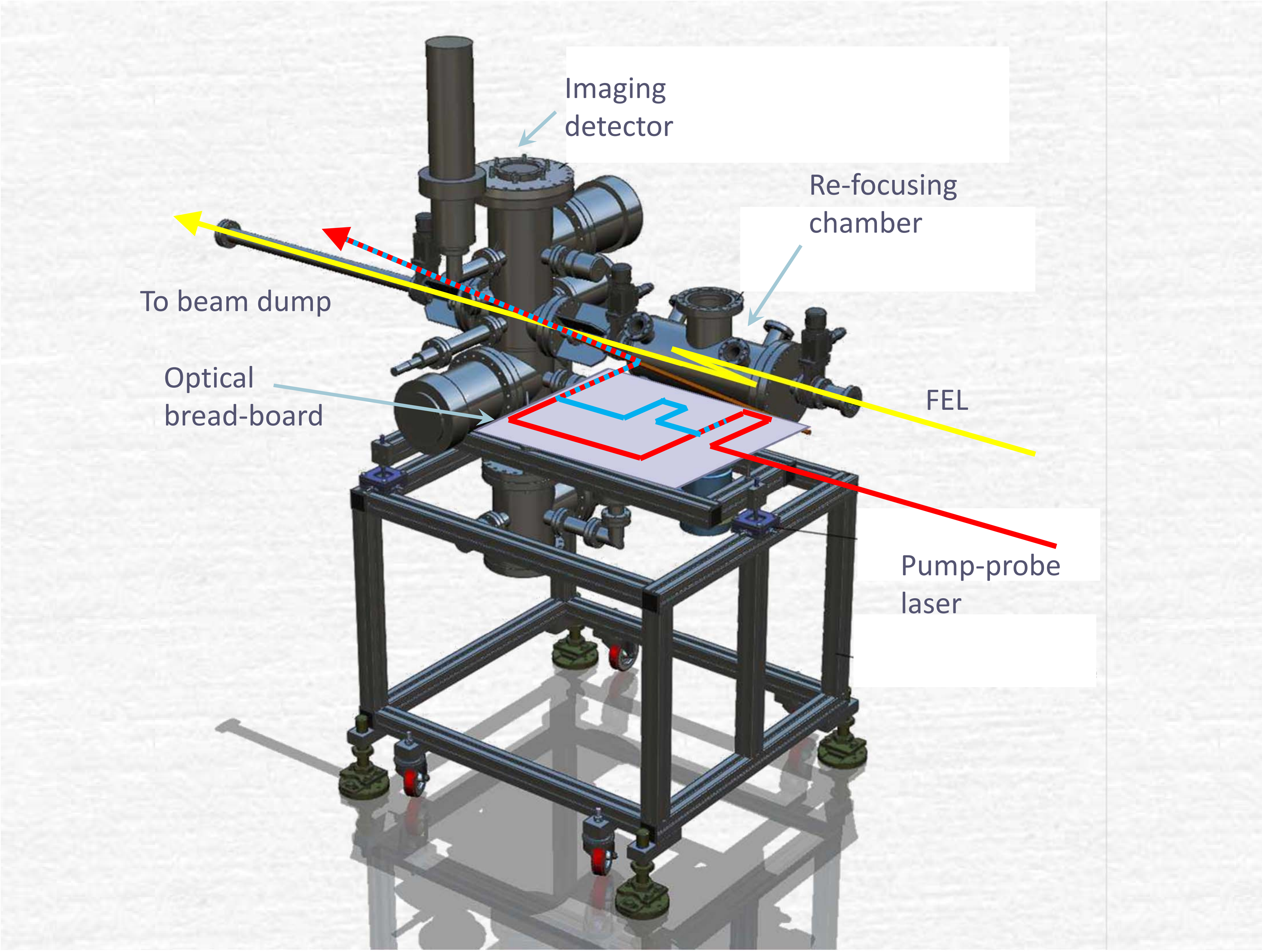






Impulsive orientation of molecules to <cosθ>=0.74 demonstrated, extension to appr. 0.96 plausible

O. Ghafur et al.,
Nature Physics 5, 289 (2009)

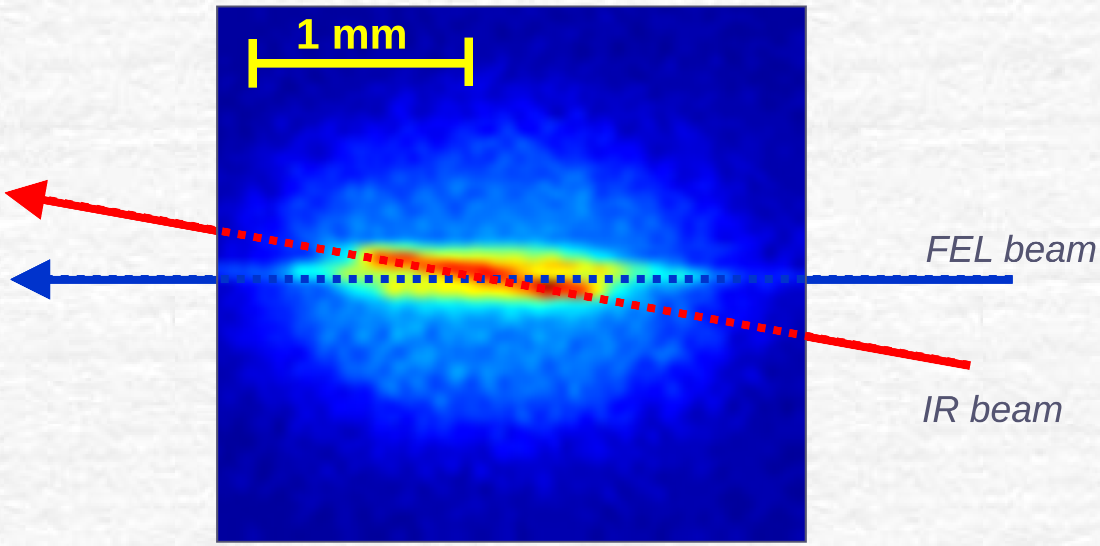


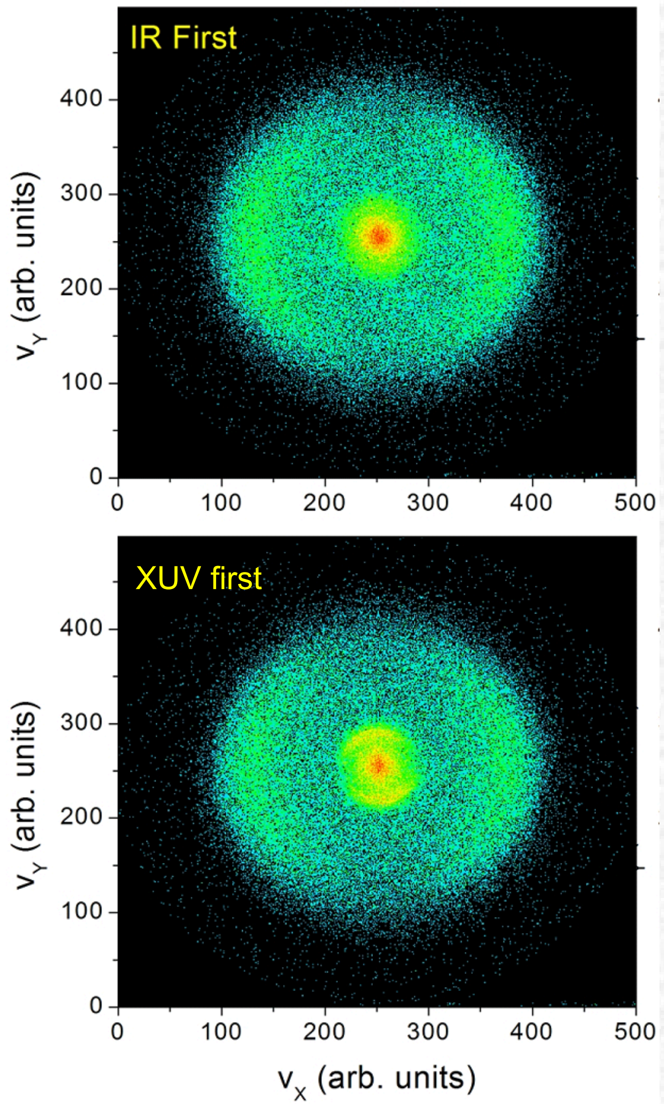
Imaging detector
Re-focusing chamber
To beam dump
Optical bread-board
FEL
Pump-probe laser

Pump-probe experiment on CO_2 alignment (FLASH Campaign 2008, BL2)

Finding the two-color overlap

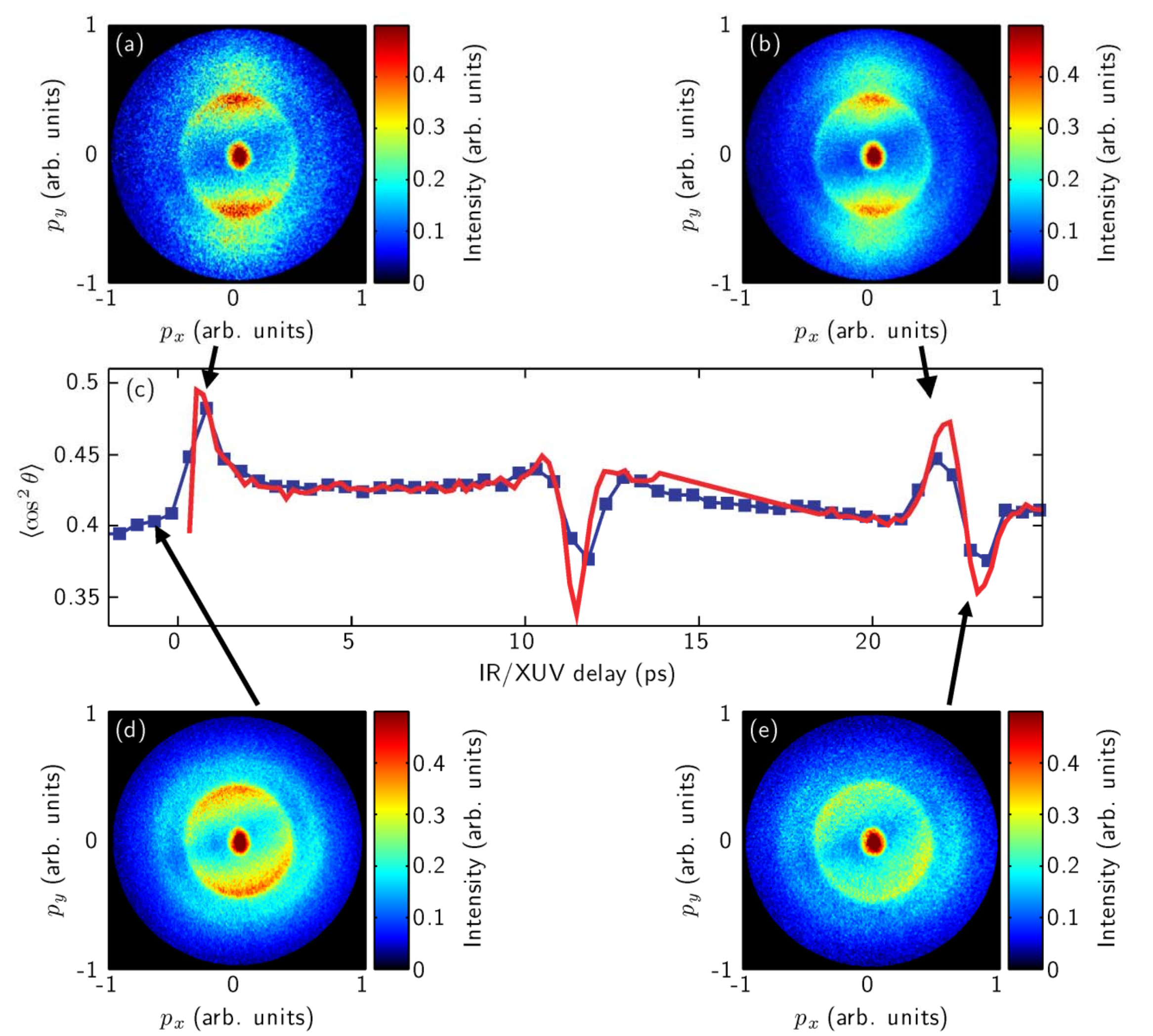
- Use bond-softening in H_2
- XUV-production of H_2^+
- IR-dissociation into H^+ + H
- Velocity and angle-resolved detection of H^+





P. Johnsson et al., Opt. Lett. 35, 4163 (2010)

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

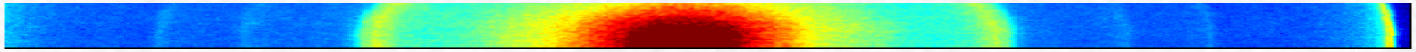


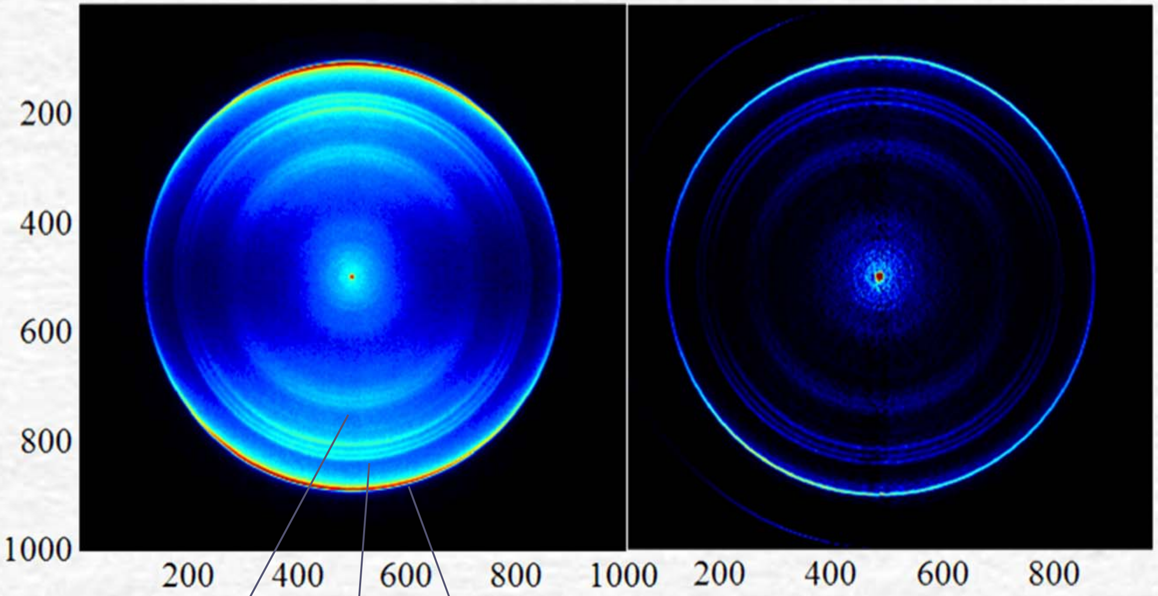
Raw data

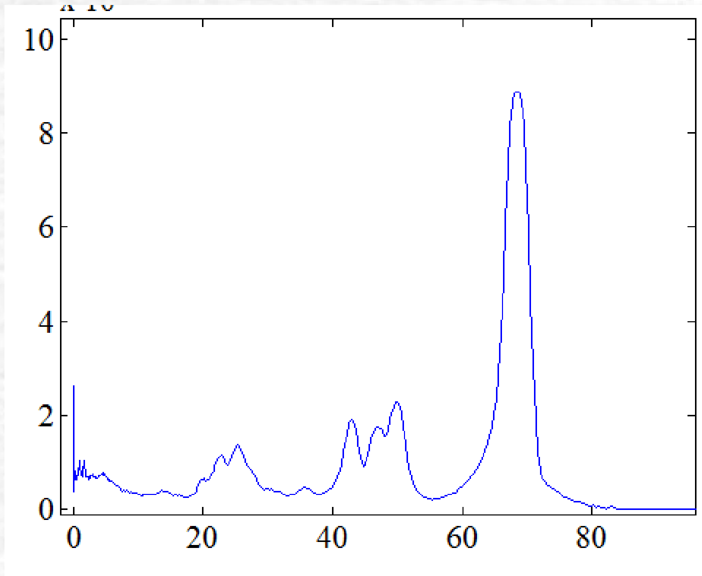
Sorted data using timing electro-optical (TEO) system (<100fs)

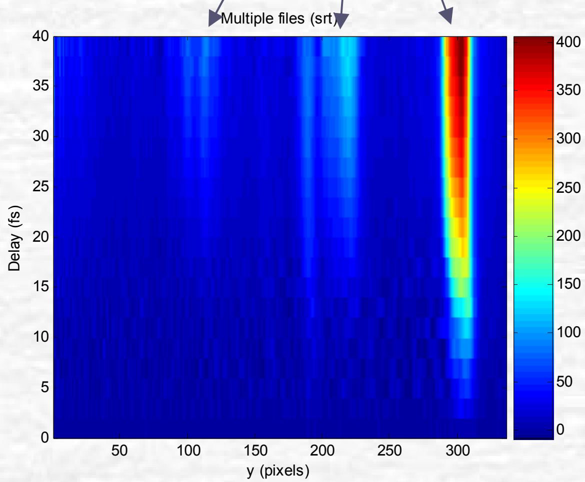
P. Johnsson et al., J. Phys. B 42, 134017 (2009)

Neon PAD spectra (June 2009)





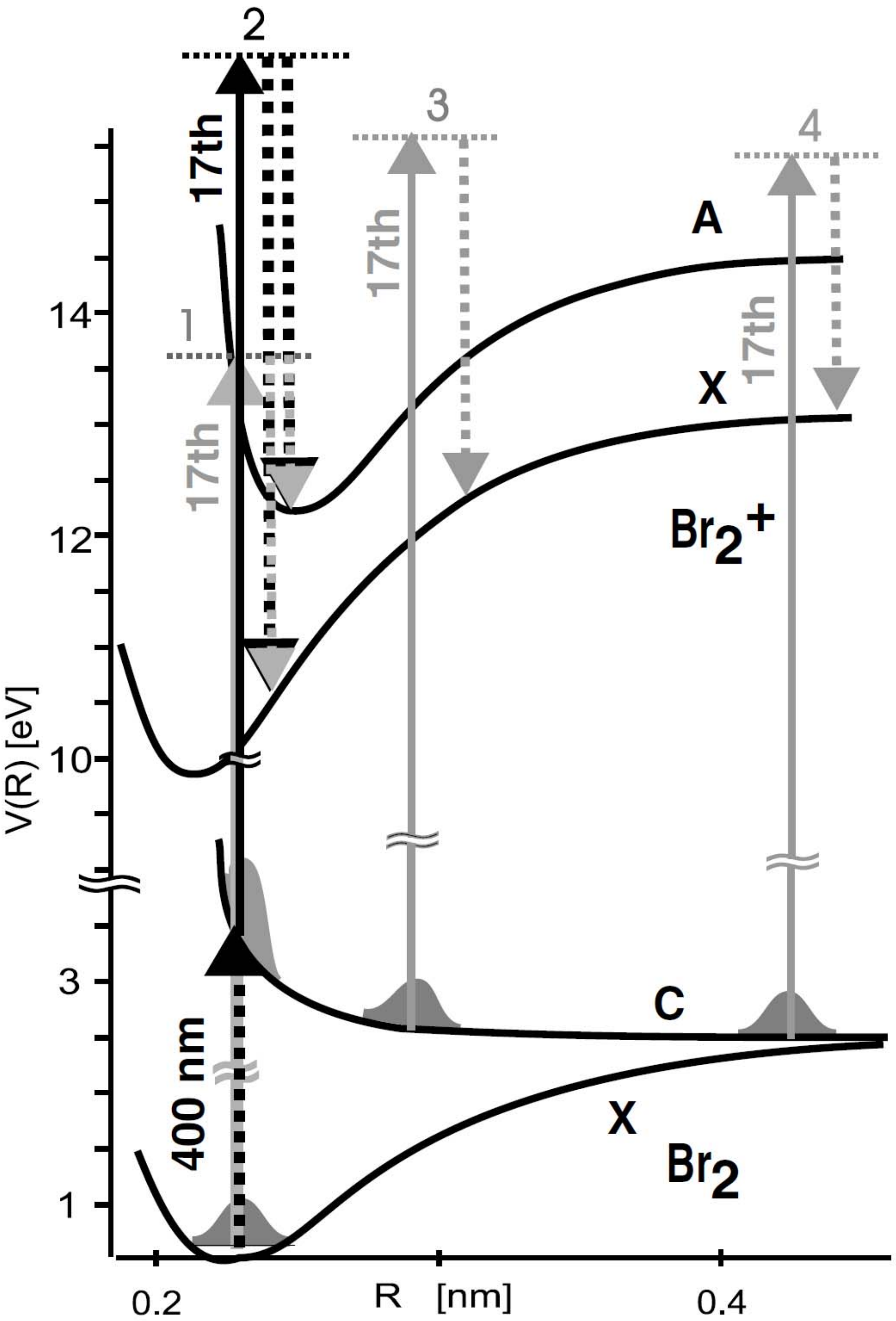




Sorted data using GMD: Allow to determine which channel is linear or non-linear with FEL energy

A. Rouzee et al, Phys. Rev. A 83, 031401 (2011)

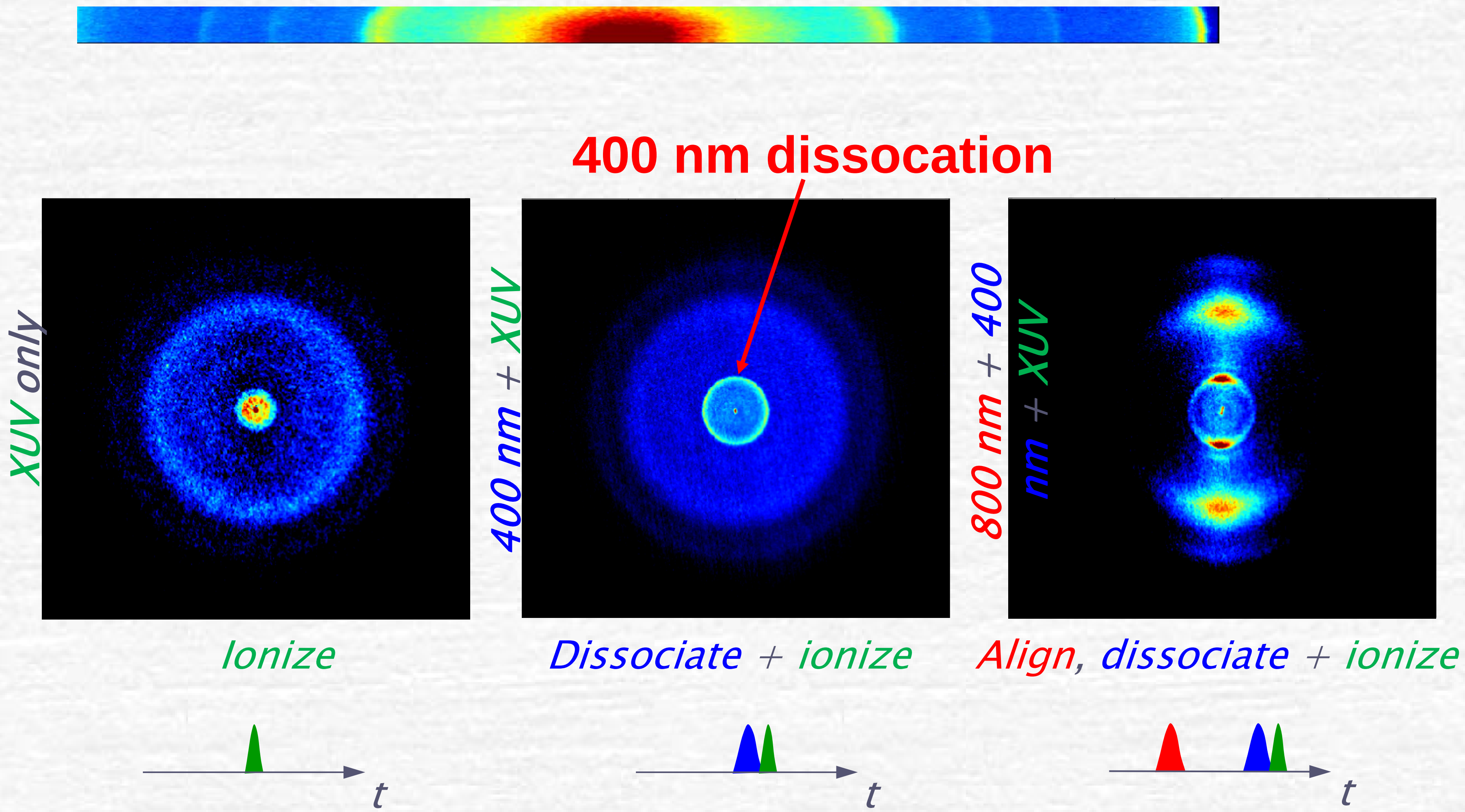
1	69,3 eV
2	49,9
3	46.9
4	42.8
5	35.6
6	25.4
7	22.7
8	20.0
9	1.6
10	0.9

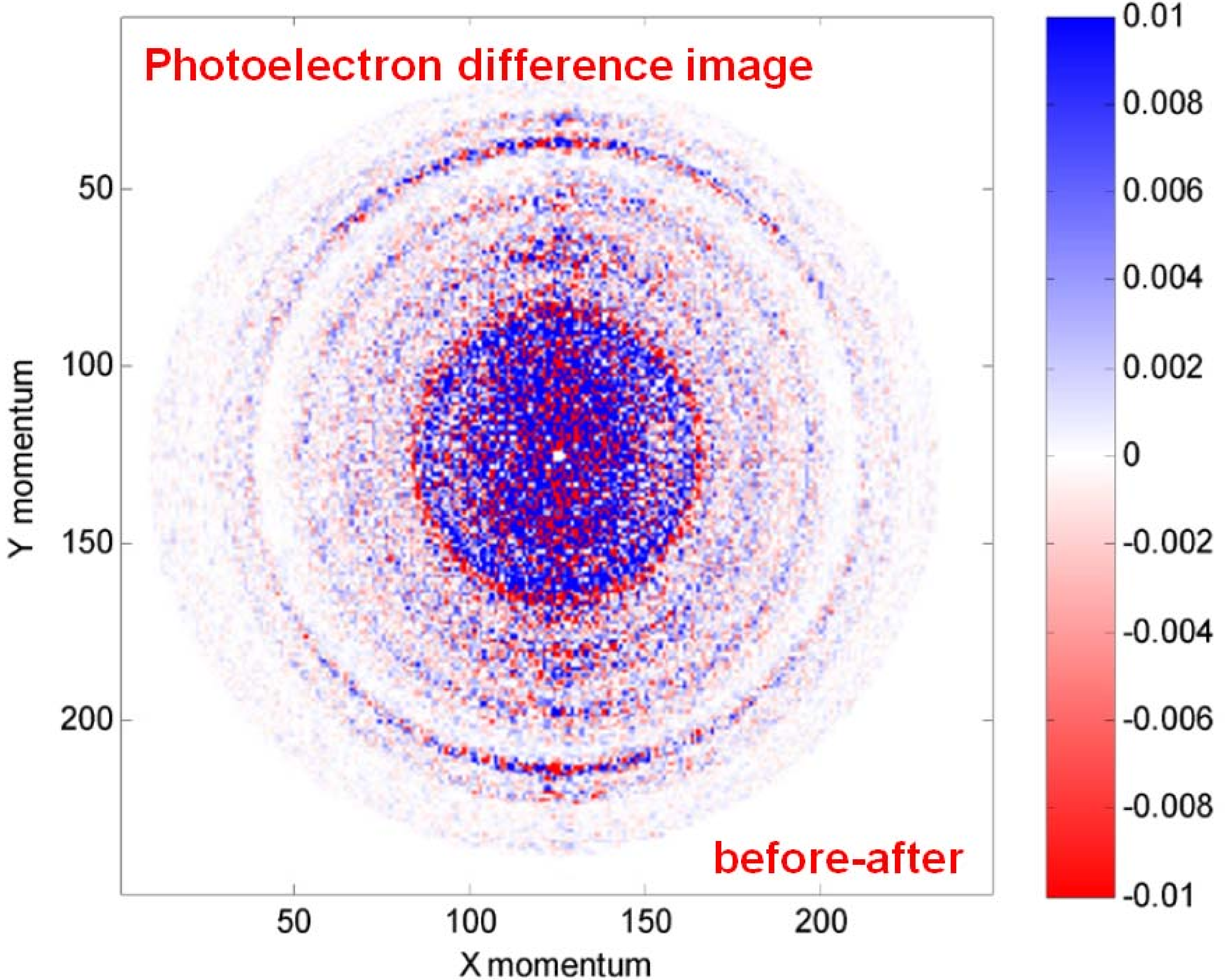


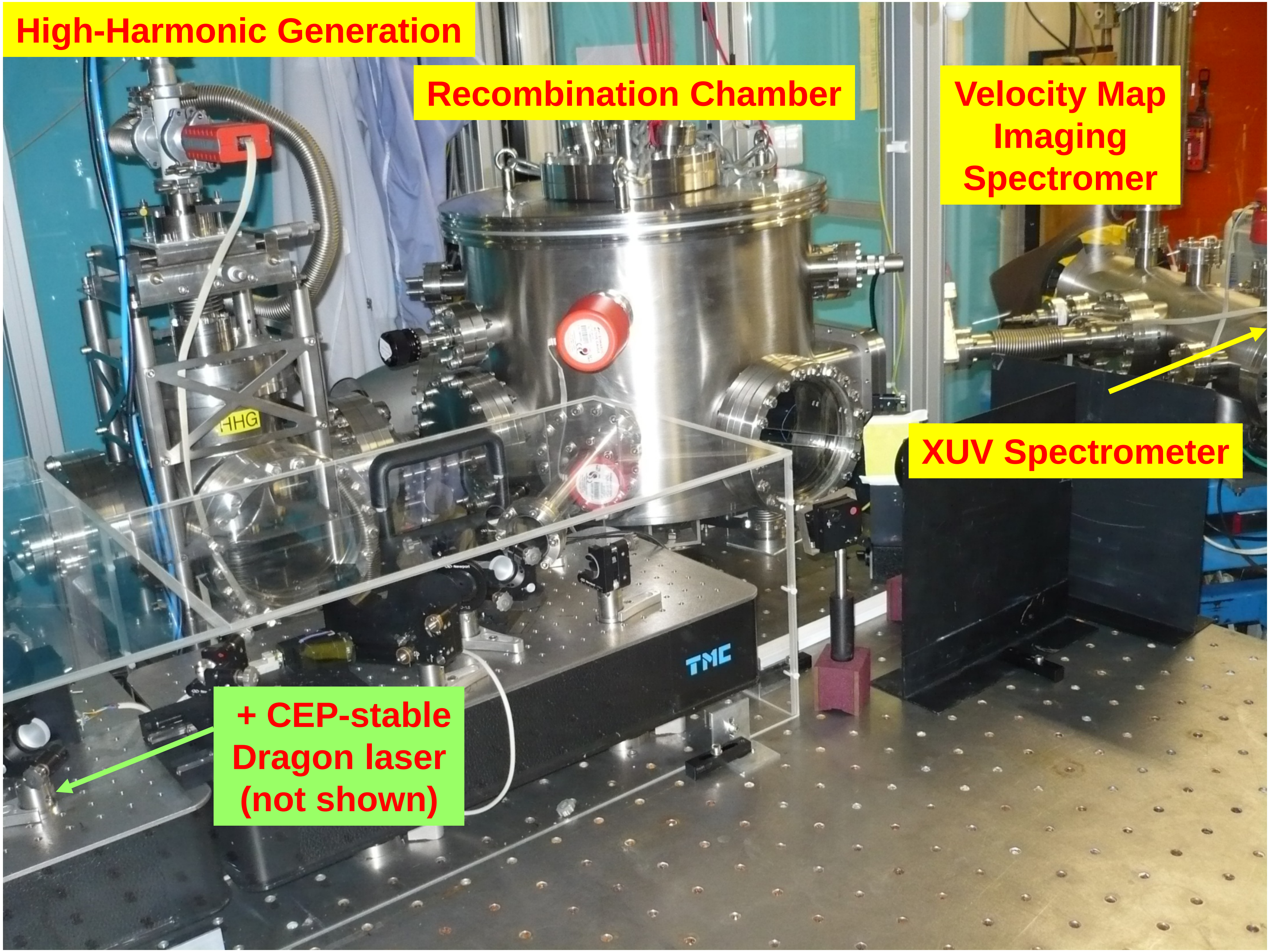
Br_2 photodissociation at FLASH in Hamburg + LCLS in Stanford

- ❖ High vapor pressure
- ❖ Only moderately fast dynamics
- ❖ Easy to align (Rosca et al., J. Phys. B 34, 4919 (2001))
- ❖ Photodissociation at 400 nm
- ❖ Previous experiments with XUV probing (Leone et al., PRL 87, 193002 (2001), Wernet et al. PRL 103, 013001 (2009))

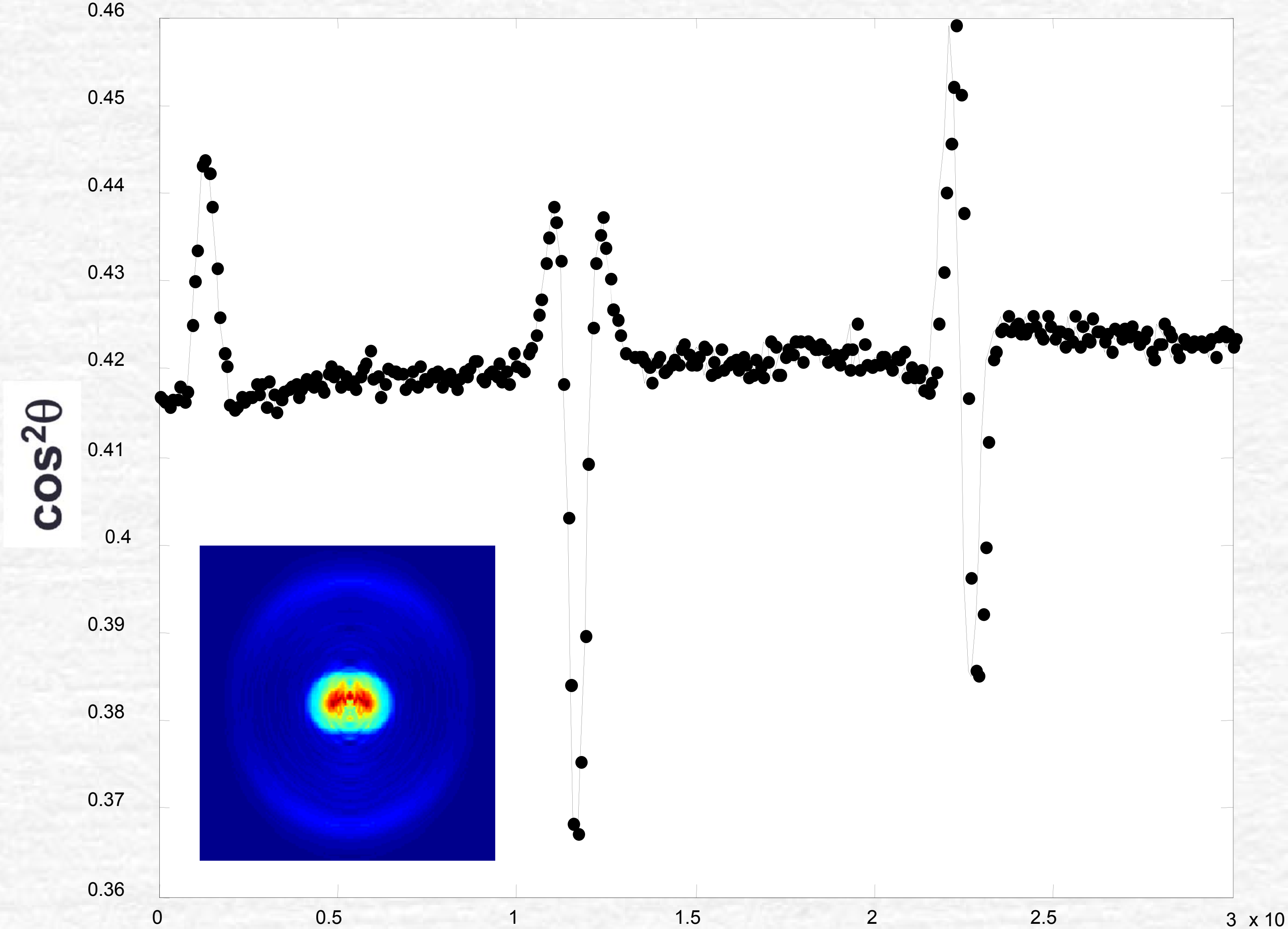
Alignment and Planar Delocalization



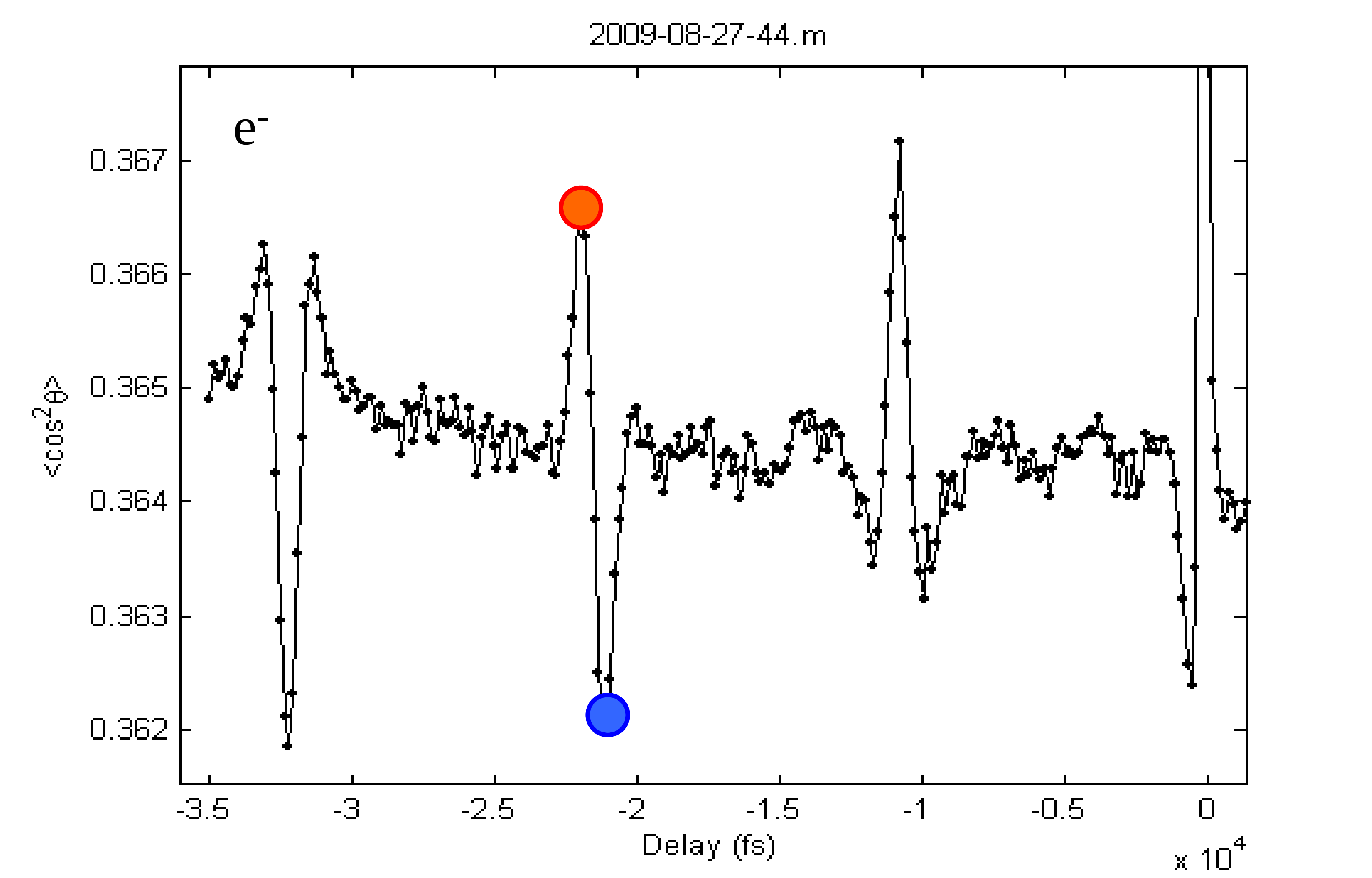

Photoelectron difference image
before-after
Y momentum
X momentum
50
100
150
200
0.01
0.008
0.006
0.004
0.002
0
-0.002
-0.004
-0.006
-0.008
-0.01

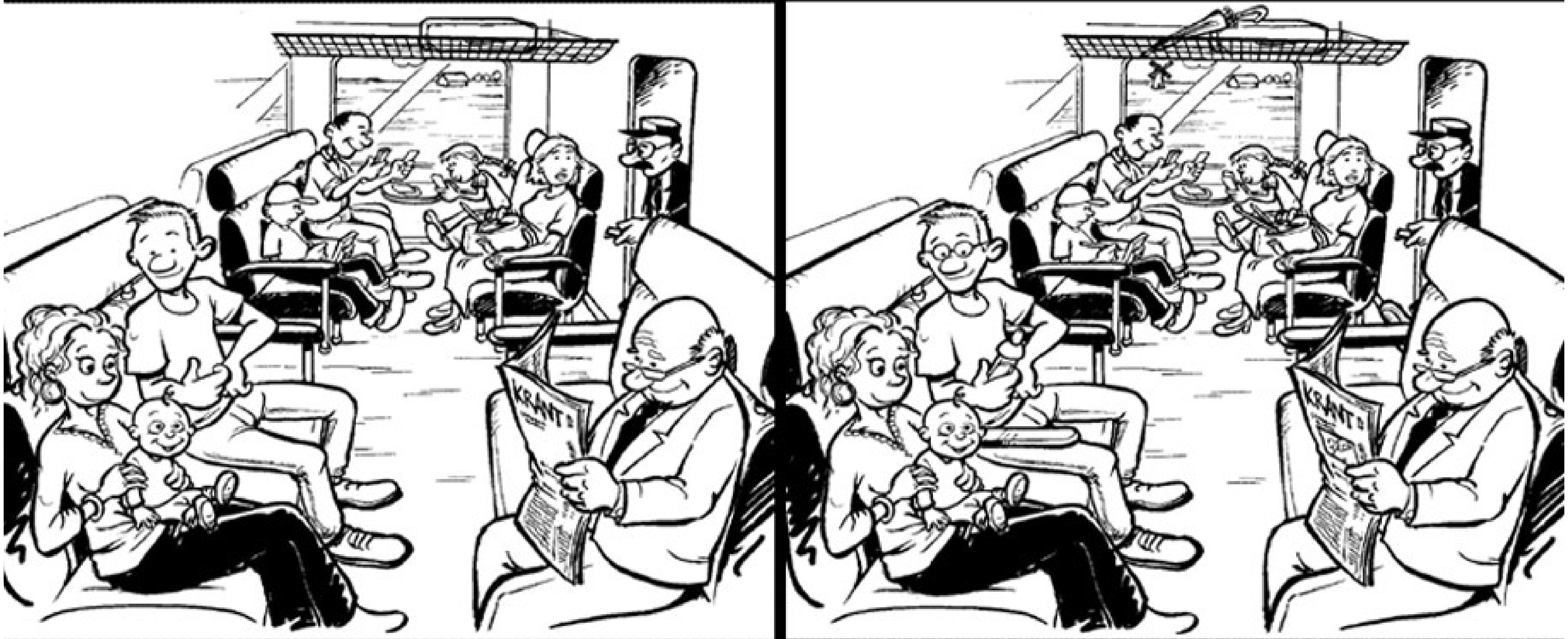

High-Harmonic Generation
Recombination Chamber
Velocity Map
Imaging
Spectromer
HHG
TMC
XUV Spectrometer
+ CEP-stable
Dragon laser
(not shown)

Dynamic Molecular Alignment of CO_2



Photoelectron angular distributions from aligned CO_2 molecules

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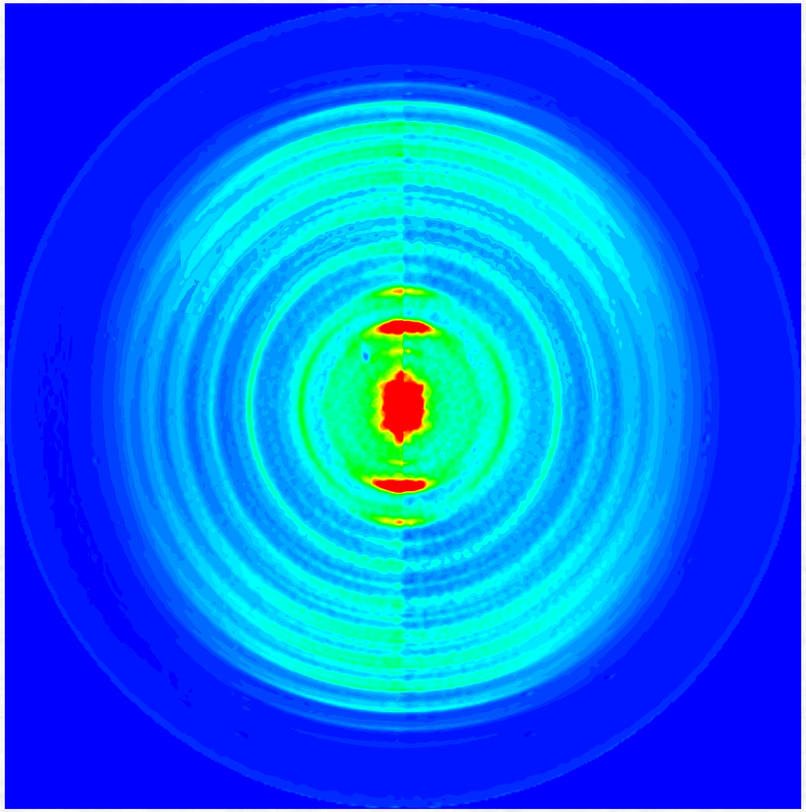
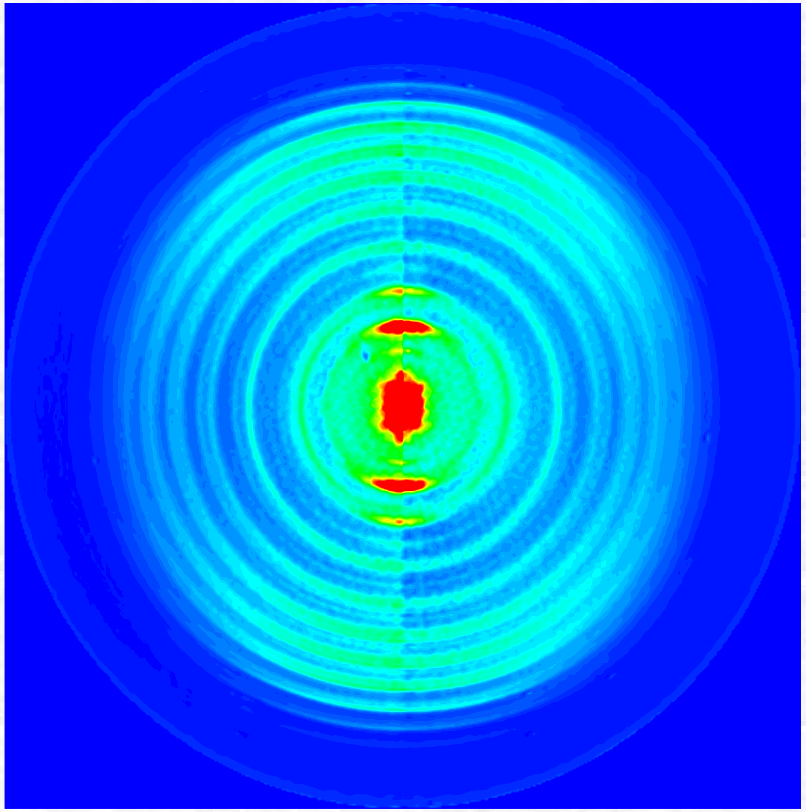
Photoelectron angular distributions from aligned CO_2 molecules

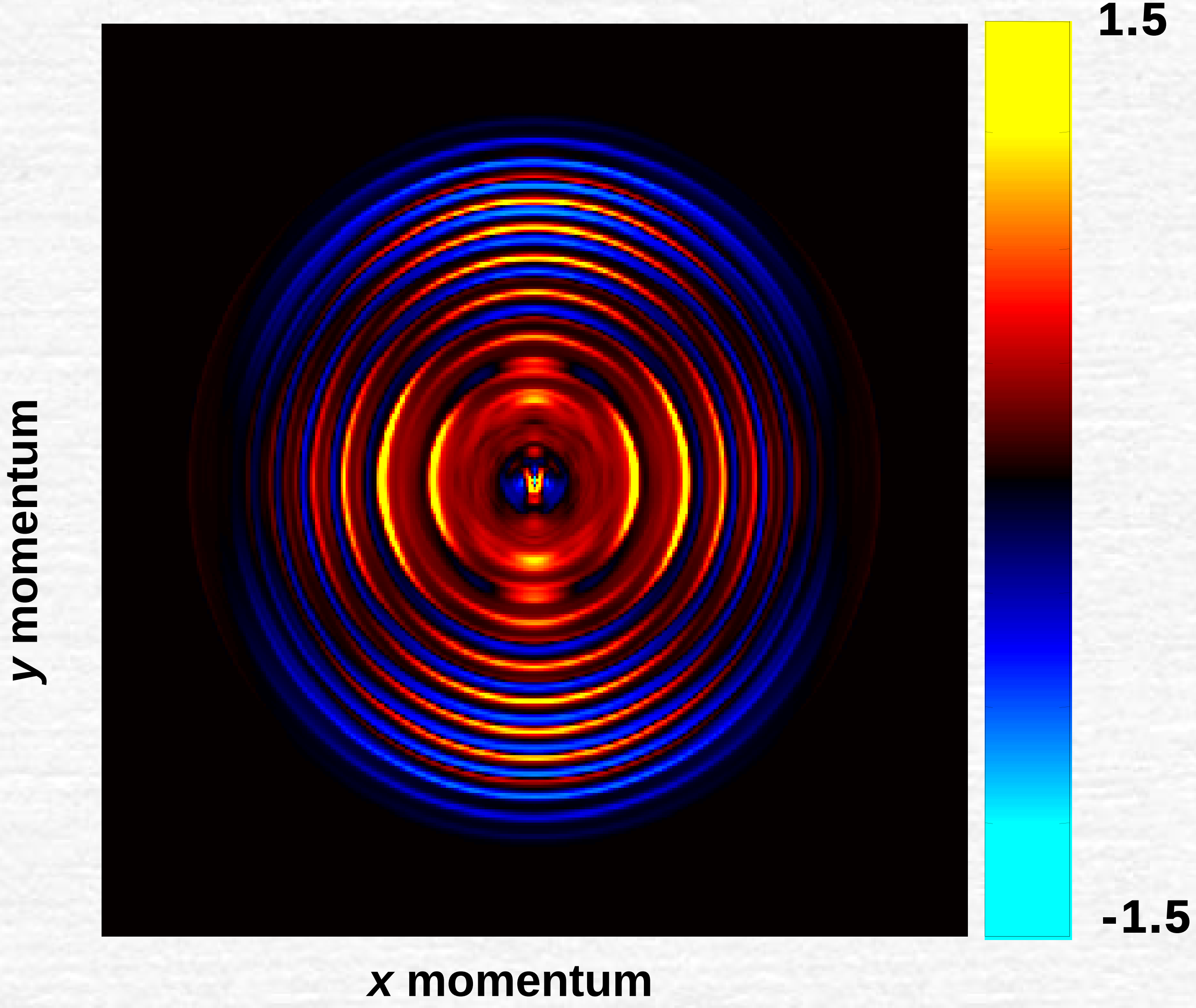


Alignment



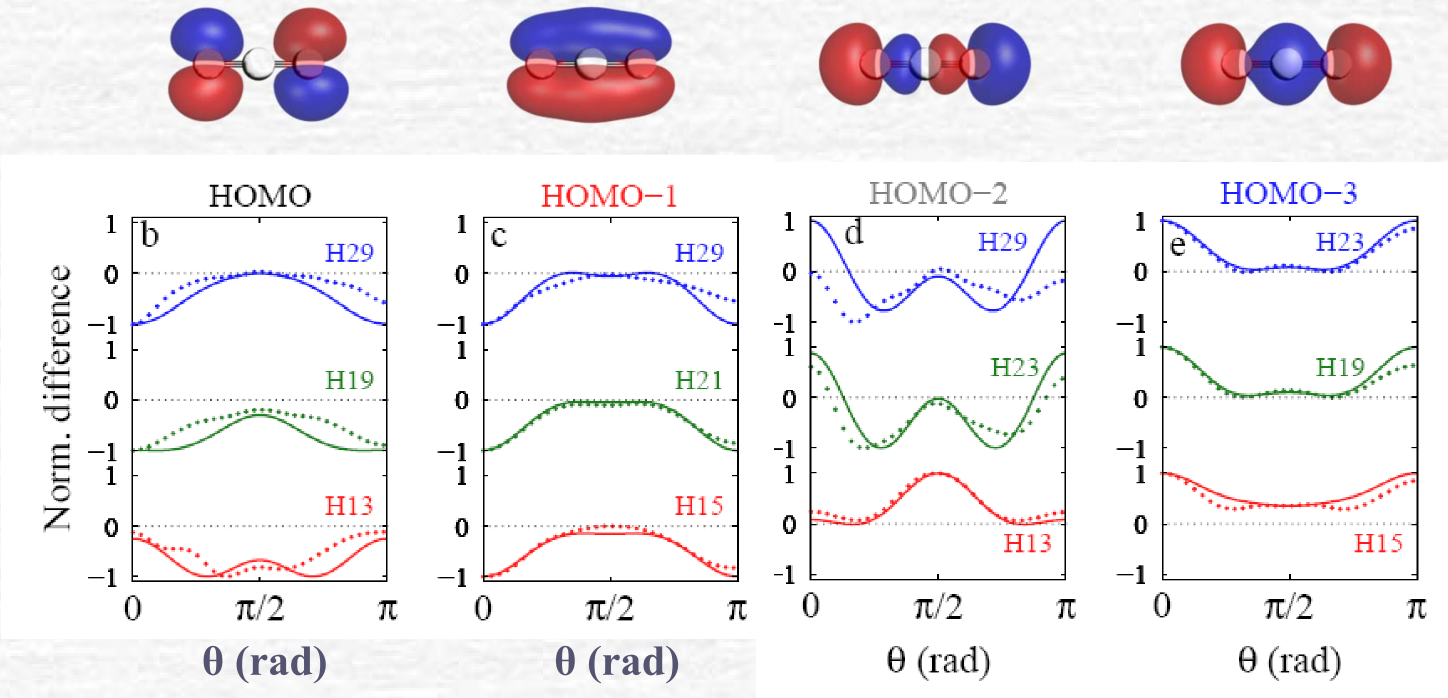
Planar Delocalization

Differential PAD: alignment – anti-alignment



F. Kelkensberg et al., PRA 84, 051404 (R) (2011)

Angular distributions evolve with energy



1. **Angular distribution sensitive to electronic structure**
2. **Energy dependence from interaction with molecular Coulomb field → molecular structure**

F. Kelkensberg et al., PRA 84, 051404 (R) (2011)

Prospects for moving to higher photon energy – two-color HHG

λ_{THz} (μm)	E_{THz} (mJ)*	$I_{mid\text{-}infrared}$ (W/cm^2)	$U_{p,mid\text{-}infrared}$ (eV)	$E_{cut\text{-}off}$ (eV)
4	0.8	10^{14}	149	490
6	0.4	$5\text{x}10^{13}$	168	550
8	0.25	$3.2\text{x}10^{13}$	190	620
10	0.16	$2\text{x}10^{13}$	186	606

Future approach:

- use HHG@MBI for high density samples and to further develop the technique
- use FELs for low density samples (complex molecules)

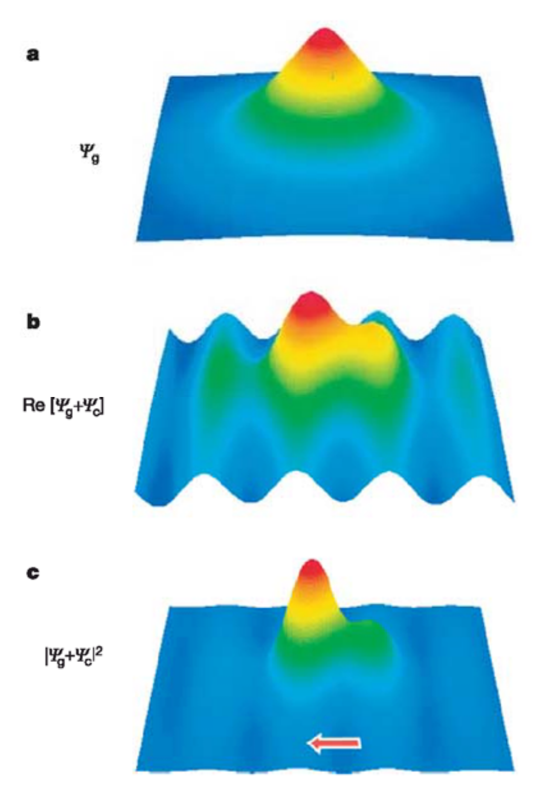
Studying Time-Resolved Molecular Dynamics using Mid-Infrared Strong-Field Ionization

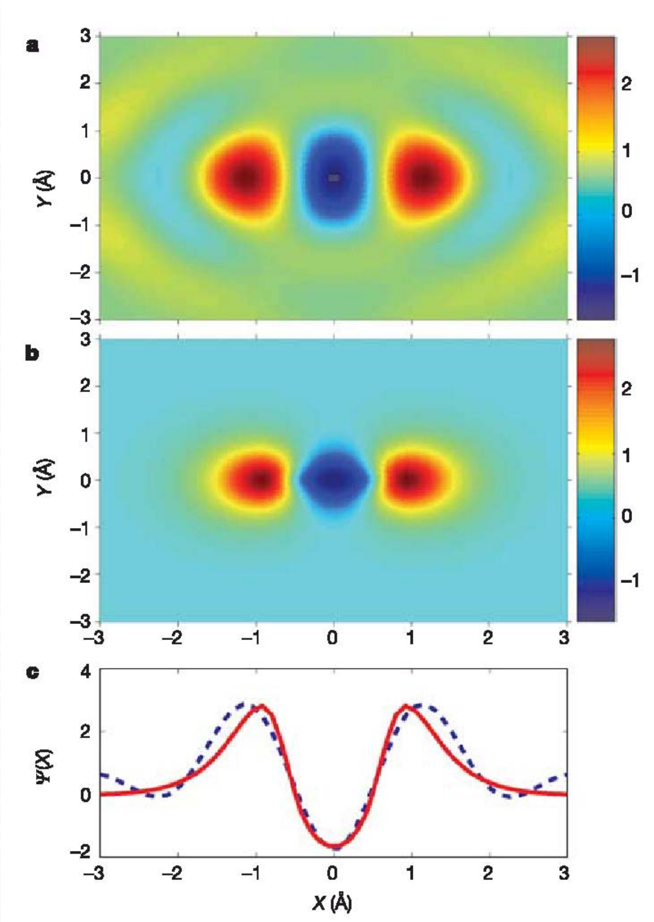
Novel XUV / x-ray sources (HHG and FELs)	**Near-IR / Mid-IR strong field ionization**
Electron dynamics *Example:* *Attosecond time-resolved pump-probe spectroscopy*	*Example:* *Observations of the breakdown of the single-active electron approximation in ATI*
Nuclear dynamics *Example:* *Molecular frame XUV/X-ray photo-emission*	*Example:* *Strong field photoelectron holography*

Recollision electrons can probe wave functions

$$\mathbf{d}(\omega;\theta) = <\psi(\mathbf{r};\theta)|\mathbf{r}|\exp[ik(\omega)x]>$$

Experimentally determined N_2 ground state orbitals

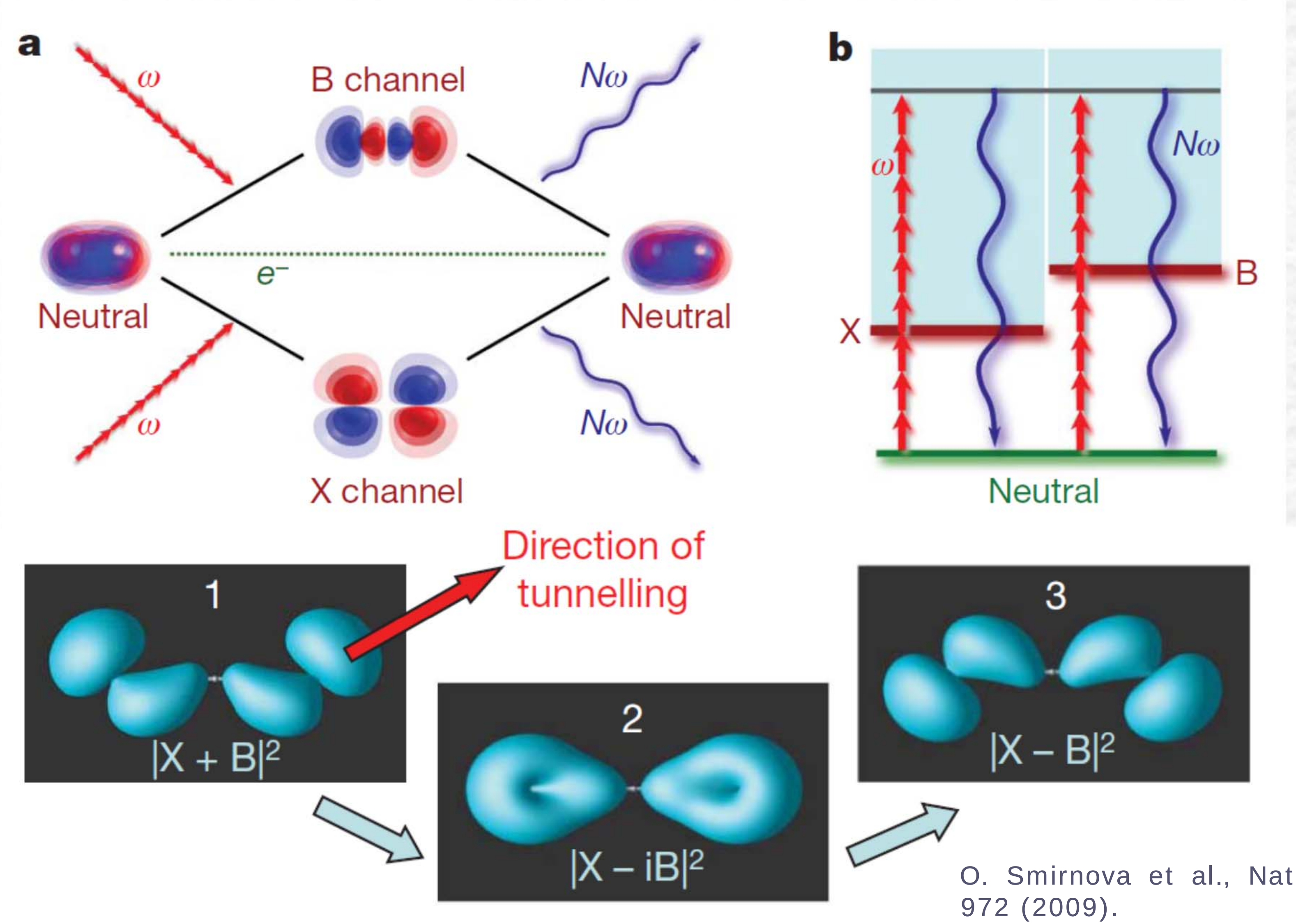




The oscillating dipole that radiates the harmonics is formed from the overlap of the ground and continuum state wavefunctions

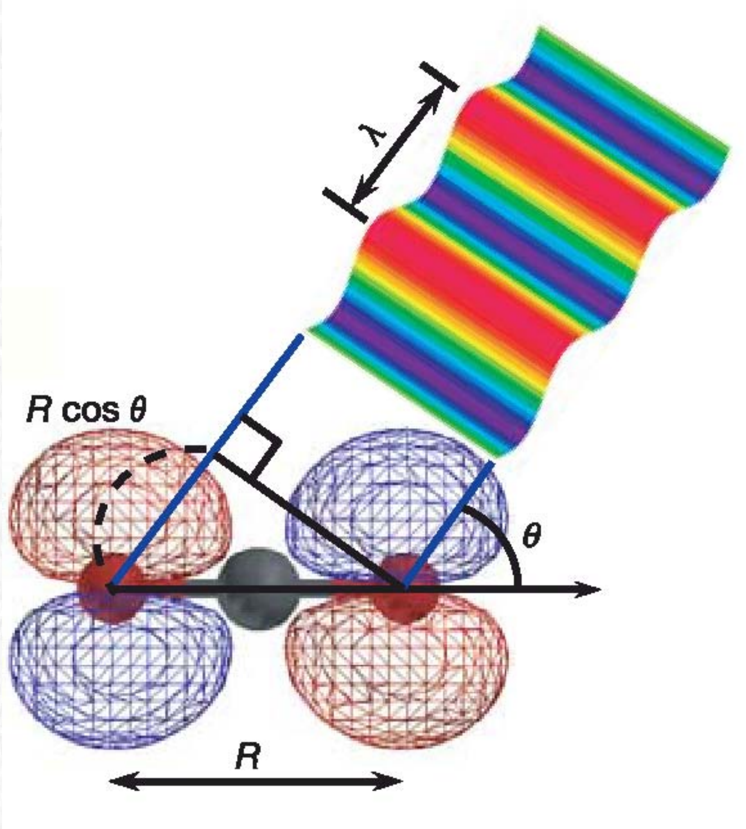
D.M. Villeneuve et al., Nature 432, 867 (2004).

Recollision electrons can probe electron dynamics

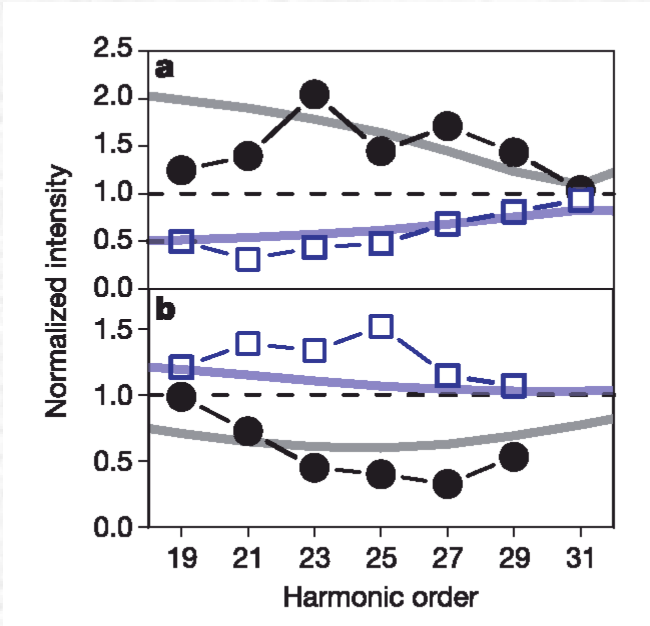


O. Smirnova et al., Nature 460, 972 (2009).

Recollision electrons can probe molecular structure



Diffraction of the recollision electron in the molecular frame shows up in the harmonic yield versus alignment angle.



Attractive: the structural information shows up via diffraction, which relaxes the requirements on the availability of spectroscopic knowledge

H. Sakai etal., Nature 435, 470 (2005).

Recollision electrons can probe molecular structure

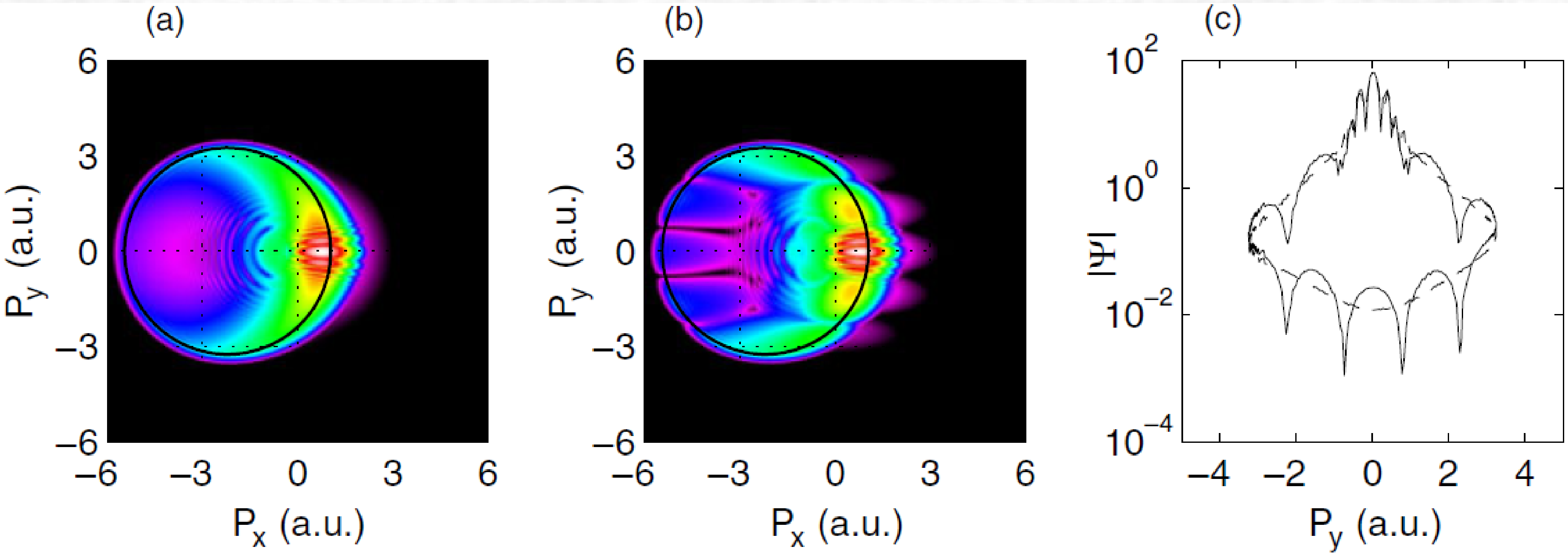
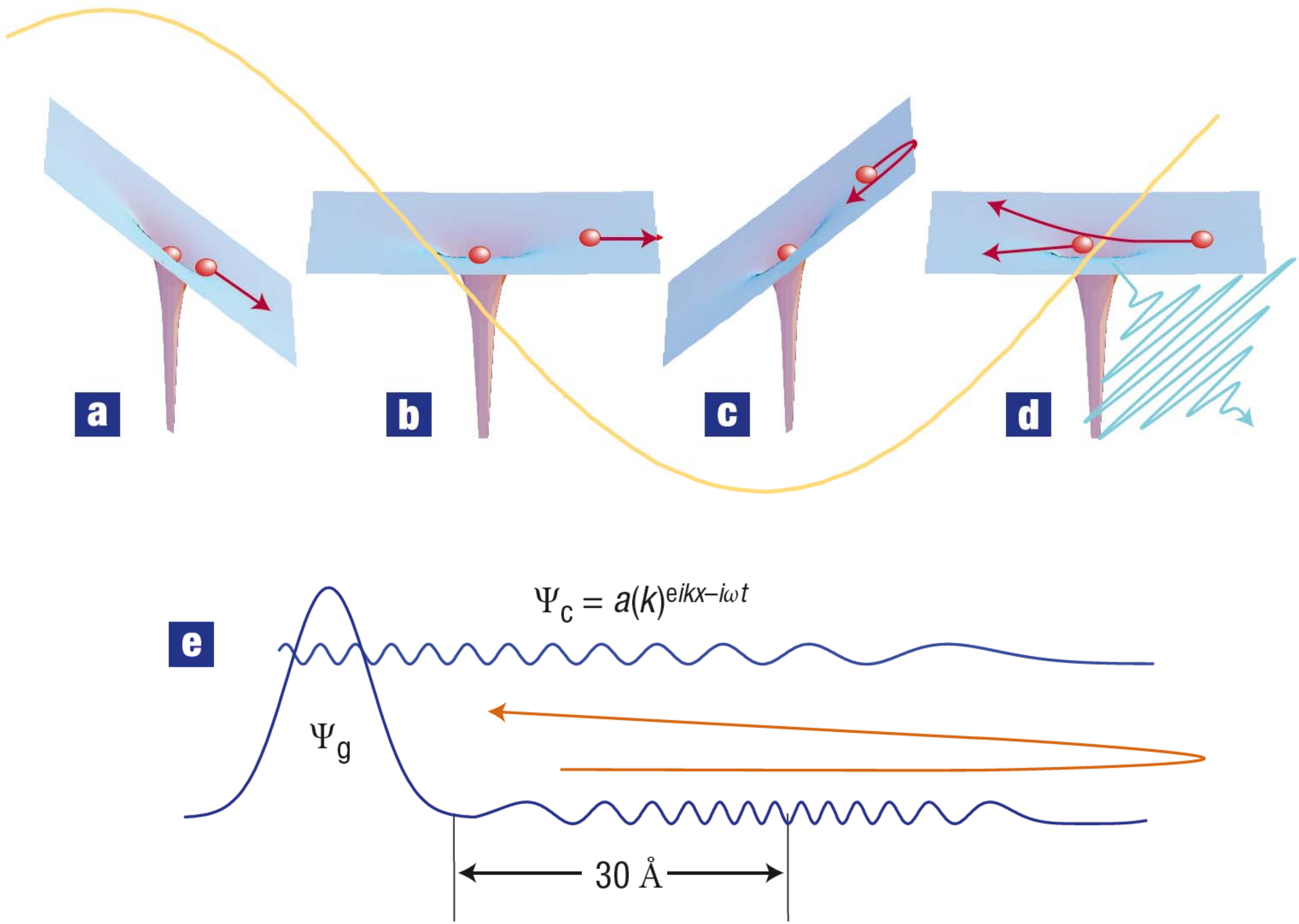


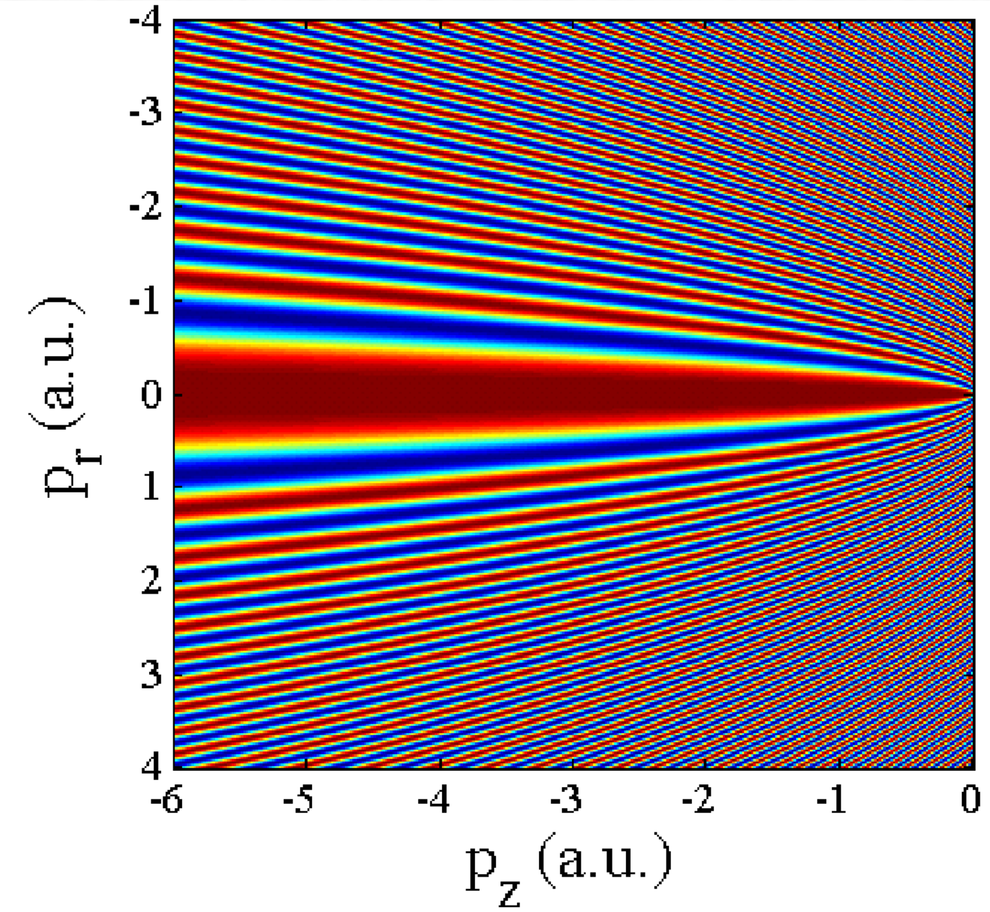
Figure 2. Recollision-induced diffraction for a single phase of birth. (a) Reference signal $|\Psi(v_x, v_y)|$ for a model atom, each new colour corresponds to the next order of magnitude; (b) $|\Psi(v_x, v_y)|$ for a model diatomic molecule; (c) circular cuts for the atom (dashed) and the molecule (solid).

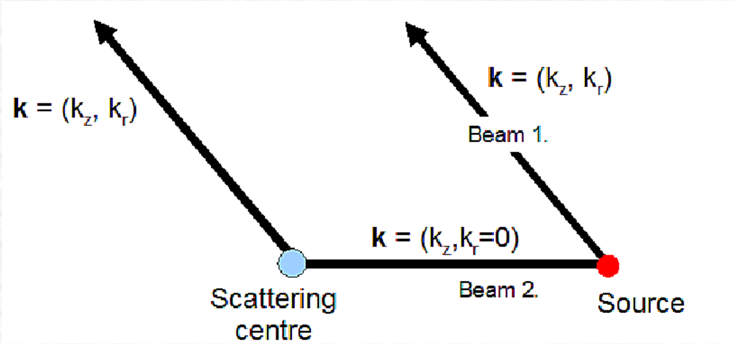
M. Spanner et al., J. Phys B 37, L243 (2004)



P. Corkum and F. Krausz, Nature Physics 3, 381 (2007)

Ionization of metastable Xe atoms using the FELICE mid-infrared free electron laser

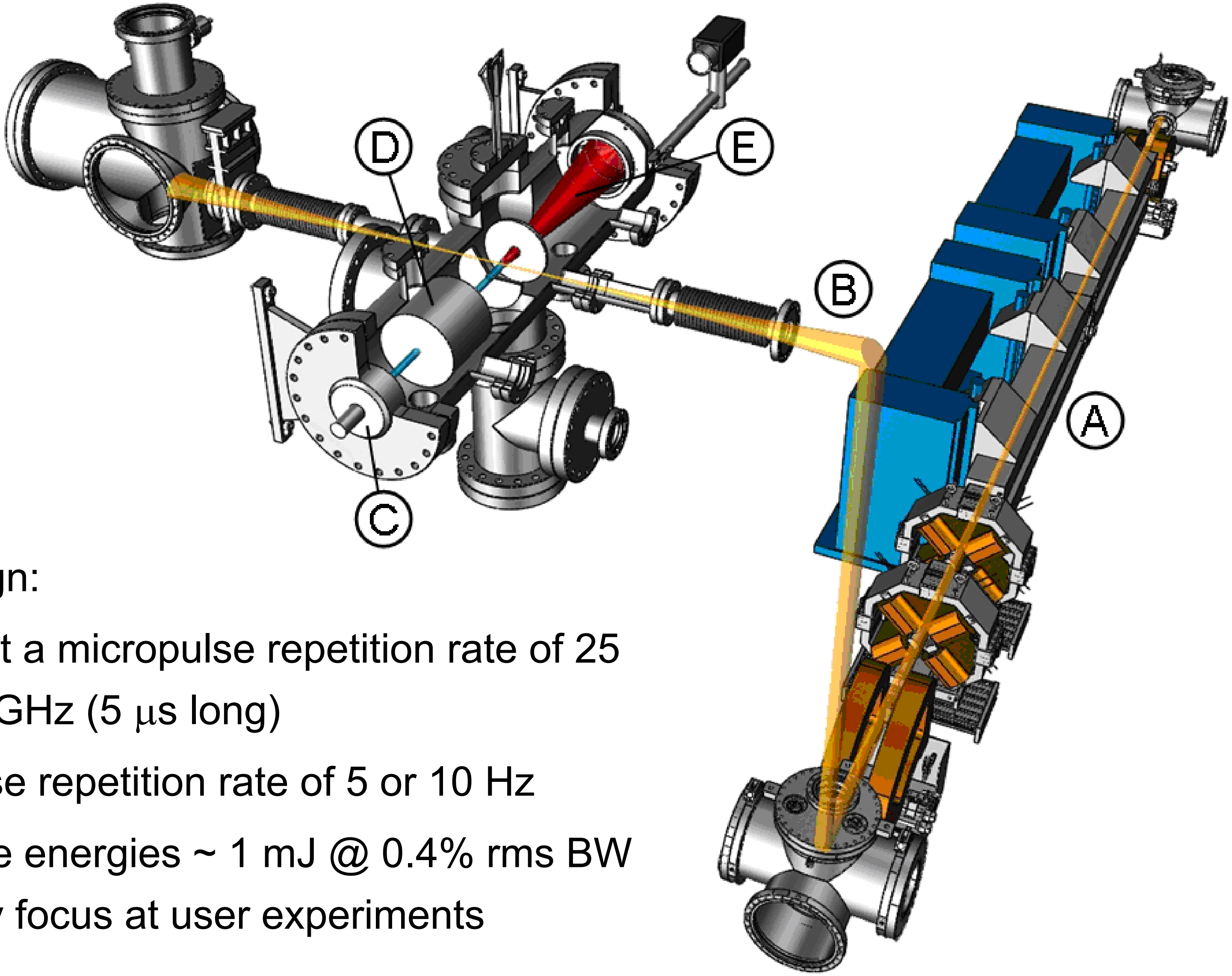




Tunnel ionization produces a source that emits a reference and signal wave

But: in this simple description there is no Coulomb potential and no laser field → is it realistic???

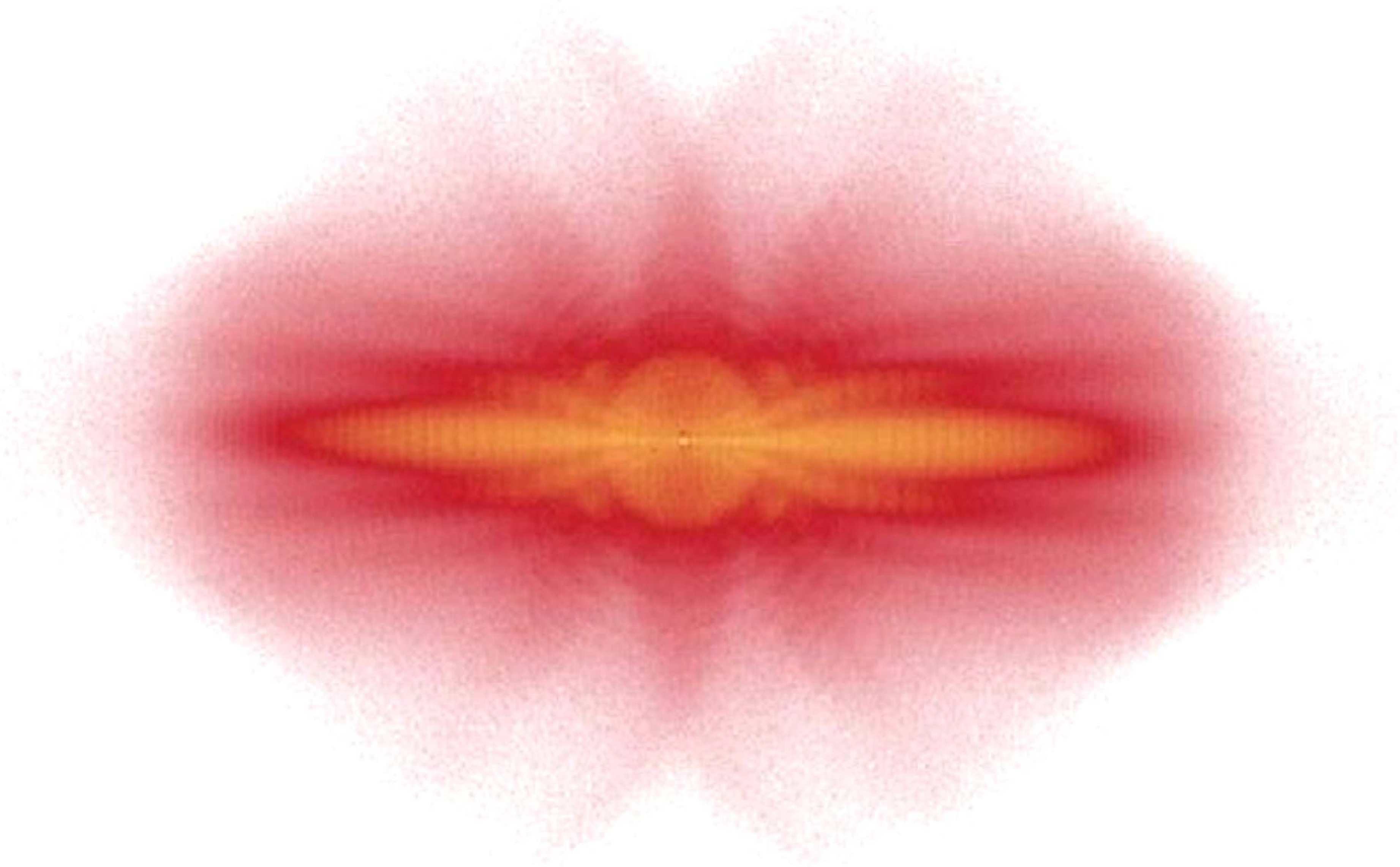
Ionization of metastable Xe atoms using the FELICE mid-infrared free electron laser



FELICE design:

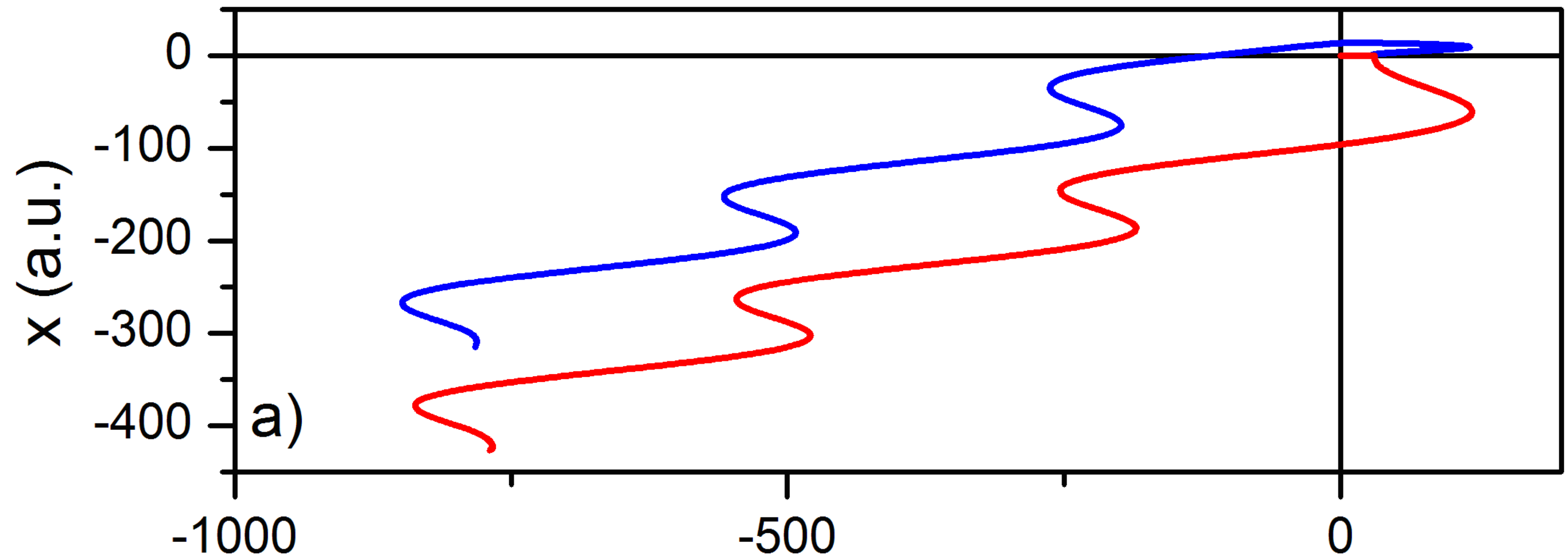
- 4-40 μm at a micropulse repetition rate of 25 MHz or 1 GHz (5 μs long)
- macropulse repetition rate of 5 or 10 Hz
- micropulse energies ~ 1 mJ @ 0.4% rms BW
- secondary focus at user experiments

Xenon 6s at 7μm



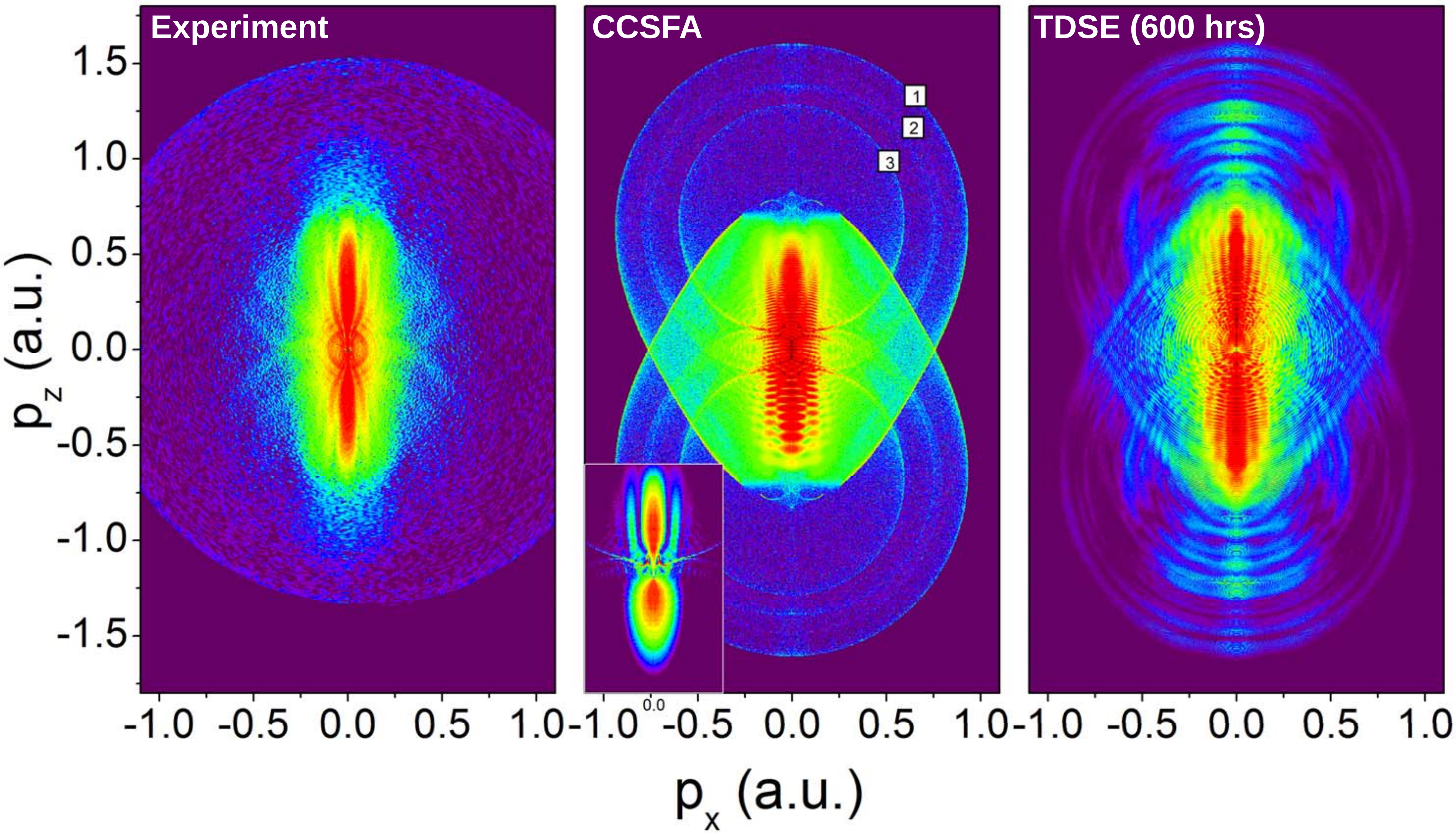
Y. Huismans, M.J.J. Vrakking, et al., Science 331, 61 (2011)

Strong-field ionization of Xe(6s) using 7 μm radiation



Y. Huismans, M.J.J. Vrakking, et al., Science 331, 61 (2011)

Compare with CCSFA and with TDSE calculation of ionization of Xe(6s) using 7 μm radiation



Y. Huismans, M.J.J. Vrakking, et al., Science 331, 61 (2011)

More detailed understanding from a semi-analytical theory

$$\Delta\phi = \phi_{signal} - \phi_{ref} = -\frac{1}{2}\int_{t_0^{signal}}^{t_C} v_z^2 d\tau + \frac{1}{2}\int_{t_0^{ref}}^{t_C} v_z^2 d\tau - \boxed{\frac{1}{2} p_r^2 \left(t_C - t_0^{ref}\right)} + IP\Delta t_0 + \Delta S^{\mathrm{Im}}$$

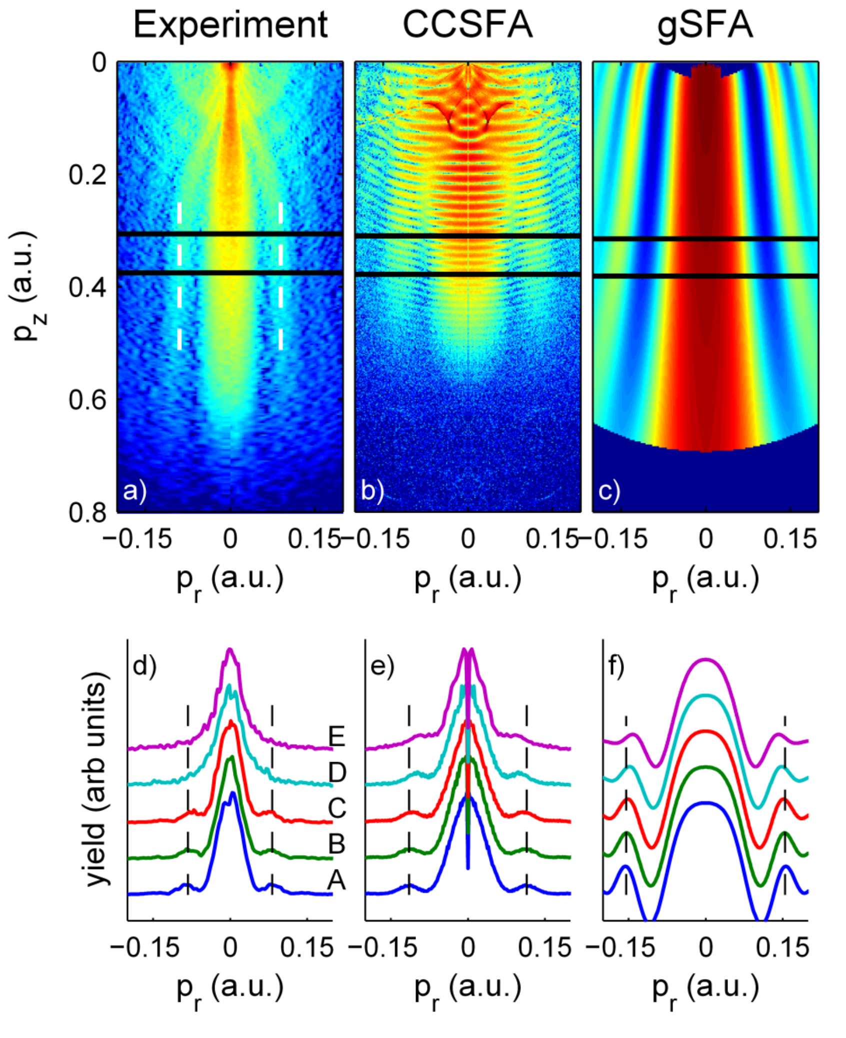
Dominant term

So we would predict that the hologram depends predominantly on the difference between the time that the reference wave leaves the atom and the time that the signal wave scatters off the atom

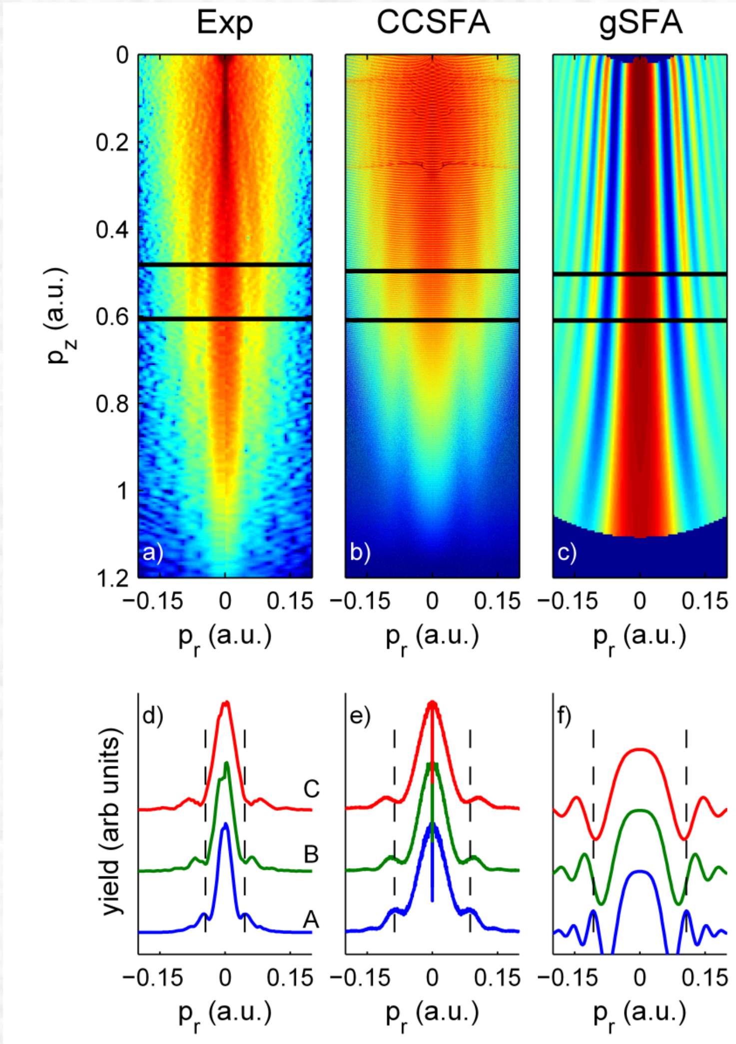
These two times mostly depend on the length of the laser optical cycle (i.e. the laser wavelength) and **not** on the laser intensity and pulse duration

Y. Huismans et al, submitted for publication

More detailed understanding from a semi-analytical theory



A 7x10[11] W/cm[2] – E 1.9x10[11] W/cm[2]



A 16 μm – C 8 μm

Y. Huismans et al, submitted for publication

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- *Various schemes involving strong-field ionization at THz to XUV/X-ray wavelengths*

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Nuclear dynamics *Example:* *Molecular frame XUV/X-ray photo-emission*	*Example:* *Strong field photoelectron holography*	**Lab-based lightsources and FELs**

Collaborators

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Lex van der Meer
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