HHG spectroscopy

Caterina Vozzi

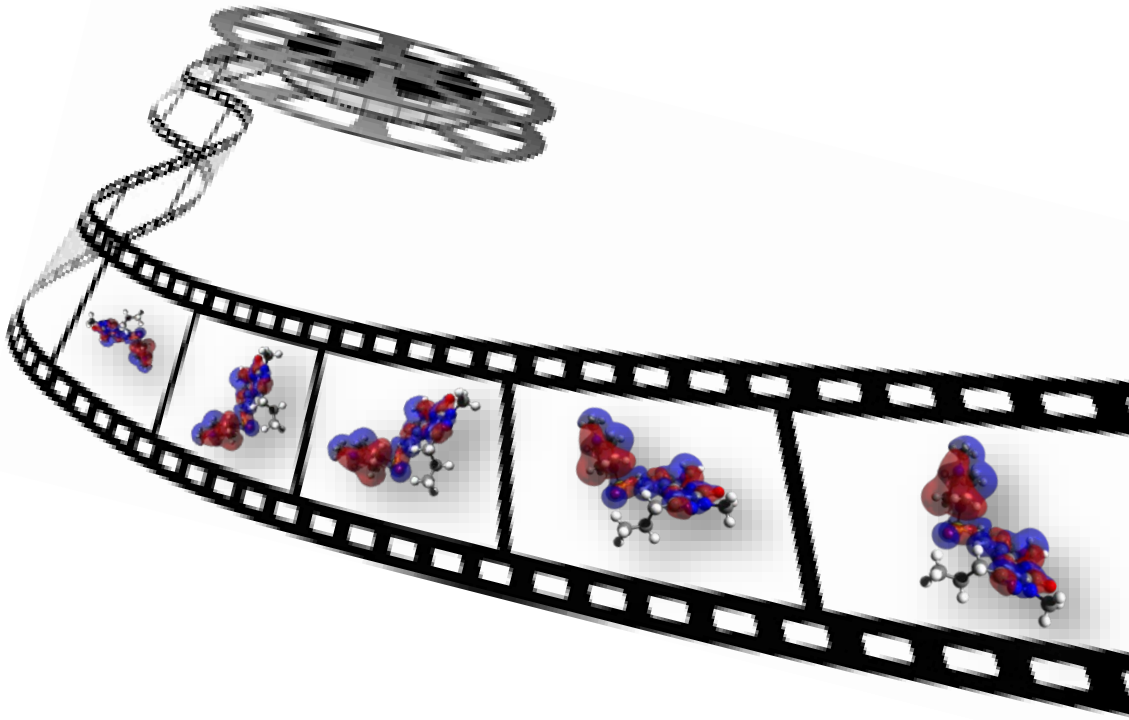
CNR- Istituto di Fotonica e Nanotecnologie

& Politecnico di Milano

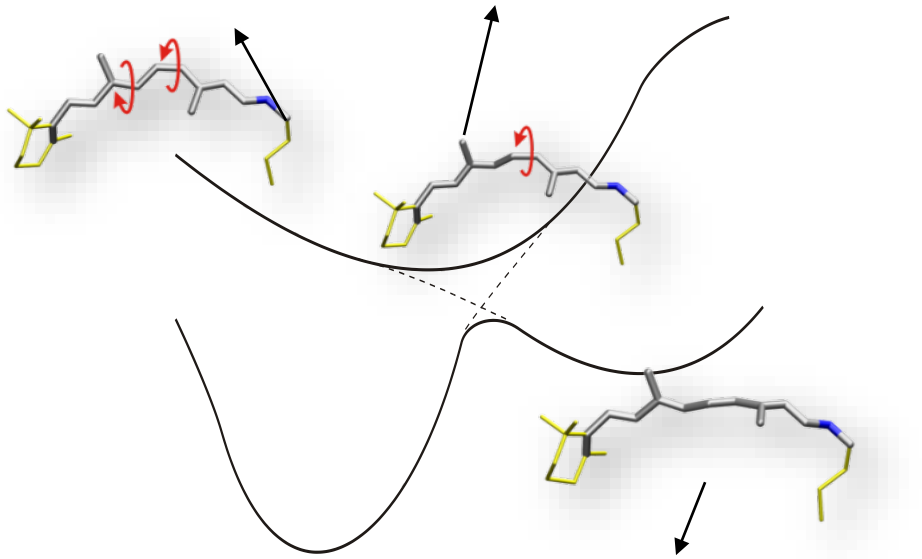
Motivation

Shooting the "molecular movie":

study of the femtosecond and attosecond dynamics of the outermost electronic structure by high order harmonic spectroscopy



Motivation



Use HHG spectroscopy and attosecond science for imaging structural changes in molecules

- direct access to excited states
- visualization of conical intersections
- precursor of coherent control
- benchmark for quantum chemistry calculation

Outline

(1) HHG spectroscopy

(2) Alignment of molecules with laser pulses

(3) Molecular orbital tomography

(4) State of the art in HHG tomography

1. High-order harmonic generation: a strong-field laser-driven process

P. Corkum, *Phys. Rev. Lett*. **71**, 1994 (1993).
M. Lewenstein et al., *Phys. Rev. A* **49**, 2117 (1994).
F. Krausz, M. Ivanov, *Rev. Mod. Phys.* **81**, 163 (2009).

Strong-optical-field phenomena

Optical phenomena are said in “strong field regime” when the electric-field component of light becomes comparable to the atomic Coulomb field

Modern laser technology provides access to this regime:

1 atomic unit of electric field $\mathbf{E_a = 5.14\times10^{11}\ V/m}$

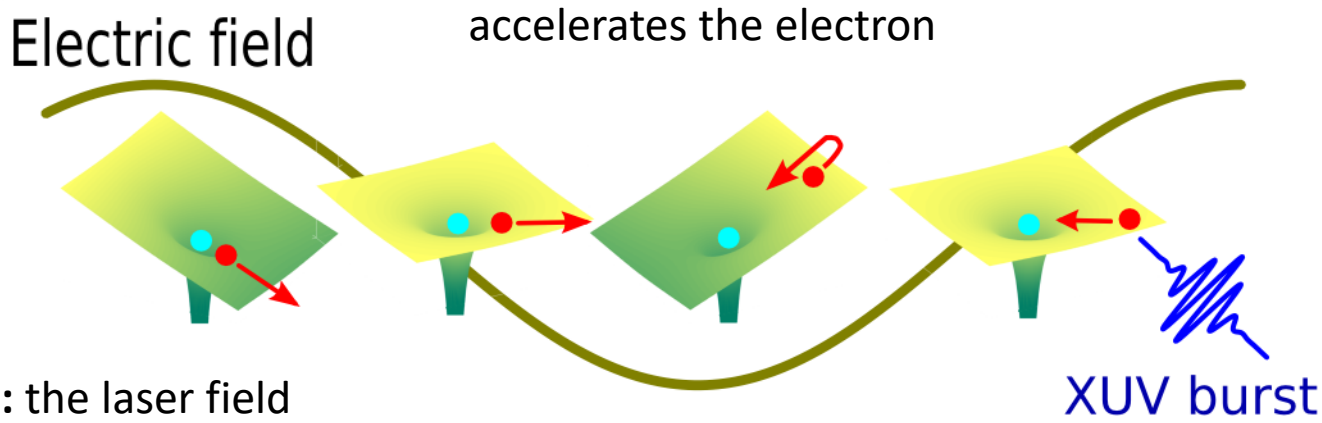
Peak intensity of a laser pulse with energy of 15 mJ, duration of 25 fs, focused to a spot of 30-μm radius: $\mathbf{I = 2\times10^{20}\ W/m^2}$

Peak electric field $\mathbf{E_p = \sqrt{\frac{2I}{c\varepsilon_0}} = 4\times10^{11}\ V/m}$

HHG: three-step model

- K. J. Schafer et al., Short-Pulse High-Intensity Lasers and Applications II (1993)
- P. B. Corkum, Phys. Rev. Lett. 71, 1994 (1993)

2: the laser field
accelerates the electron



1: the laser field
ionizes the electron

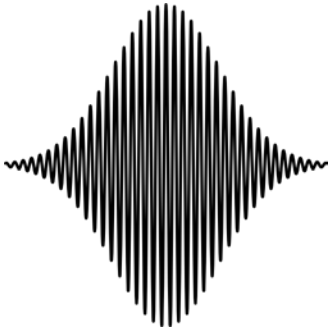
3: the electron collides with the parent ion emitting a burst of XUV-soft X light

- XUV (eXtreme Ultra Violet) : 10-300 eV
- soft X Rays: 300-3000 eV

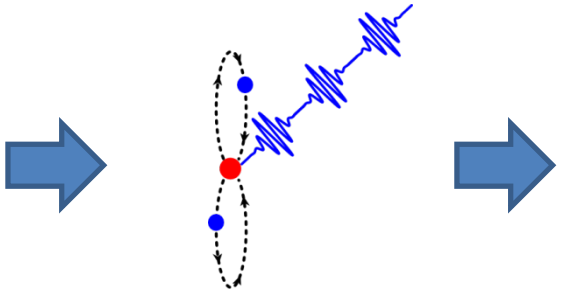
HHG: three-step model

- K. J. Schafer et al., Short-Pulse High-Intensity Lasers and Applications II (1993)
- P. B. Corkum, Phys. Rev. Lett. 71, 1994 (1993)

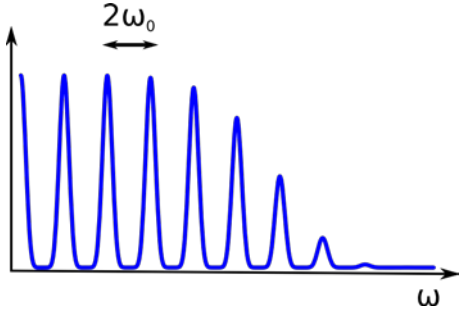
"Long" laser pulse



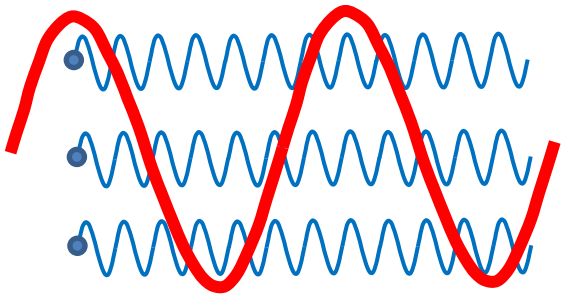
Multiple XUV bursts



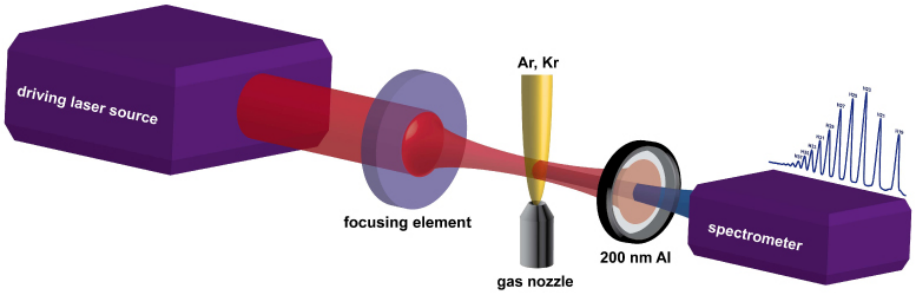
Odd harmonics
in spectral domain (HHG)



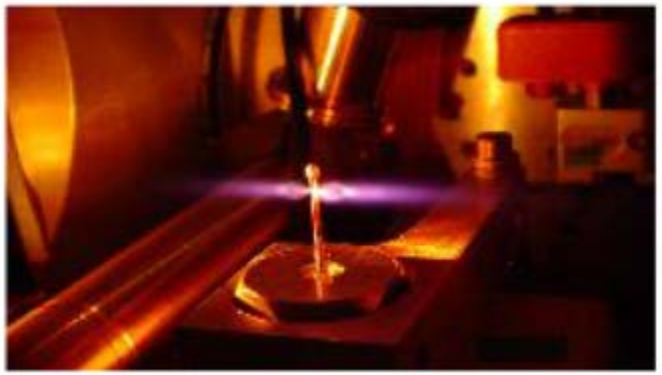
HHG is a coherent process:
all the atoms in the macroscopic medium are driven by the same laser field



Typical HHG spectra

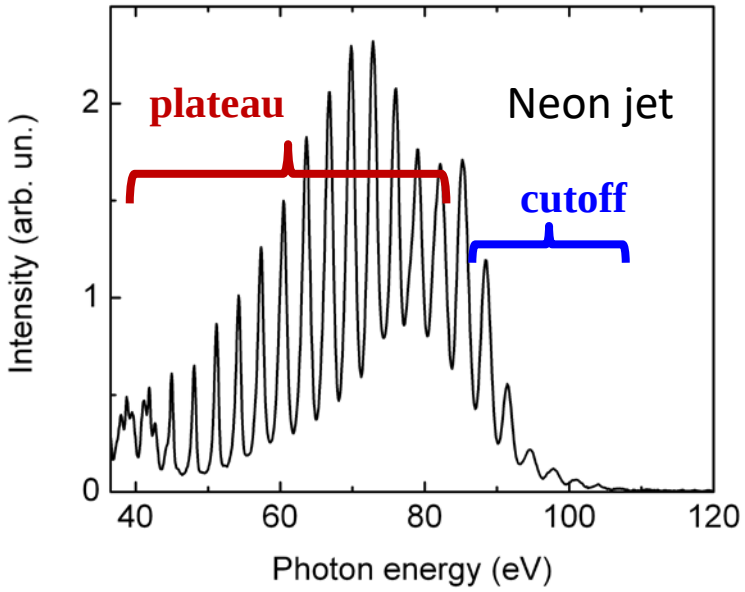


from: S. Hädrich et al., *Opt. Express* **18,** 20242 (2010)



from: J. Seres et al., *Photonics* **2**, 104 (2015)

Acquired in our laboratory (2016)



HHG spectra are typically produced in gas jets/cells inside vacuum chambers

Spectral analysis performed with grazing-incidence XUV spectrometers

The HHG spectra present a plateau and a cutoff region

HHG as a probe of matter

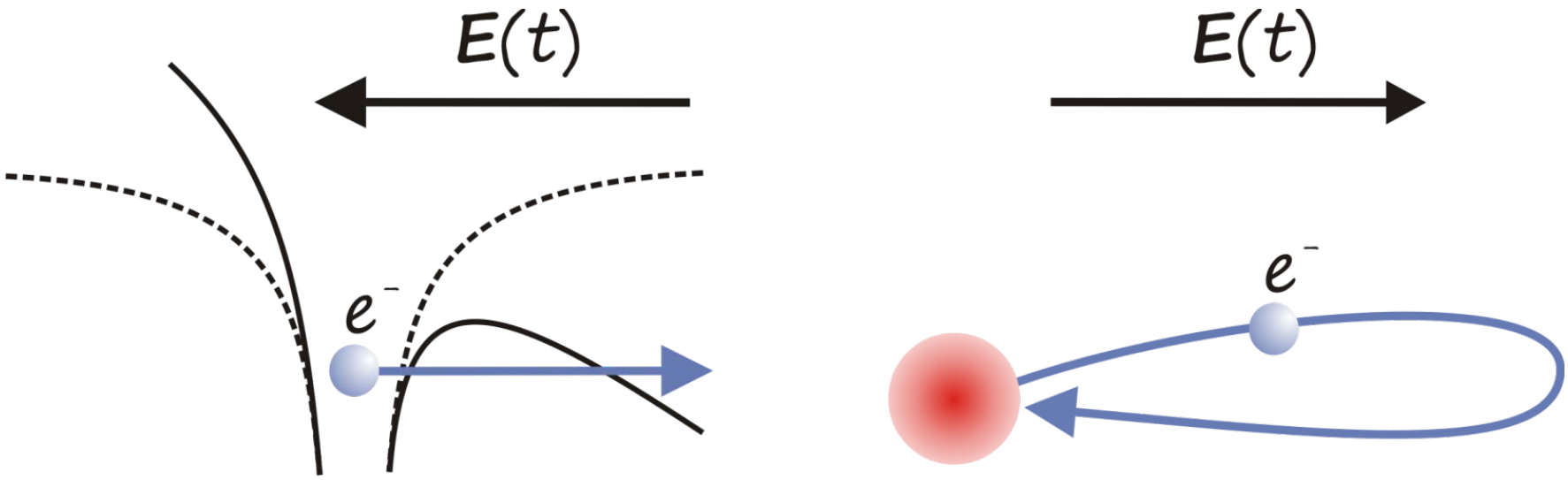
The electron wavepacket responsible for HHG collides with the parent ion (3rd step in HHG)

It "probes" its own parent ion (self probing)

Emitted harmonic radiation carries information about the probed atom/molecule with **extreme spatial (~Å) and temporal (< 1 fs) resolution**

A quantitative model of HHG is required for the extraction of the sought information

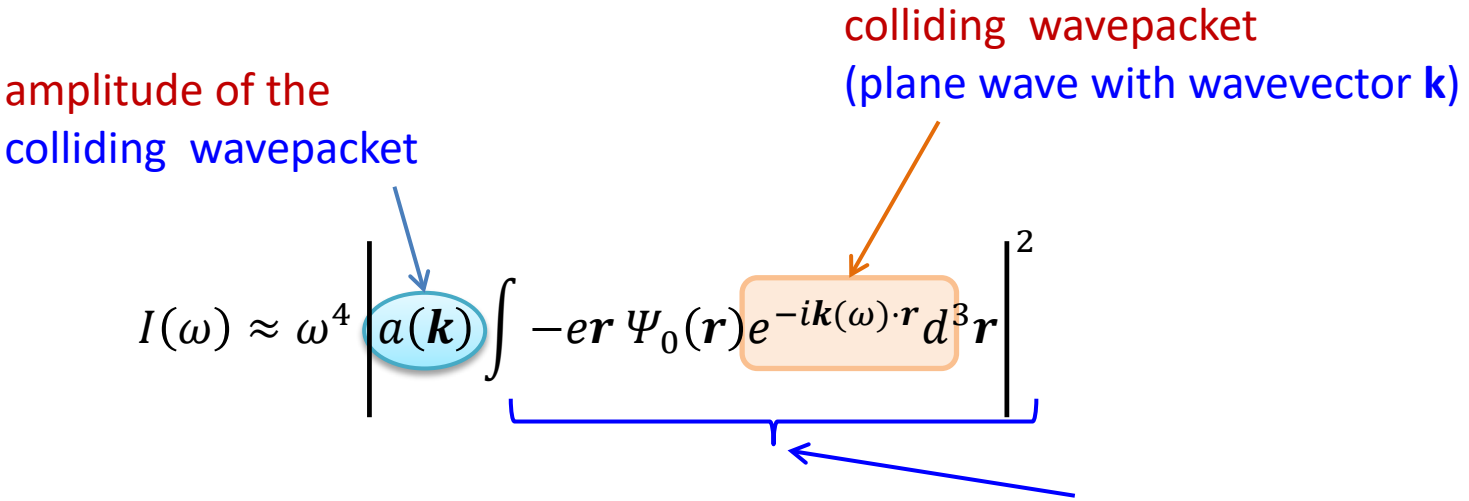
HHG as an interferometer



tunnel ionization → beam splitter
electron wave-packet motion → delay line
re-collision → interference

Structural information in HHG spectra

The spectral intensity of harmonic radiation can be approximated as:



The wavevector **k** of the colliding electron is related to the emitted photon energy $\hbar\omega$ owing to **energy conservation**

Atomic vs. molecular targets

Atoms are centrosymmetric systems

HHG readily provides information on the “atomic structure”

On the contrary, molecules are anisotropic and randomly oriented in nature

HHG may provide structural information only if all the molecules are aligned along a given direction

Molecular alignment is essential for HHG-based spectroscopy and imaging of molecules

2. Alignment of molecules with laser pulses

H. Stapelfeldt, T. Seideman, *Rev. Mod. Phys.* **75**, 543 (2003).
L. D. Landau, E. M. Lifshitz, *Mechanics* (Pergamon Press, Oxford 1976).
H. W. Kroto, *Molecular rotation spectra* (Dover Phoenix Editions, Mineola NY, 2003)

Molecular alignment

By controlling the alignment/orientation of molecules one can investigate:

- How chemical reactions occur
- How molecular bonds dissociate
- How molecular photoionization depends on light polarization
- Which are shape and properties of molecular orbitals

How to do that: by aligning molecules with an electric field E

Intense laser pulses align molecules impulsively

How it works (a classical model)

1. The laser pulse induces a transient dipole in the molecule:

polarizability tensor

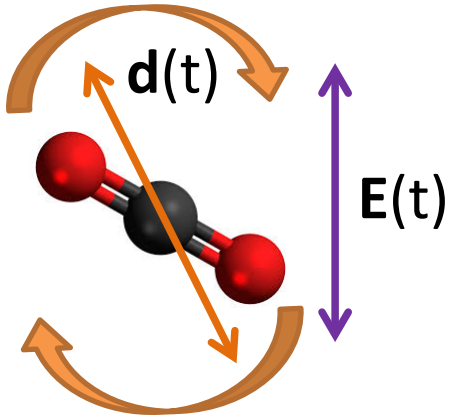
electric field (i=x,y,z)

hyperpolarizability

$$d_i(t) = d_{0i} + \sum_k \alpha_{ik} E_k(t) + \sum_{j,k} \beta_{ijk} E_j(t) E_k(t) + \cdots$$

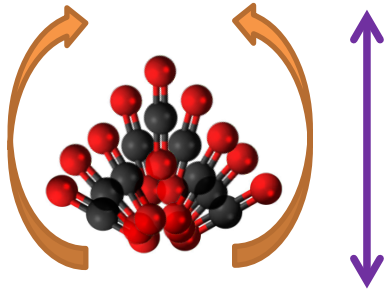
permanent dipole

induced dipole



2. A torque $\boldsymbol{\tau} = \mathbf{d} \times \mathbf{E}$ force rotation of molecules towards the direction of the laser polarization.

3. A delayed alignment appears along the **E** direction.



Quantum model of alignment

Interaction energy U_{int} of a molecule in the laser electric field **E**(t):

$$U_{int}(t) = -\left(\sum_i d_i E_i + \frac{1}{2}\sum_{i,k} \alpha_{ik} E_i E_k + \cdots\right)$$

Rotational Schrödinger equation (RSE):

$$\left[\hat{H}_{rot} + U_{int}(t)\right]|\Psi\rangle = i\hbar \frac{\partial|\Psi\rangle}{\partial t}$$

where, **for linear rigid molecules** with rotational constant *B*:

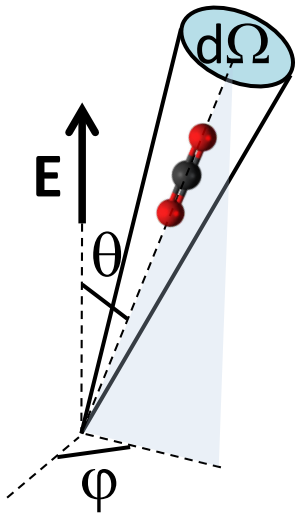
$$\hat{H}_{rot} = -B\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$$

and $f(\theta,\varphi,t) = |\Psi|^2$ is the angular distribution of molecules.

Measuring the alignment degree

Angular distribution $f(\theta,\varphi)$

$f(\theta,\varphi)d\Omega$: probability for a molecule inside the solid angle $d\Omega$ located around θ and φ

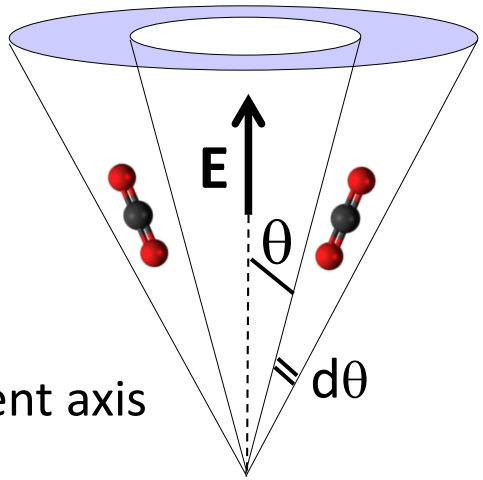


Population $N(\theta)$

$N(\theta)d\theta$: probability for a molecule between θ and $\theta+d\theta$ ➡ $N(\theta) = \sin\theta \int_0^{2\pi} f(\theta,\varphi)d\varphi$

Alignment factor $\langle\cos^2(\theta)\rangle$

$$\langle\cos^2(\theta)\rangle = \int_0^{\pi} N(\theta)\cos^2(\theta)d\theta$$



$\langle\cos^2(\theta)\rangle$ =
- 0 all the molecules are perpendicular to alignment axis
- 1/3 for random molecular alignment
- 1 all the molecules parallel to the alignment axis

However…

- Molecules are often complex (not linear, not rigid etc.)

Solving the RSE might be onerous

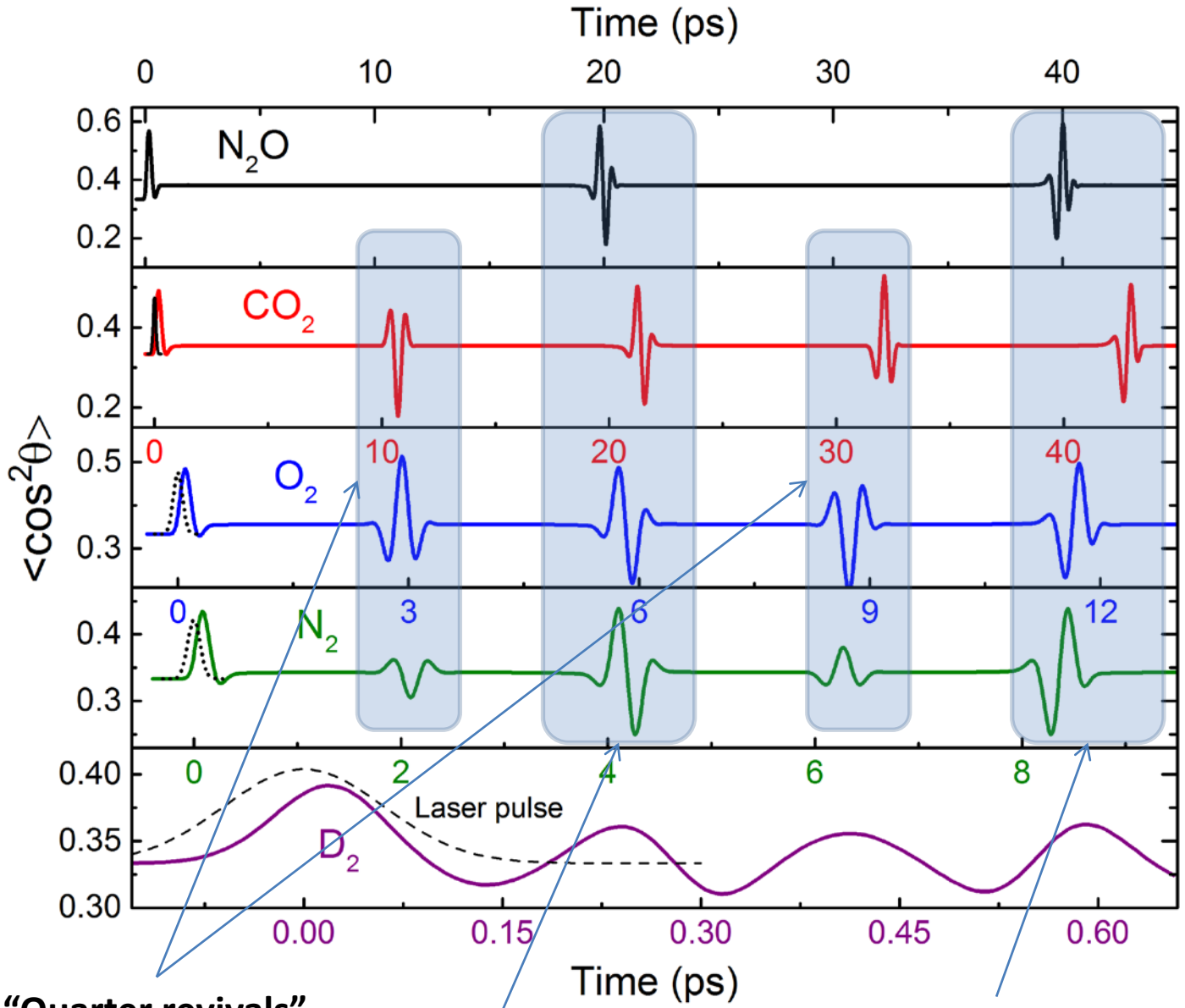
- Nuclear spin isomers and molecular isotopes are present

Selection rules for rotational transitions to be considered

- Molecular gases are complex systems (“mixed states”)

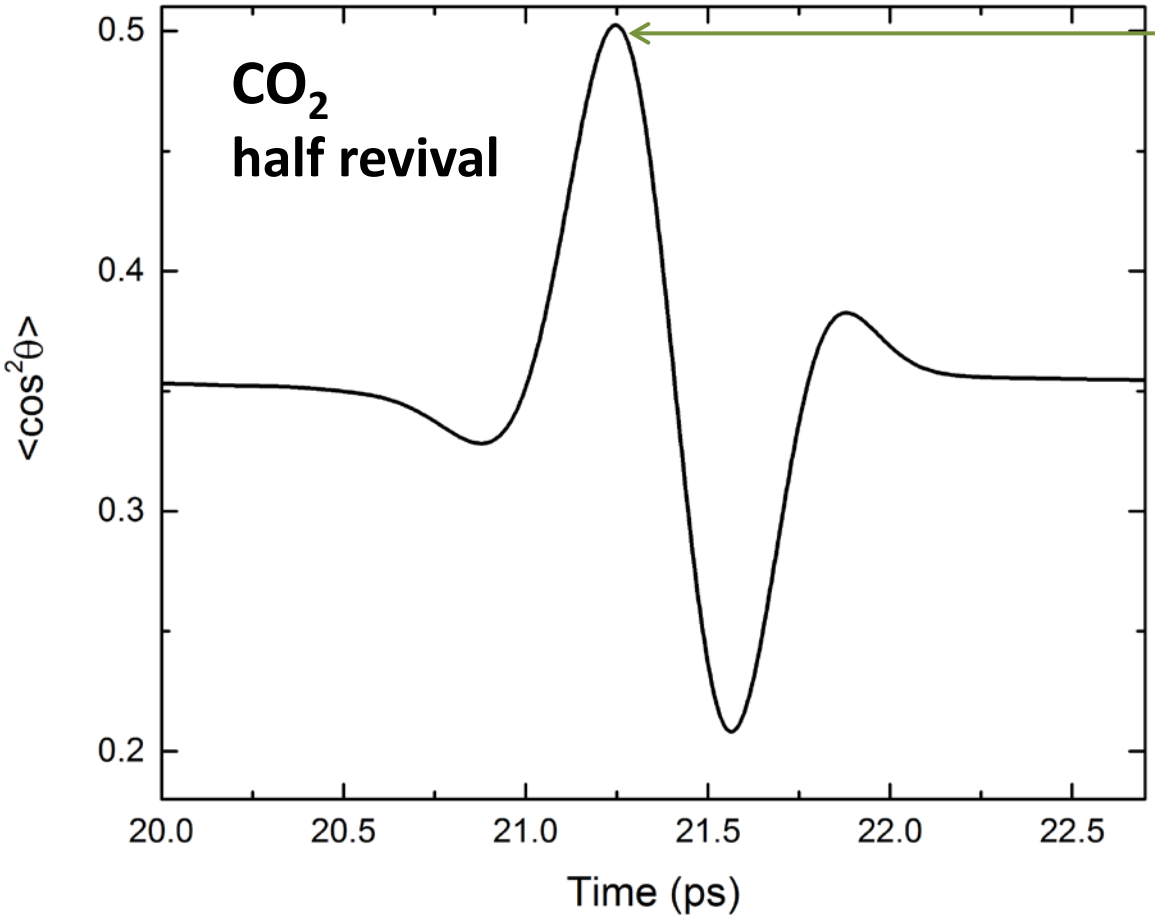
Density matrix formalism is required

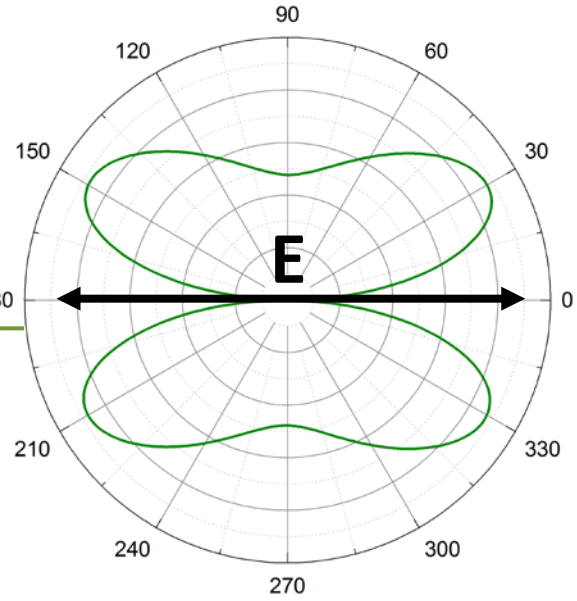
Rotational revivals in "real" gases



How molecules are distributed in space?

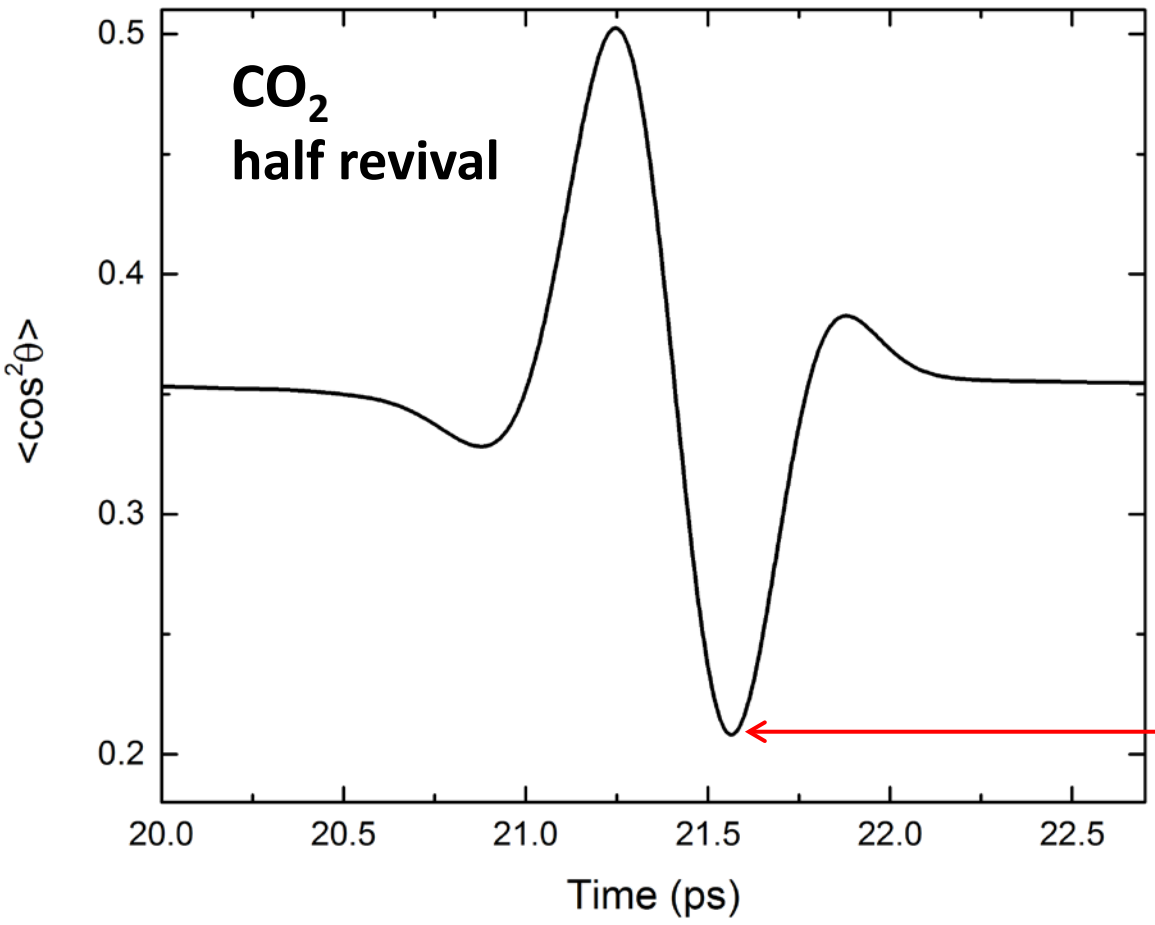
At **alignment** molecules are mostly aligned at **~30°** ! ***Perfect alignment is not possible.***

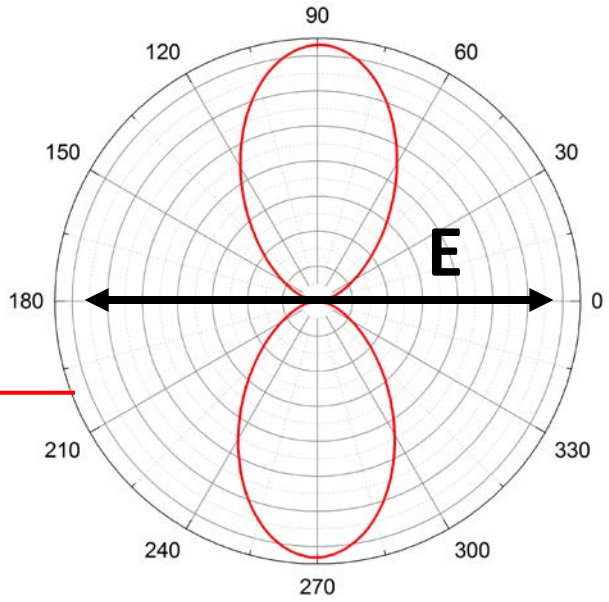




How molecules are distributed in space?

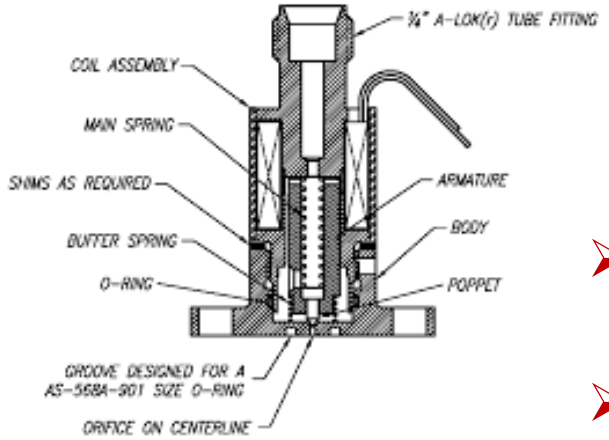
At **antialignment** molecules are orthogonal
to the alignment laser polarization



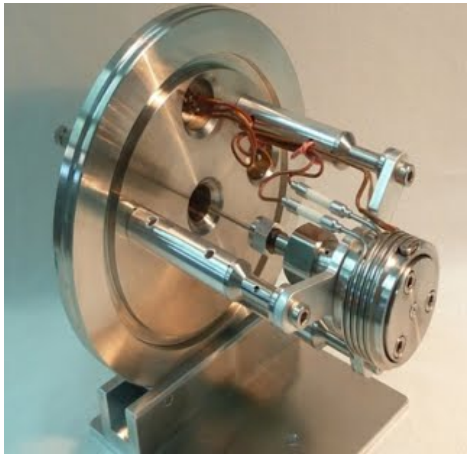


Practical issues in molecular alignment

Standard gas valve



Even-Lavie valve



Impulsive molecular alignment is effective in **cold gases** (50-100 K)

- Supersonic expansion of gas jets in vacuum is exploited for gas cooling
- Supersonic jets are collimated (high gas density)
- Performances strongly depend on valve temperature, gas type, stagnation pressure, nozzle shape etc.

Issues

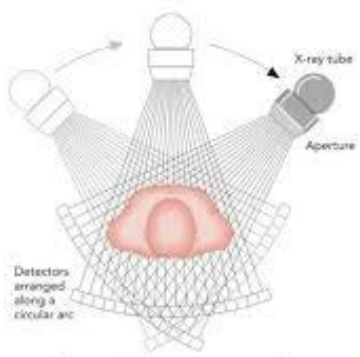
- High stagnation pressure or low temperatures are detrimental since **clustering** appears
- Current technology limited to kHz rep. rate

3. Molecular orbital tomography

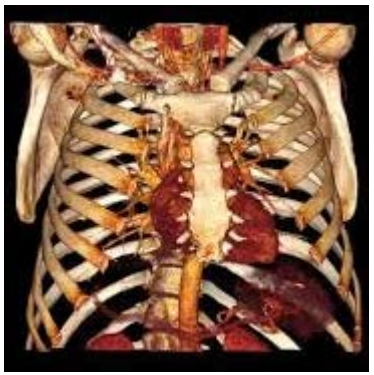
J. Itatani et al., *Nature* **432**, 867 (2004).
C. Vozzi et al., *Nature Phys.* **7**, 822 (2011).
J. B. Bertrand et al., *Nature Phys.* **9**, 174 (2013).

Molecular orbital tomography

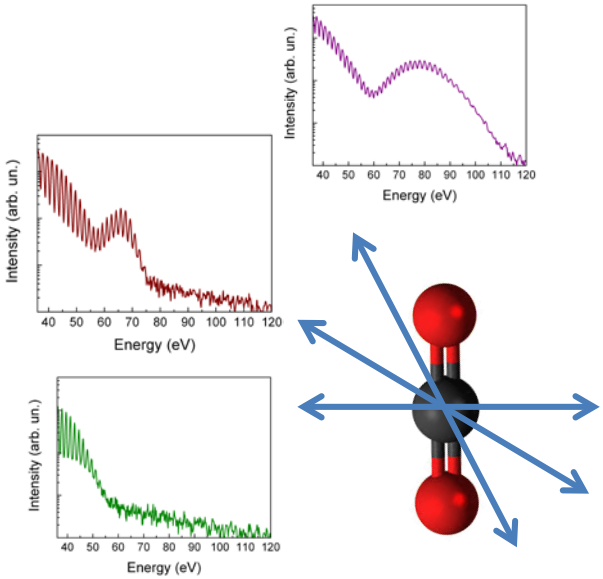
Computed tomography of a human being



Some complex algorithm



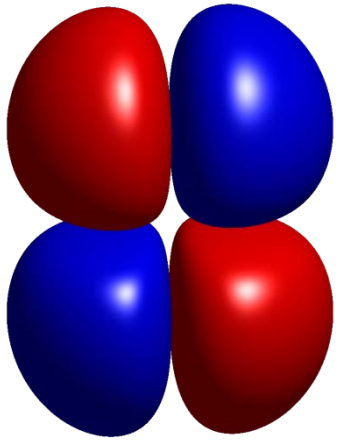
IDEA: tomography of a molecule with HHG



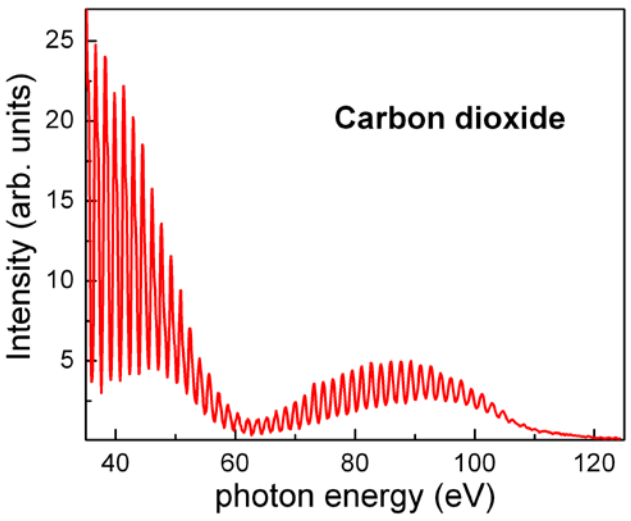
Some complex algorithm

Laser pulses at different polarization directions

Molecular orbital



HHG and molecular tomography



Orbital structure and symmetry are encoded in the HHG spectrum *I(ω).*

I(ω) depends on the recolliding wavepacket and the molecular HOMO $\Psi_0(\boldsymbol{r})$:

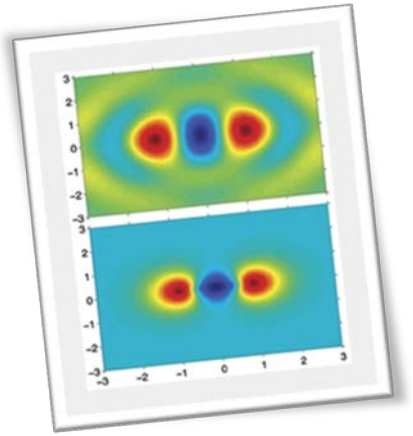
$$I(\omega) \propto \omega^4 \left| a(\boldsymbol{k}) \mathcal{F}_{\boldsymbol{k}(\omega)} \{ \boldsymbol{r}\, \Psi_0(\boldsymbol{r}) \} \right|^2$$

which is in practice the spatial Fourier transform of $\boldsymbol{r}\Psi_0$ in the $\boldsymbol{k}$ direction

Tomographic molecular orbital reconstruction:

Spatial Fourier transform of the molecular orbital obtained from HHG spectra acquired in aligned molecular gas

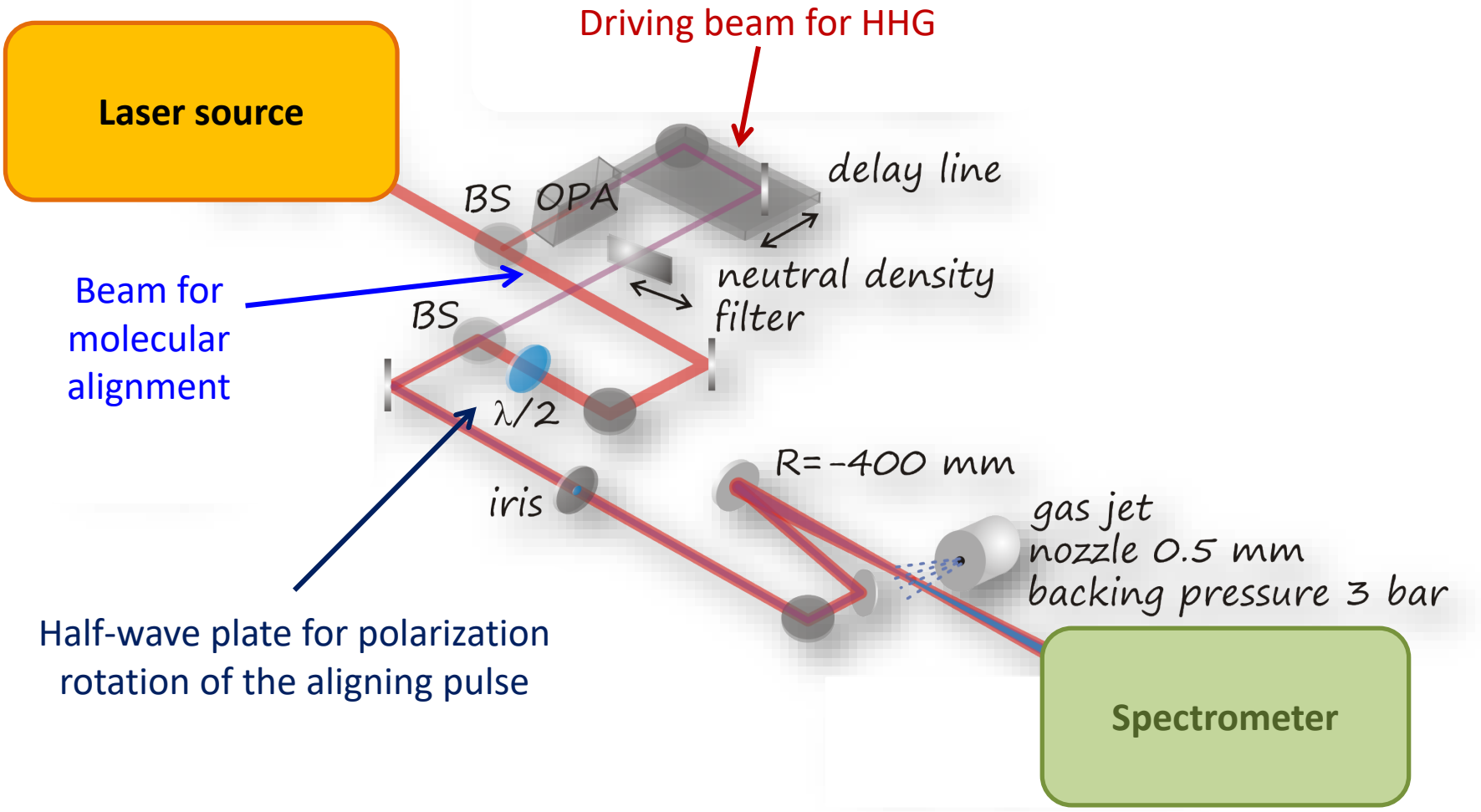
Molecular orbital reconstructed by inverse Fourier transformation



Orbital reconstruction in Nitrogen.

J. Itatani et al., *Nature* **432**, 867 (2004)

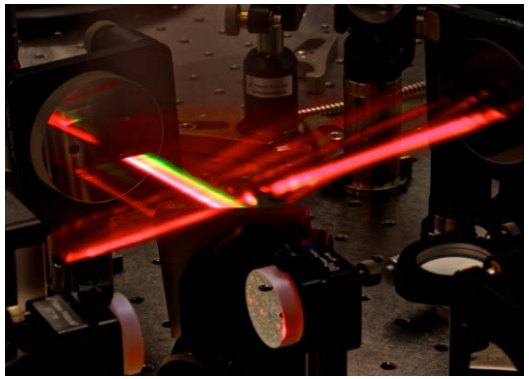
Experimental setup for HHG tomography



An HHG tomography lab

Typical driving laser source (Ti:Sapphire laser):

- ❑ <25 fs pulses
- ❑ 15-mJ energy
- ❑ 1-kHz repetition rate



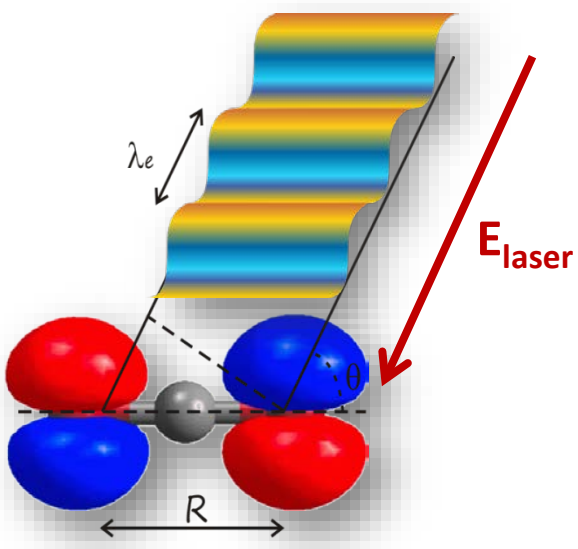
Light pulse manipulation

- ❑ Temporal compression
- ❑ Wavelength down- or up-conversion
- ❑ Multi-color laser pulse combining

HHG beamline:

- ❑ Vacuum chambers hosting:
  - ➢ HHG section with gas jet
  - ➢ Harmonics beam transport to diagnostics
  - ➢ Harmonics polarization analyzer
  - ➢ Grazing-incidence XUV-soft X spectrometer

HHG tomography: basic procedure

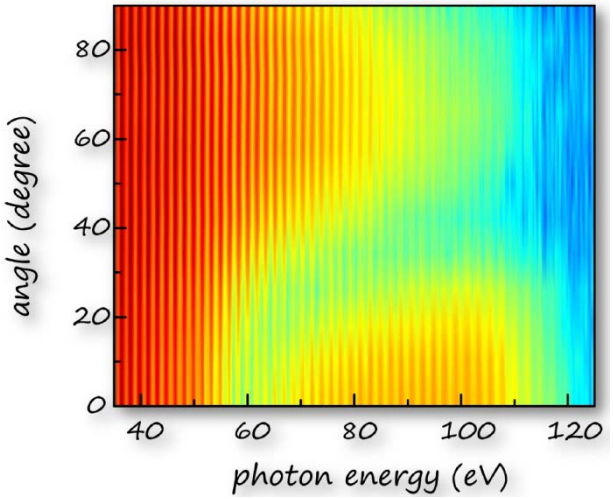


Tomography of the ground state orbital Ψ(r):

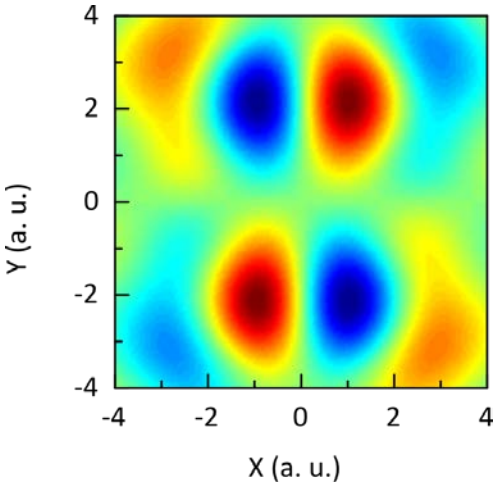
1) align the target molecules (e.g. @half revival)

2) collect HHG spectra $I(\omega,\theta)$ at different angles θ between the molecular axis and the laser E field

3) obtain $\omega^4 \left|a(\boldsymbol{k})\mathcal{F}_{\boldsymbol{k}(\omega)}\{\boldsymbol{r}\,\Psi_0(\boldsymbol{r})\}\right|^2$ from HHG spectra by mapping the optical frequencies ω to the spatial frequencies k



4) make some assumptions on $a(\boldsymbol{k})$, on the phase of $\mathcal{F}_{\boldsymbol{k}}\{\boldsymbol{r}\,\Psi_0(\boldsymbol{r})\}$ and on the orbital symmetry; then inverse transform.



Issues in HHG tomography (1)

The wavepacket amplitude $a(\boldsymbol{k})$ is not know *a priori*

Idea:
the amplitude of the wavepacket weakly depends on the atom/molecule if the ionization potential is similar

Solution:
determine $a(\boldsymbol{k})$ *from the HHG spectra, acquired in the same experimental conditions,* ***in a noble gas with*** I_p ***similar to the molecule's one.***

Issues in HHG tomography (2)

The phase of HHG radiation, hence the phase of $\mathcal{F}_{\boldsymbol{k}}\{r\,\Psi_0(r)\}$, is not know (intensity measurements)

Idea:

the phase may be evaluated using theoretical models or it can be measured somehow

Solutions:

1) calculate *the phase from theoretical $\Psi_0(\boldsymbol{r})$ (useless?)*

2) use recursive algorithms *for finding the best phase (not unique solutions?)*

3) measure *the phase of the HHG radiation with interferometric techniques (very complex)*

Issues in HHG tomography (3)

HHG with long "laser pulses" does not disentangle $\mathcal{F}_{\boldsymbol{k}}\{r\,\Psi_0(r)\}$ from $\mathcal{F}_{-\boldsymbol{k}}\{r\,\Psi_0(r)\}$ *(electron collisions from both opposite sides)*

Idea:

the spatial Fourier transform of symmetric orbitals has peculiar properties

Solutions:

extend the spatial Fourier transform to "negative ***k***" taking into account the orbital symmetry (***but*** it does not work with non-symmetric molecules)

4. State of the art in HHG tomography

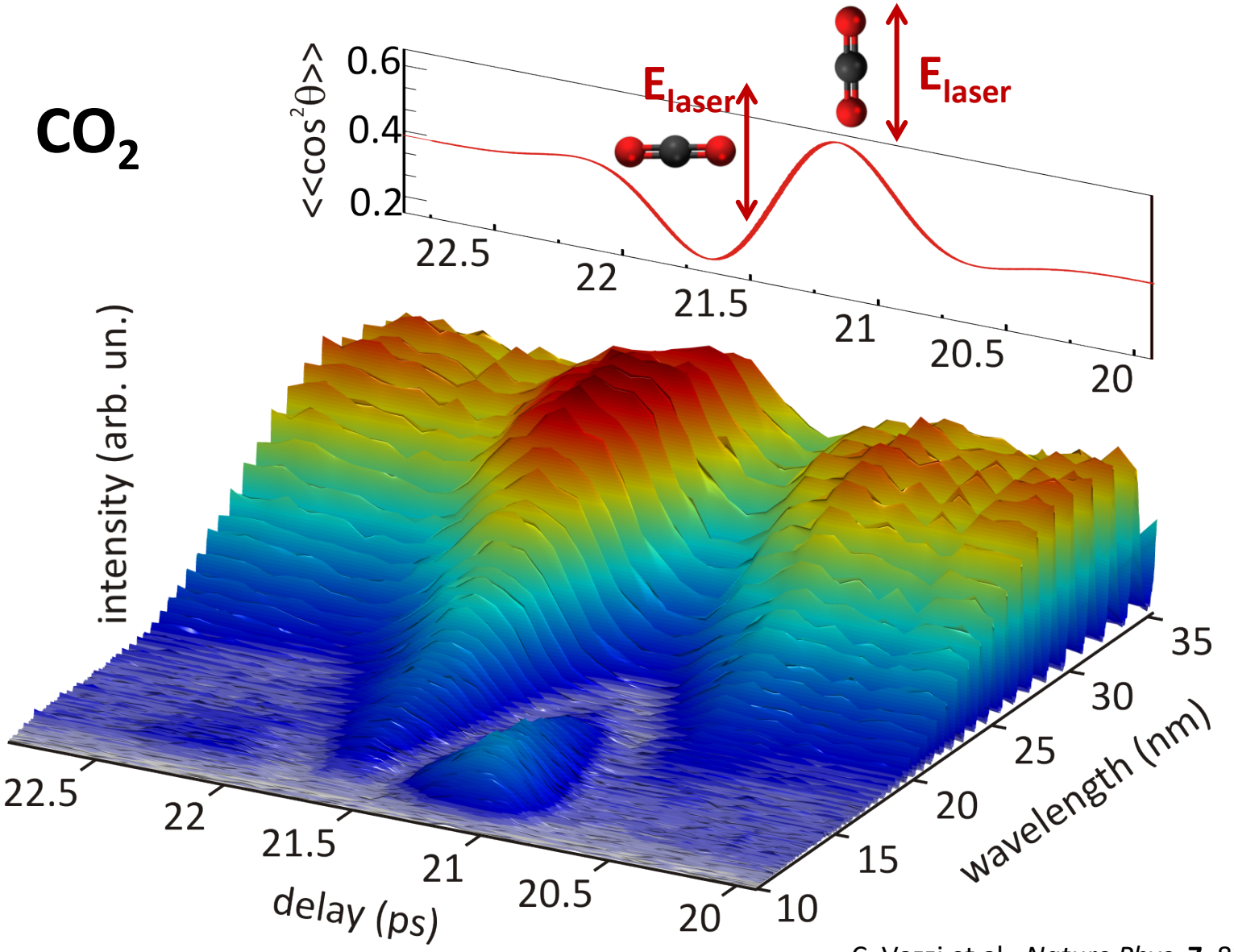
J. Itatani et al., *Nature* **432**, 867 (2004).
C. Vozzi et al., *Nature Phys.* **7**, 822 (2011).
J. B. Bertrand et al., *Nature Phys.* **9**, 174 (2013).

HHG tomography – 2nd generation

Basic HHG tomography requires to record several HHG spectra while fixing molecules aligned at different angles…

New paradigm: take HHG spectra while molecules are moving

HHG tomography – 2nd generation



C. Vozzi et al., *Nature Phys.* **7**, 822 (2011)

Modelling

$$I(\omega,\tau) \propto \left|\tilde{S}(\omega,\tau)\right|^2 = \left|\int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \; F(\theta,\phi,\tau) \; \tilde{E}(\omega,\theta)\right|^2$$

complex-valued macroscopic HHG field

angular distribution changing with time

HHG field emitted by a single molecule

'Generalized tomography':

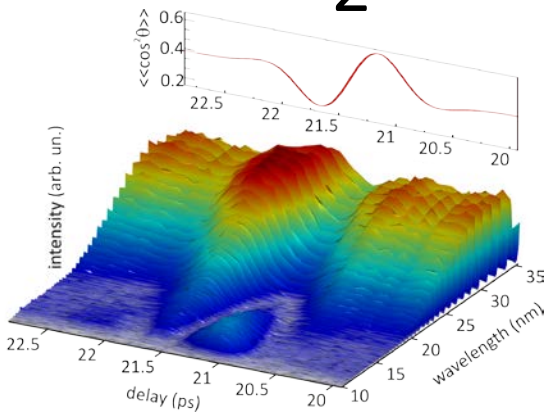
- the HHG spectrum is the coherent sum of emissions from molecules with various orientations that ***change with time***;

- deconvolve the contribution of each molecule using the (calculated) time-varying angular distribution and the redundancy of experimental data;

- it implies a *phase-retrieval problem*.

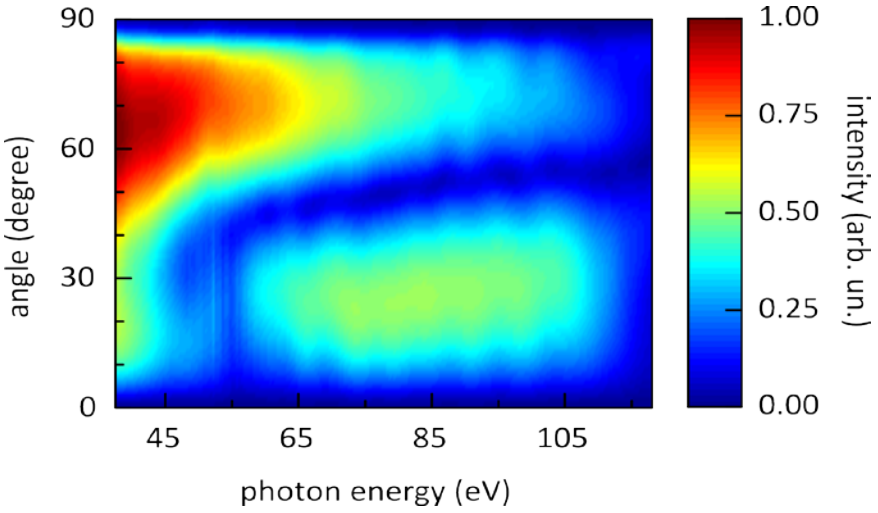
Angle-resolved HHG in CO_2

Retrieval iterative algorithm

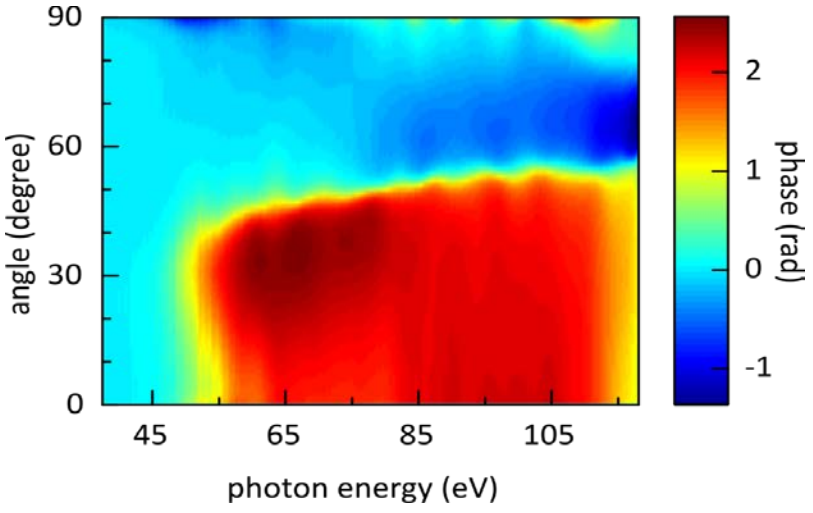


Angle-resolved XUV radiation emitted by CO_2 molecules in

Amplitude



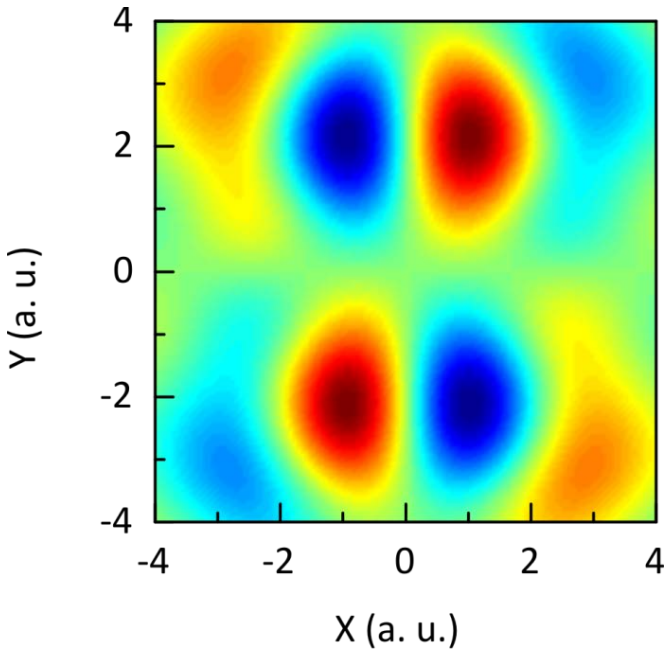
Phase



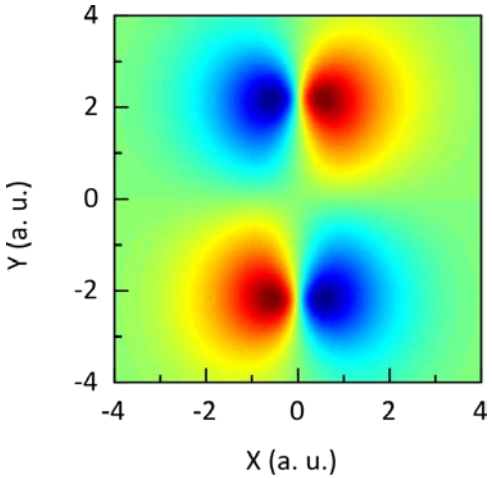
C. Vozzi et al., *Nature Phys.* **7**, 822 (2011)

CO_2 HHG tomography

From the angle-resolved HHG spectra we determine $\mathcal{F}_{\boldsymbol{k}}\{\boldsymbol{r}\,\Psi_0(\boldsymbol{r})\}$ and retrieve the molecular orbital:

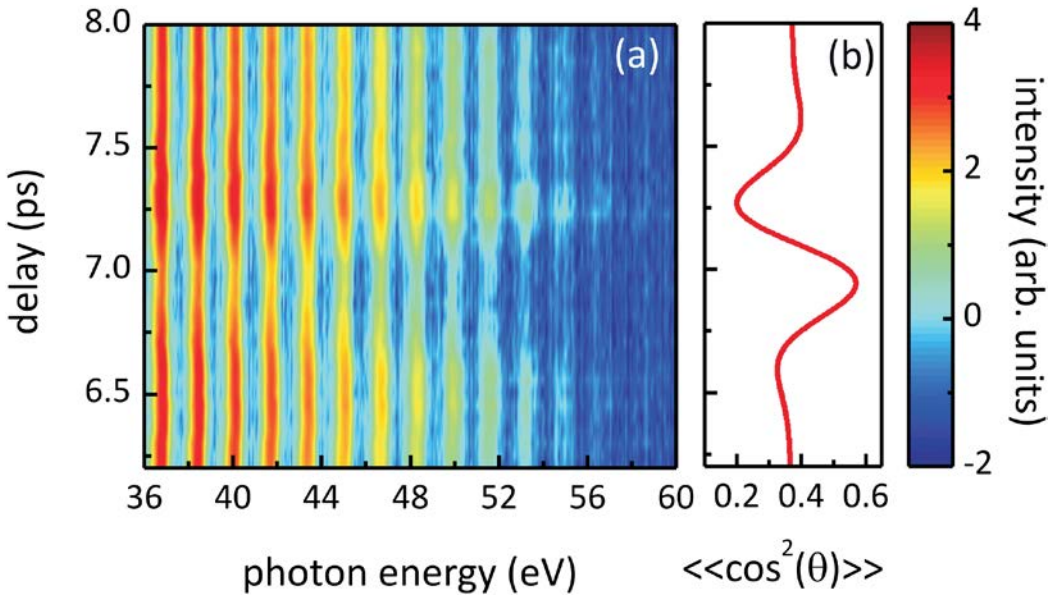


Discrepacies between the retrieved and the expected orbitals are due to clipping of the Fourier transform in the spectral domain.

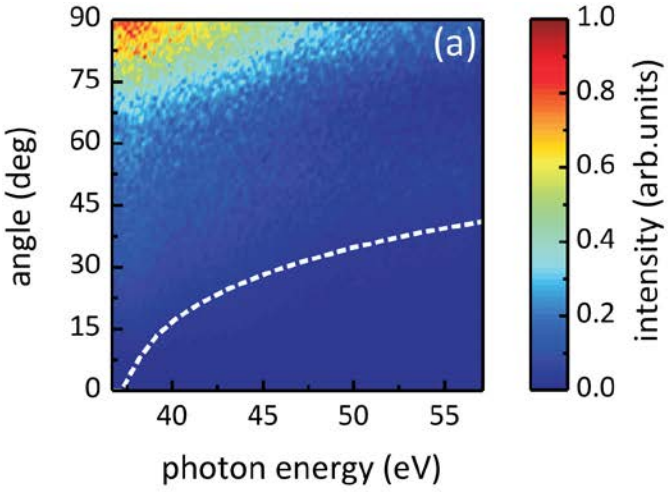


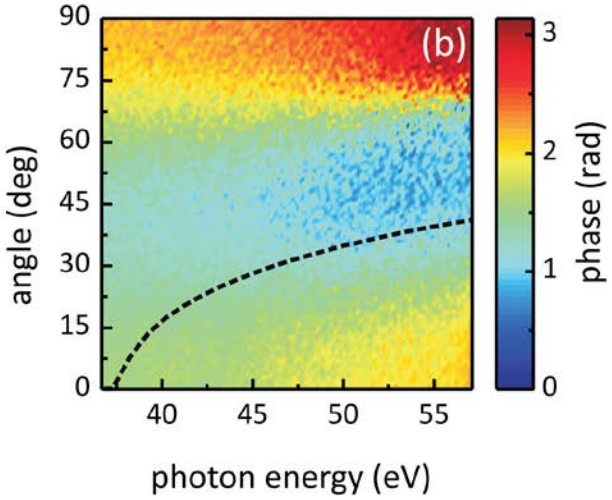
C. Vozzi et al., *Nature Phys.* **7**, 822 (2011)

Tomography in Acetylene



HHG spectra in C_2H_2 acquired along the half rotational revival

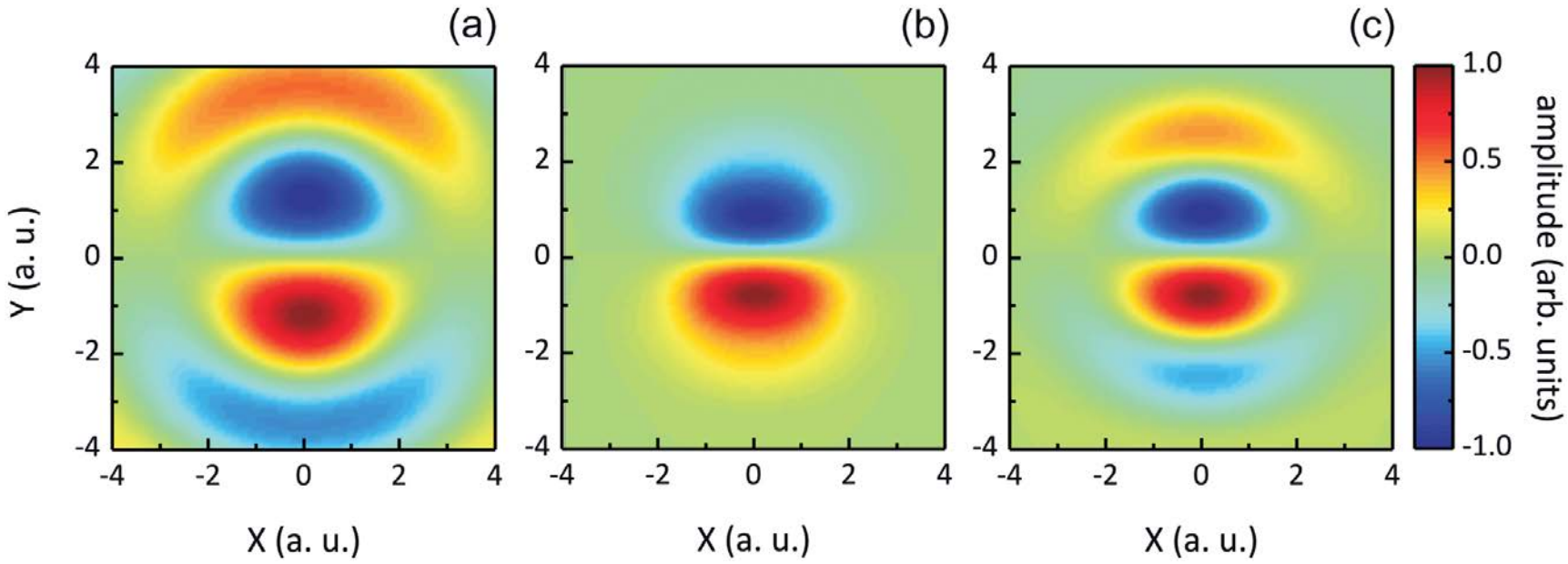




Corresponding angle-resolved XUV field in amplitude and phase

M. Negro et al. Faraday Discussions **171**, 133-143 (2014)

Tomography in Acetylene



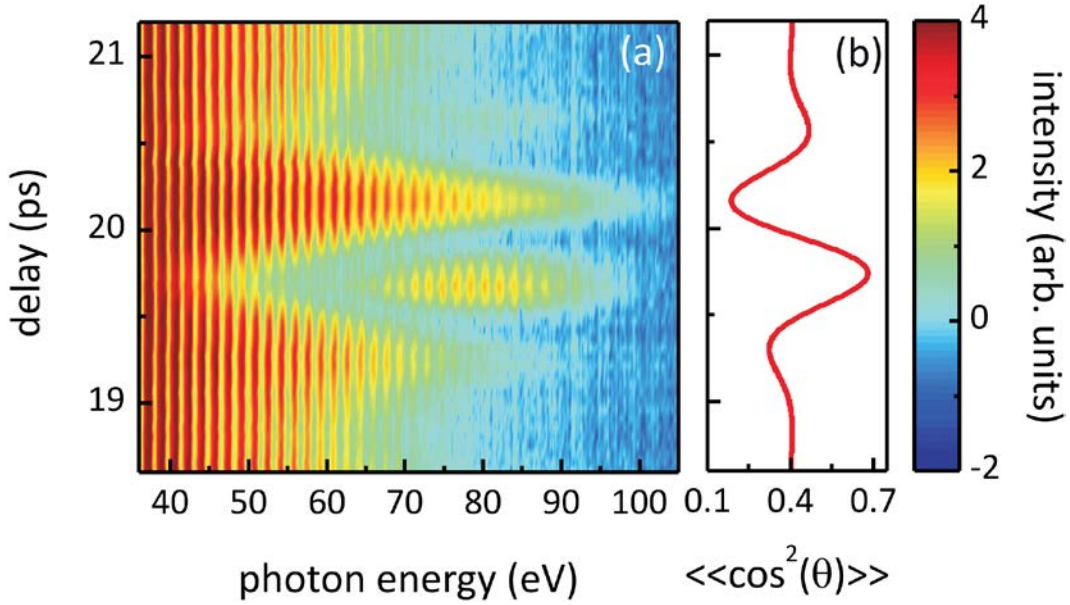
Retrieved C_2H_2 orbital

Expected C_2H_2 orbital

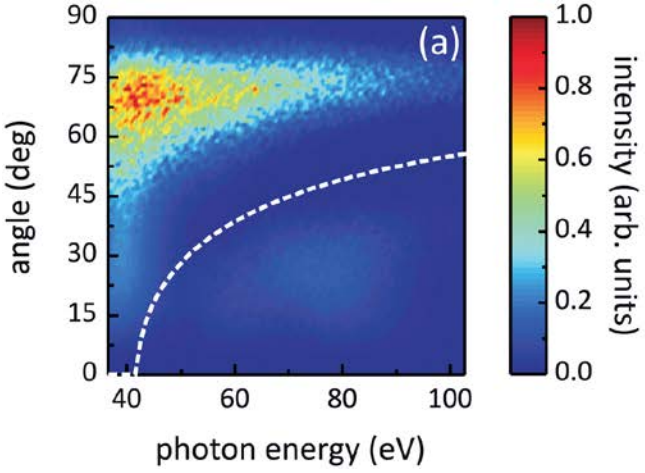
Simulated effect of spectral clipping on the expected C_2H_2 orbital

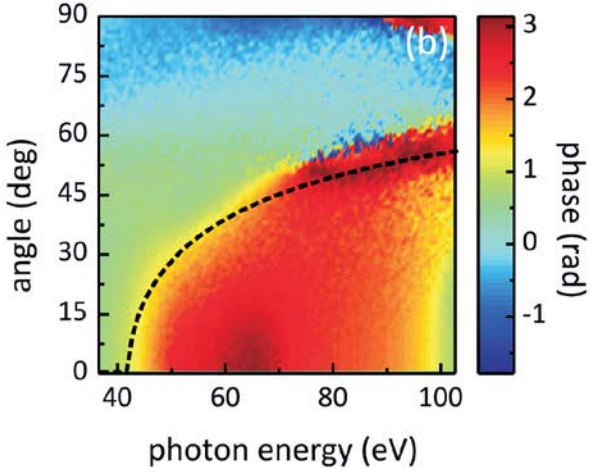
M. Negro et al. Faraday Discussions **171**, 133-143 (2014)

Tomography in N_2O



HHG spectra in N_2O acquired along the half rotational revival

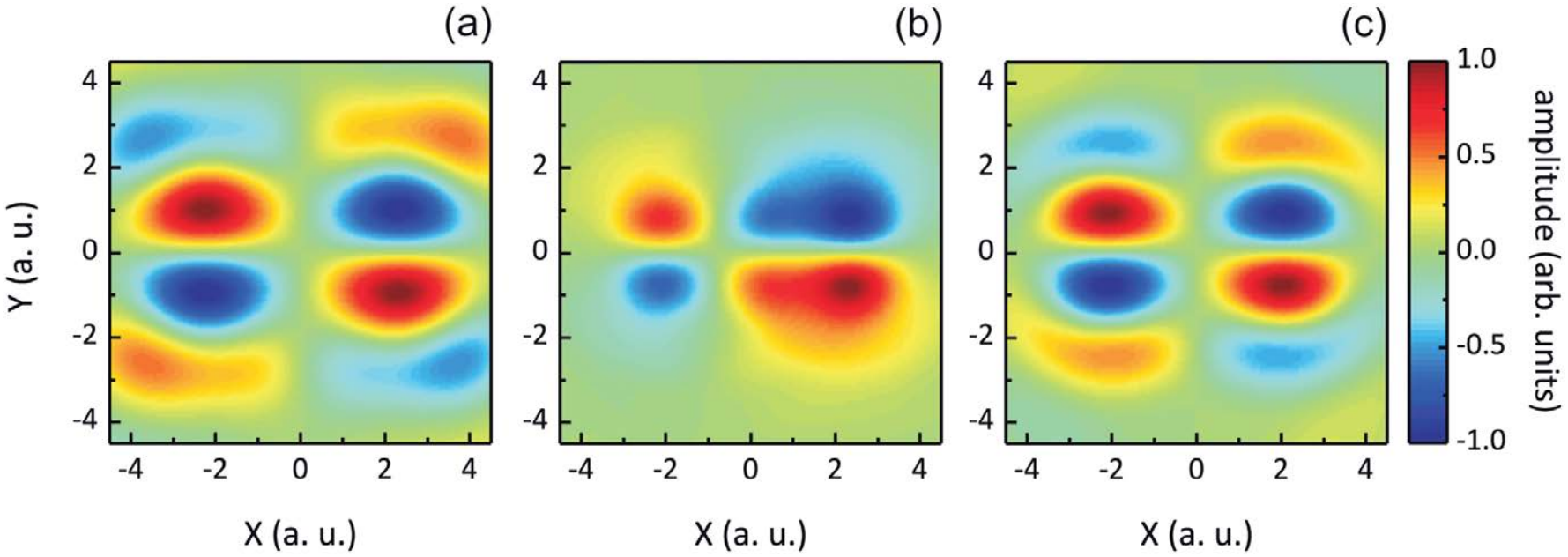




Corresponding angle-resolved XUV field in amplitude and phase

M. Negro et al. Faraday Discussions **171**, 133-143 (2014)

Tomography in N_2O



Retrieved N_2O orbital

Expected N_2O orbital

Simulated effect of spectral clipping and random molecular orientation on the expected N_2O orbital

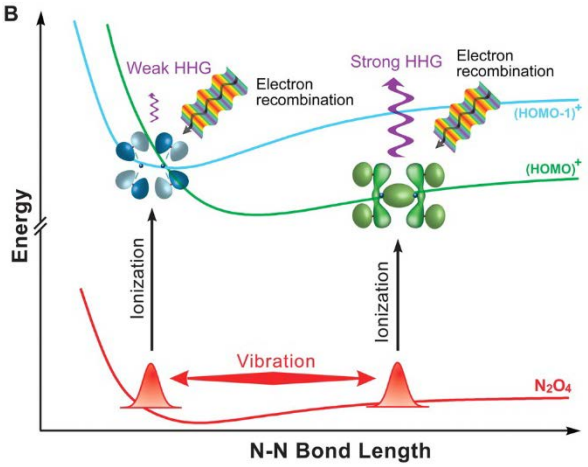
N_2O is not symmetric, alignment **AND** orientation are required

M. Negro et al. Faraday Discussions **171**, 133-143 (2014)

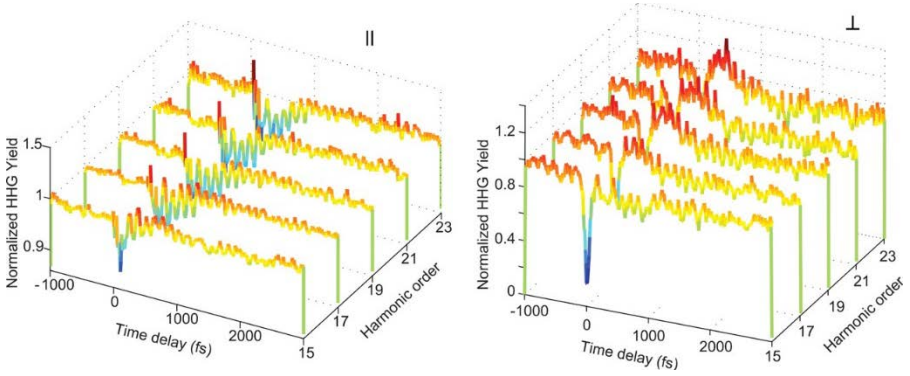
Conclusions

- HHG is a powerful tool for molecular spectroscopy and orbital tomography
- Several linear molecules have been already characterized by this tool
- Extension to nonlinear and non symmetric molecules not implemented yet

HHG spectroscopy of vibrational dynamics

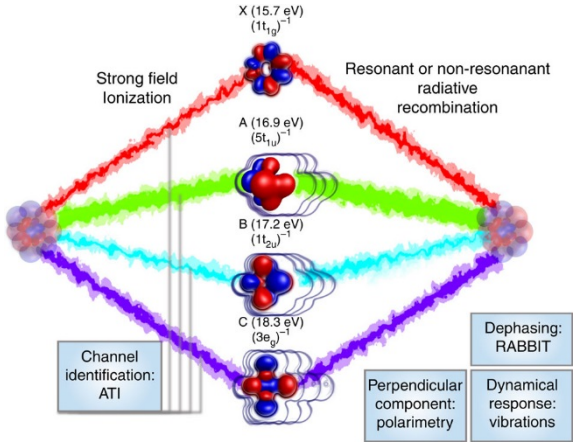


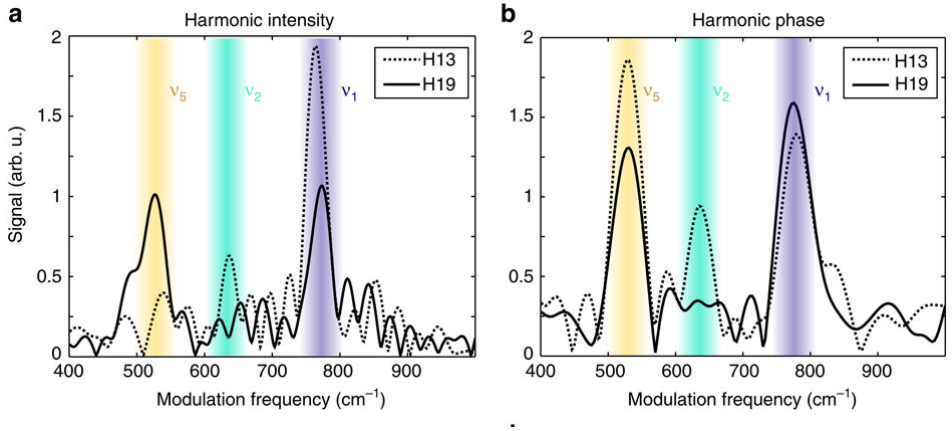
study of vibration in N_2O_4



- Wen Li et al., Science 322, 1207 2008

electronic and vibrational dynamics in SF_6

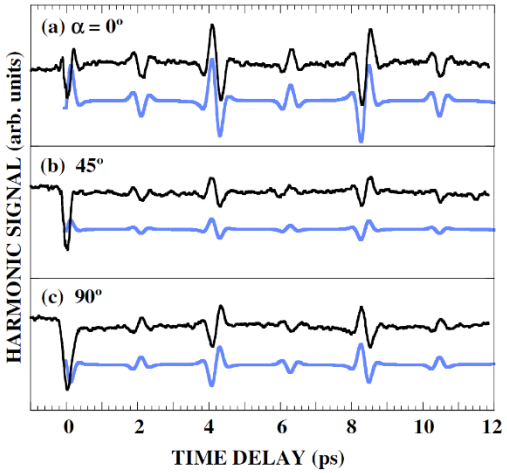


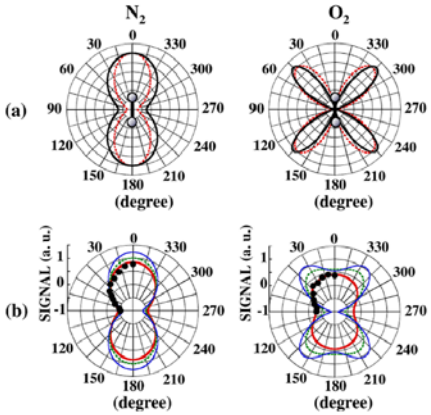


- A. Ferré et al., Nature Comm. 6, 5952 2015

HHG spectroscopy of rotational dynamics

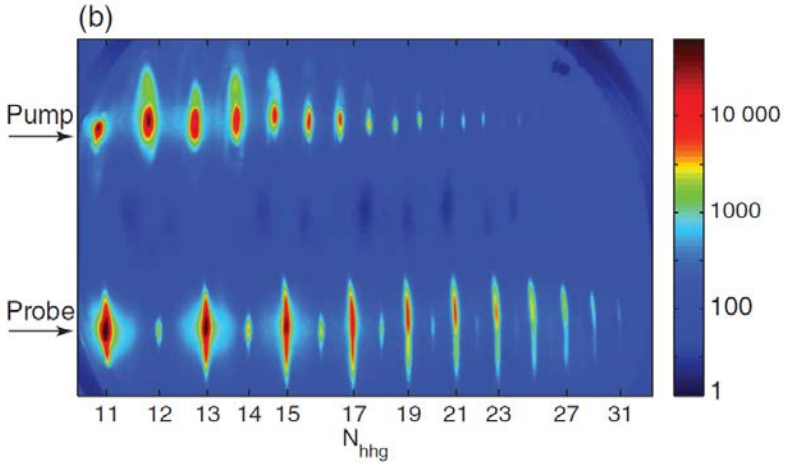
dynamic of HHG from rotating molecules

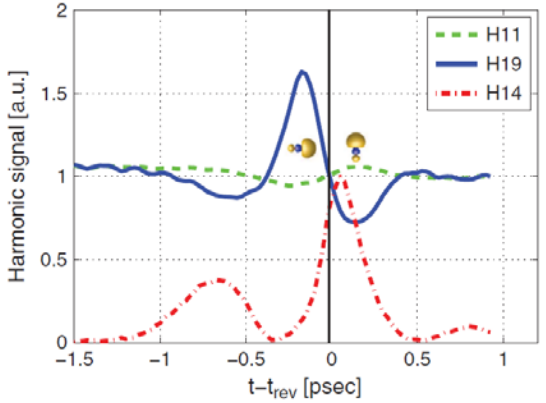




- K. Yoshii et al., Phys. Rev. Lett. 101, 183902 2008

dynamic of HHG from oriented molecules

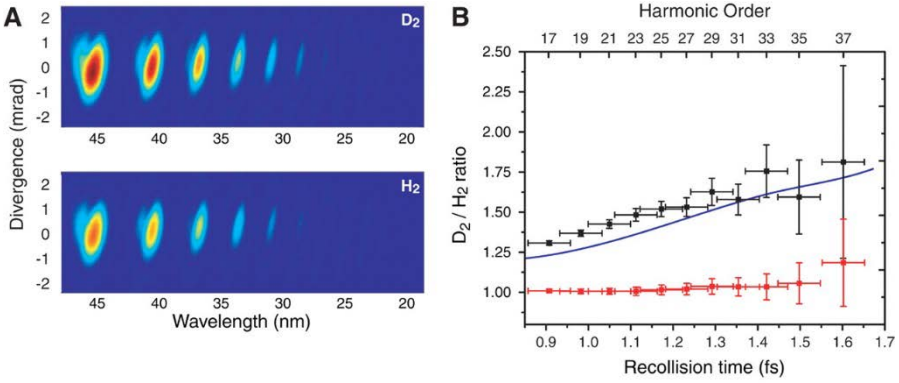


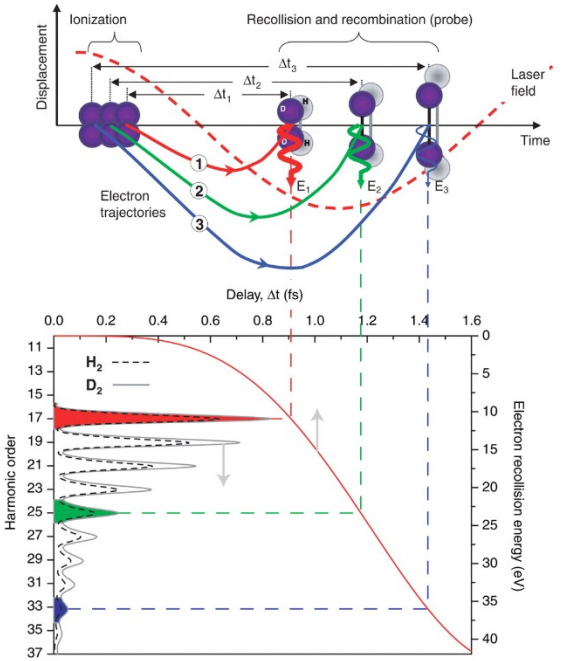


- E. Frumker et al., Phys. Rev. Lett. 109, 113901 2012

HHG spectroscopy of molecules

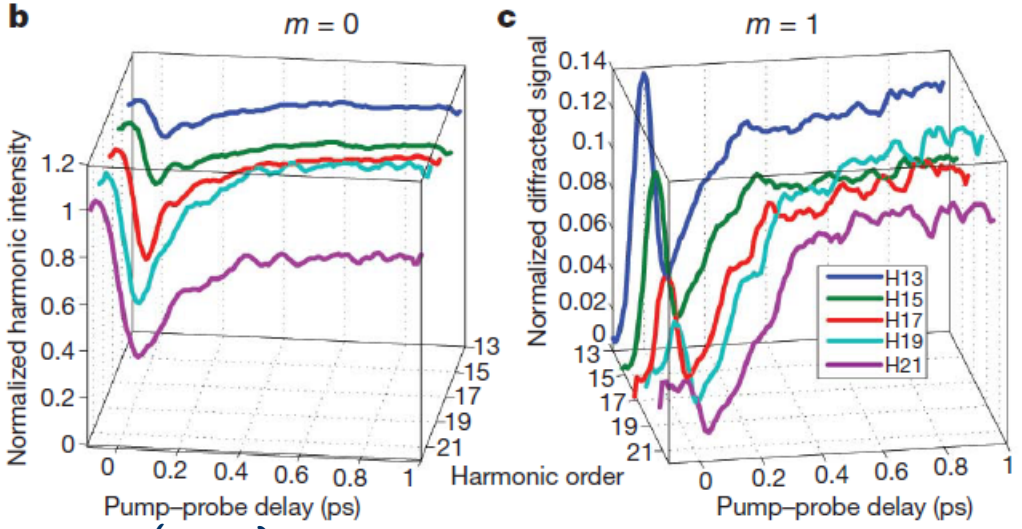
proton rearrangement in methane upon ionization





- S. Baker et al. Science 2006;312:424-427

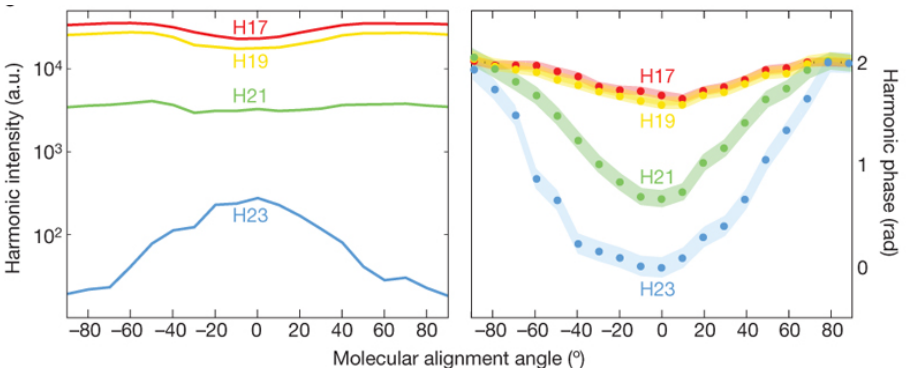
dissociation of Br_2 molecule

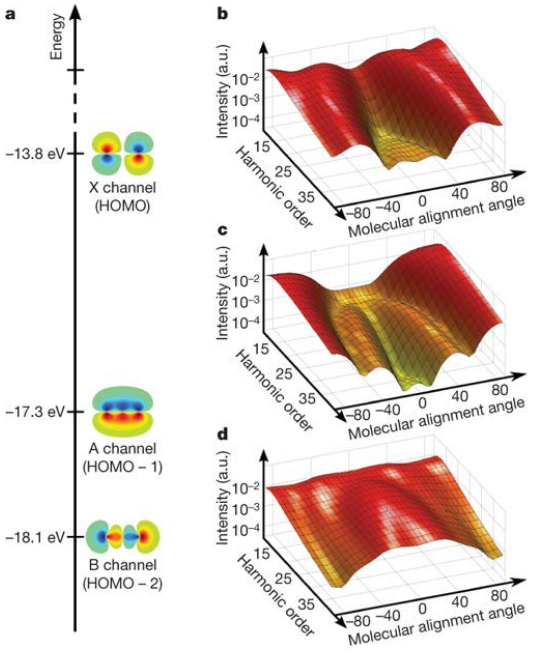


- H. J. Worner et al., Nature 466, 604 (2010)

HHG spectroscopy of molecules

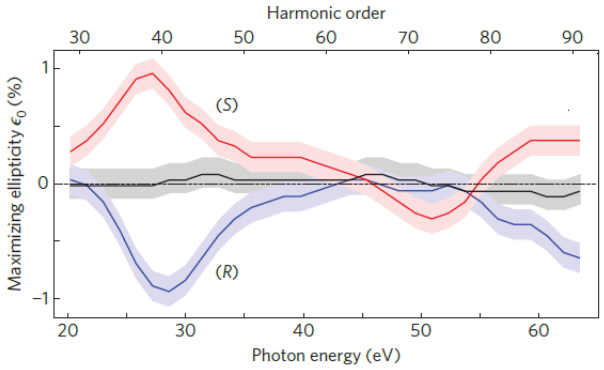
multielectron dynamics in CO_2

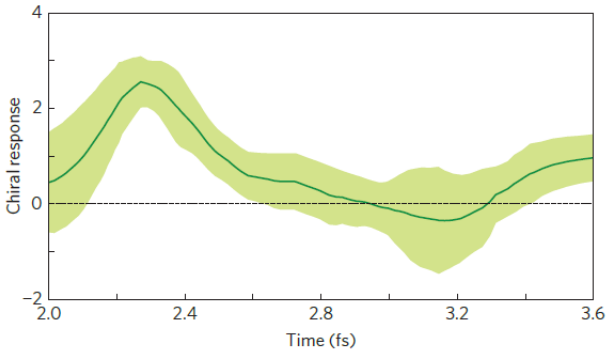




- O. Smirnova et al., Nature 460, 972 (2009)

study of chirality in organic molecules

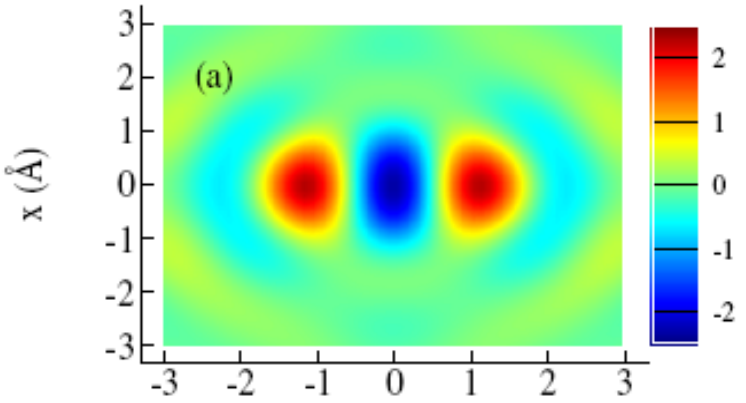




- R. Cireasa et al., Nat. Physics 11, 654 (2015)

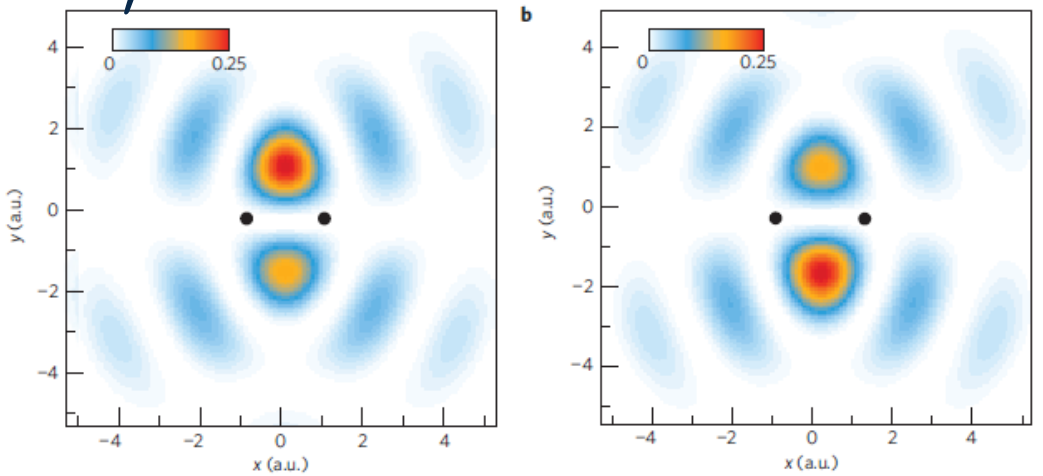
HHG recollision electron imaging

imaging of N_2



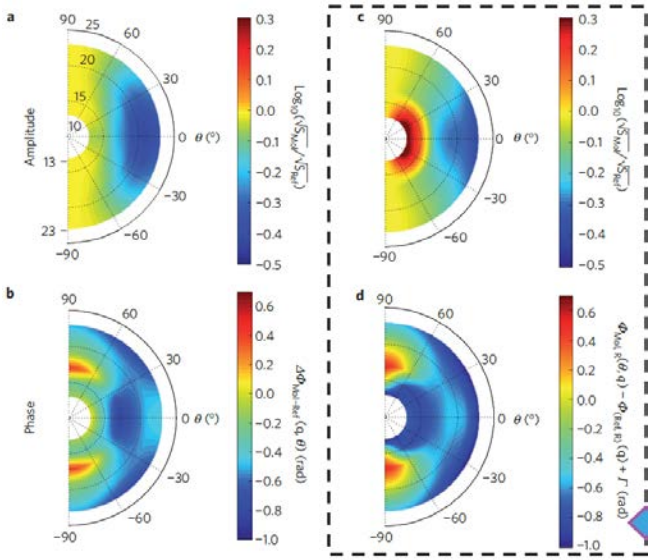
- J. Itatani et al., Nature 432, 867 (2004)

reconstruction of hole dynamic in N_2



- S. Haessler et al., Nat. Phys. 6, 200 (2010)

mixed gas interferometry multielectron effects in Br_2



- J. B. Bertrand et al., Nat. Phys. 9, 174 (2013)

caterina.vozzi@cnr.it

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- Caterina Vozzi

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- Aditya Pusala
- Prabhash Prasannan Gheeta

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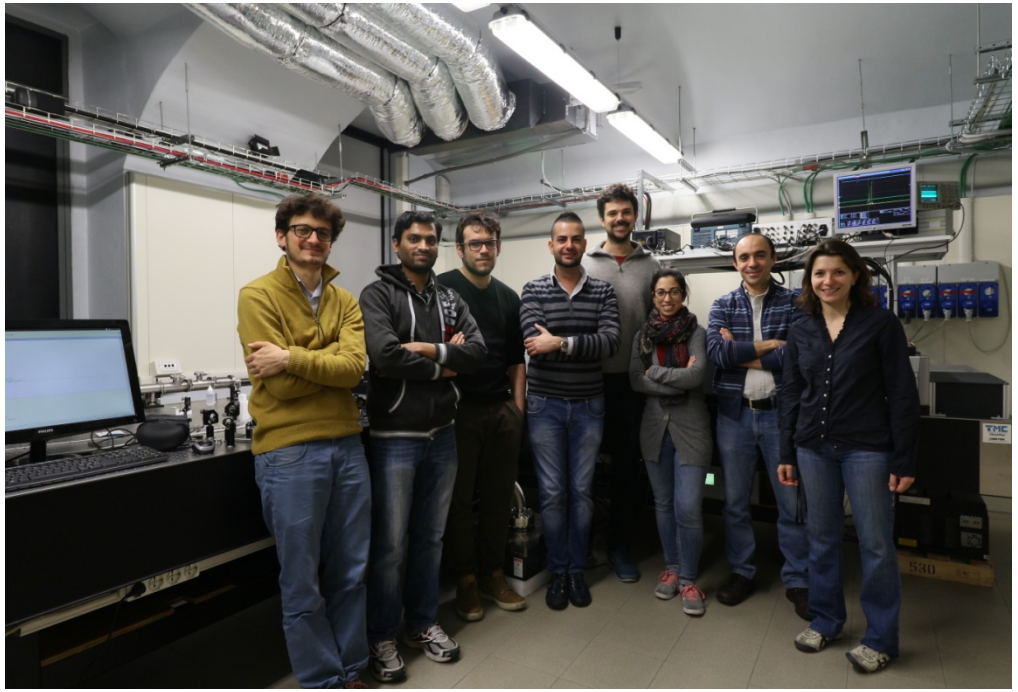
- Gabriele Crippa



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