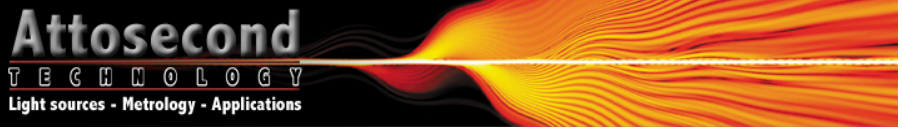


Quantum Optics and Laser Science Group
Blackett Laboratory, Imperial College London

Controlling electrons for ultrafast molecular imaging

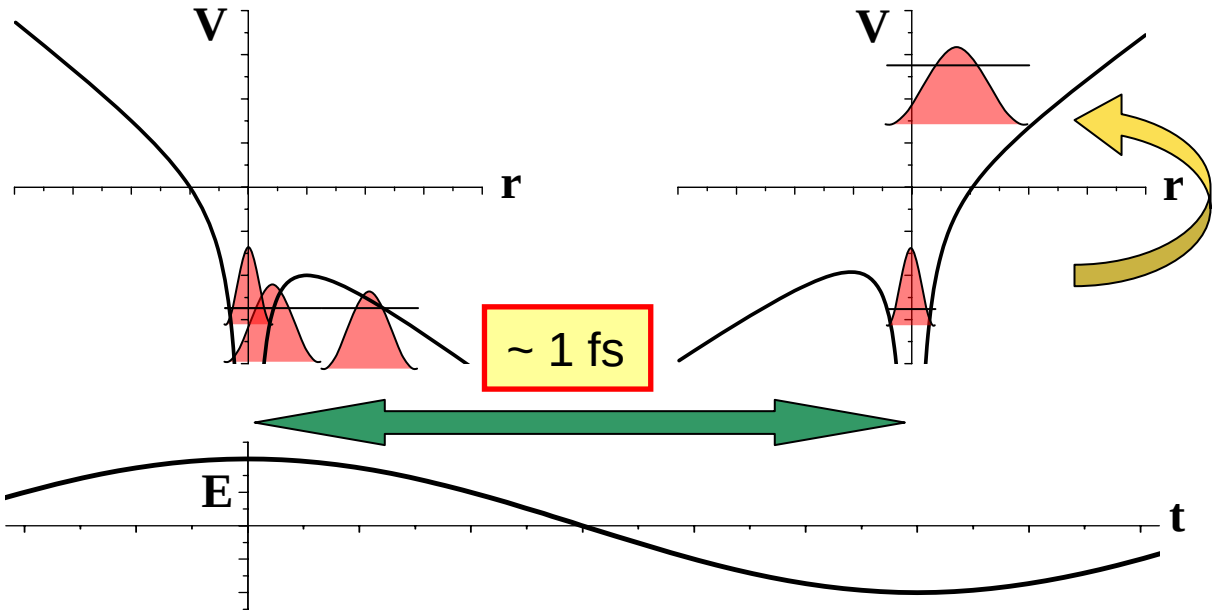
Ricardo Torres
Imperial College London, UK

KITP, Santa Barbara, May 2009

Strong laser field interaction with molecules

Laser intensity ~ 100 TW/cm^2

Tunnel ionization **Acceleration & Recollision**



e$^-$ kinetic energy ~ 100 eV

e$^-$ current density > 10^{10} A/cm^2

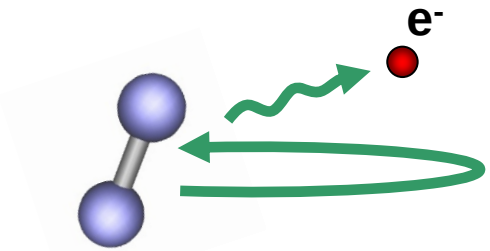
P.B. Corkum, Phys. Rev. Lett. 71, 1994 (1993)

Laser driven electrons can be used to probe molecular structure:

- **Sub-fs time resolution.**
- **Sub-Angstrom spatial resolution**
- **Broad energy spectrum**

Laser induced electron diffraction

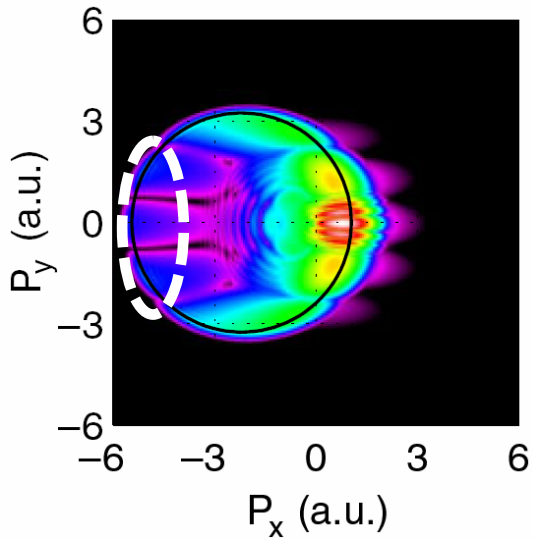
The angular distribution of rescattered electrons may exhibit **diffraction peaks/minima**; a signature of the molecular internuclear separation.



T. Zuo *et al.*, Chem. Phys. Lett. 259, 313 (1996).
M. Lein *et al.*, Phys. Rev. A 66, 051404 (2002).

Best information found at **high electron energies**.

Measuring angular distribution of such high energy electrons is **experimentally difficult**.



5-6 a.u: 340-490 eV

(Up ~ 42eV)

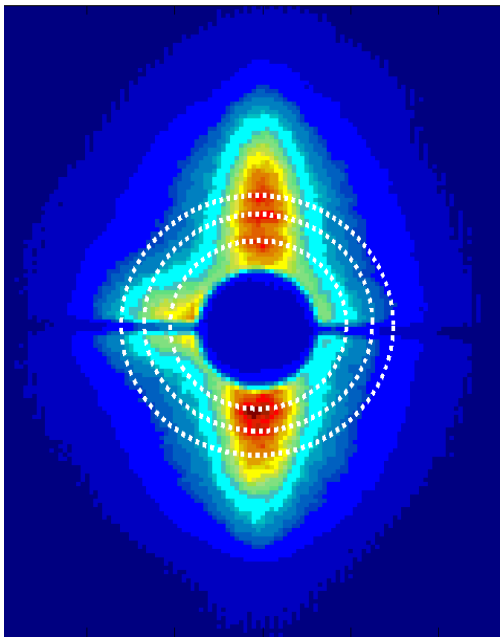
M. Spanner *et al.*,
J. Phys. B 37, L243 (2004).

Recent experimental demonstration of laser induced electron diffraction in N_2 and O_2 using COLTRIMS with electrons up to ~ 100 eV.

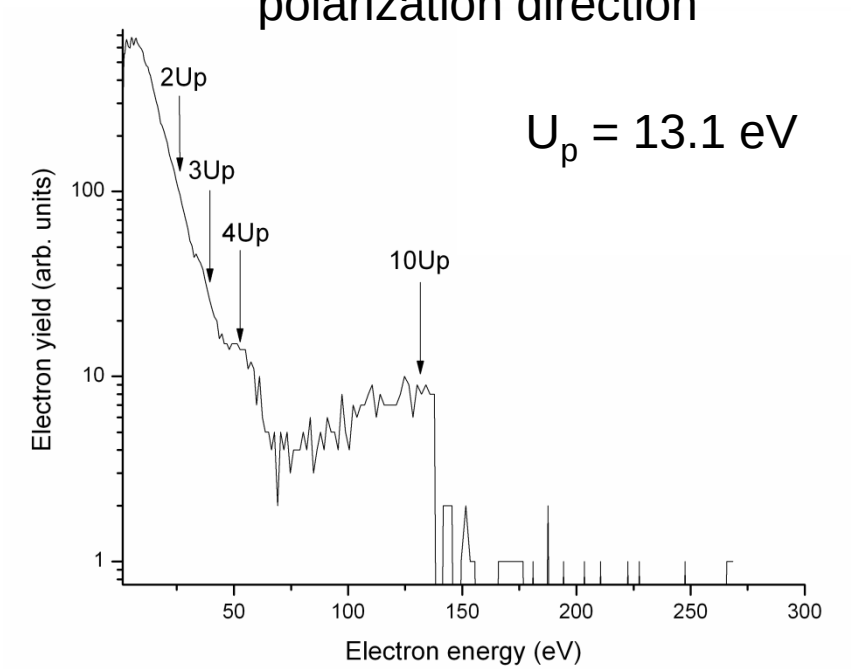
M. Meckel, *et al.* Science 320, 1478 (2008).

Laser induced electron diffraction

Development of a Velocity Map Imaging Spectrometer for measurement of velocity distribution of electrons up to 300 eV.



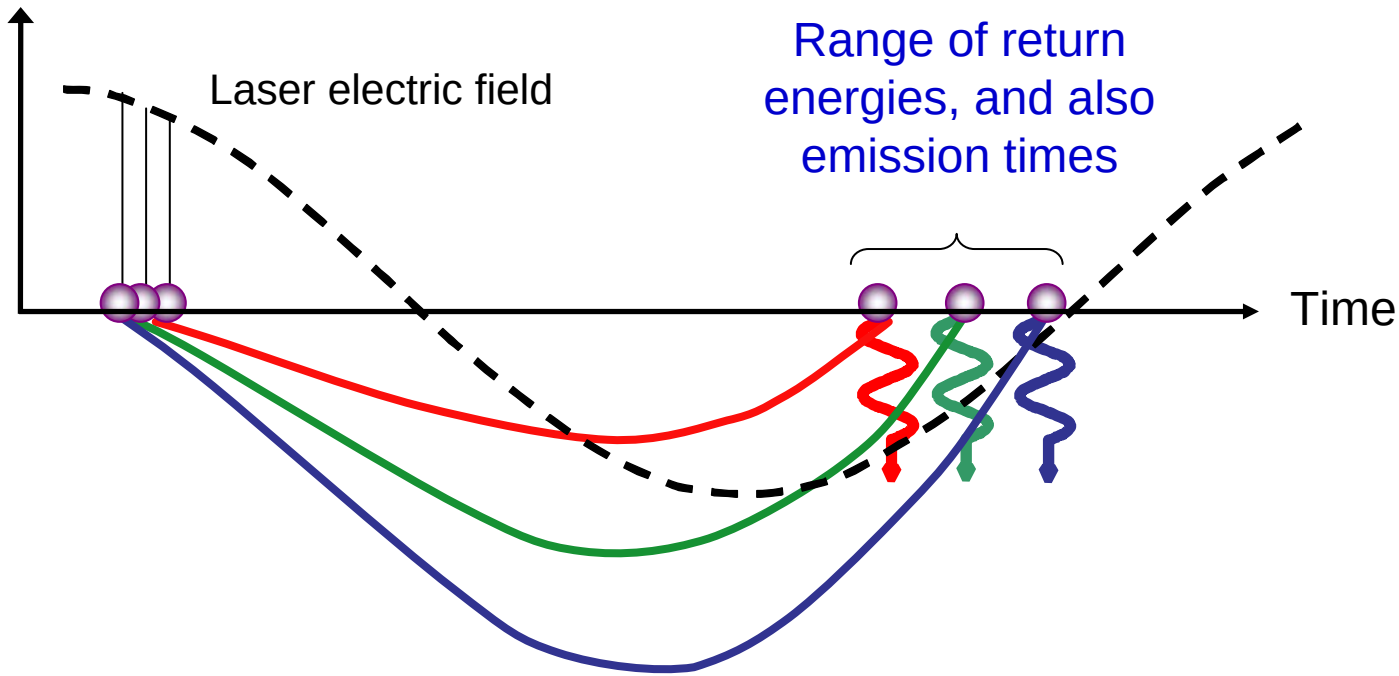
Energy distribution along polarization direction



Maximum energy electron detected ~140 eV – but limited by laser intensity, not performance of VMI spectrometer.

High order harmonic generation (HHG)

The recolliding electron wavepacket can be reabsorbed into the initial state emitting light in the form of harmonics of the fundamental laser frequency.



Structural information of the molecule **measured by the electrons** is **transferred to XUV light**.

Each harmonic carries information about a different “slice” of the molecule in momentum space and a different time.

Theoretical description of HHG

Harmonic spectrum is caused by the oscillation of the dipole moment arising from the overlap of the continuum wavefunction with the bound state.

$$\mathbf{D}(t) = \langle \psi_0 | \mathbf{r} | \psi_C \rangle$$

Bound state Continuum wavefunction

Strong Field Approximation (SFA) is useful to describe HHG in molecules.

- Continuum states are approximated as **plane waves**.

$$\psi_C(\mathbf{r}) = \int a(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{k}$$

- Ignores influence of laser field upon molecular bound state. Usually assumes single-active electron, therefore the bound state ψ_0 is a **molecular orbital**.

$$\mathbf{D}(t) \sim \mathcal{F}[\mathbf{r}\psi_0]$$

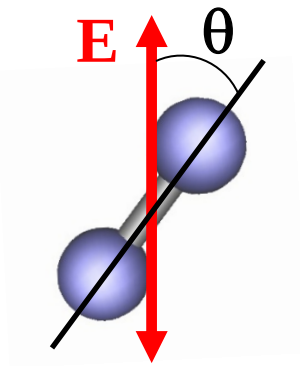
We can go beyond SFA but it is a convenient framework with which to begin

Controlling HHG

We want to control the measurements by manipulating:

1) Target (Fixing molecular alignment in space).
2) Probe (Steering the electrons with the electric field).

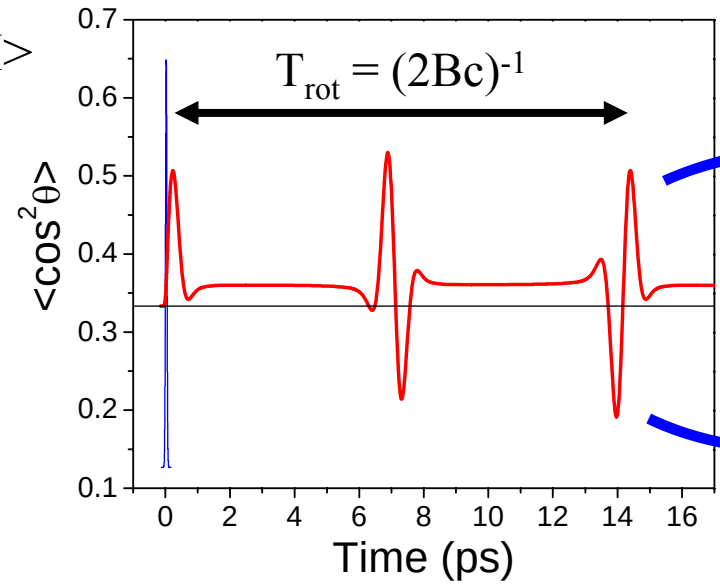
Molecular alignment

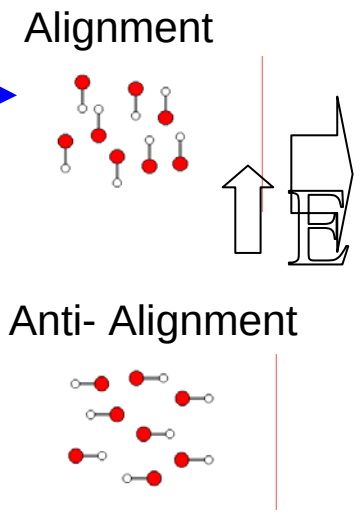


Non-resonant, linearly polarized laser field (I~10^{13} W/cm^2, τ<100 fs) produces a **wavepacket of rotational states** localizing the molecular axis around the laser field axis.

$$|J_i\, M\rangle \Rightarrow \sum_J C_{JiJ}\, |J\, M\rangle$$

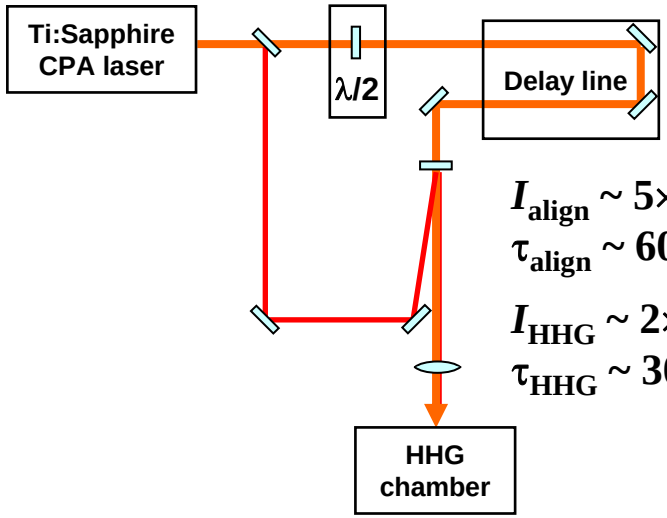
Transient aligned states revive periodically every $\Delta t = T_{rot}/2$.





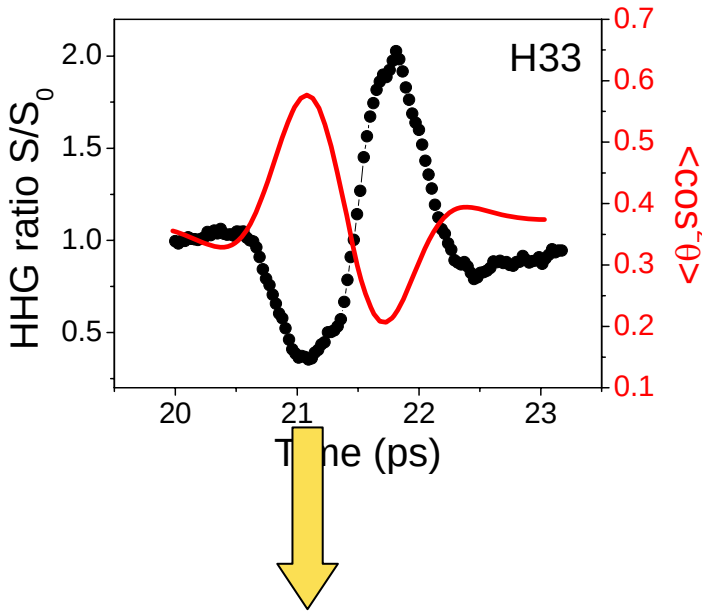
HHG in aligned CO_2

Experimental setup

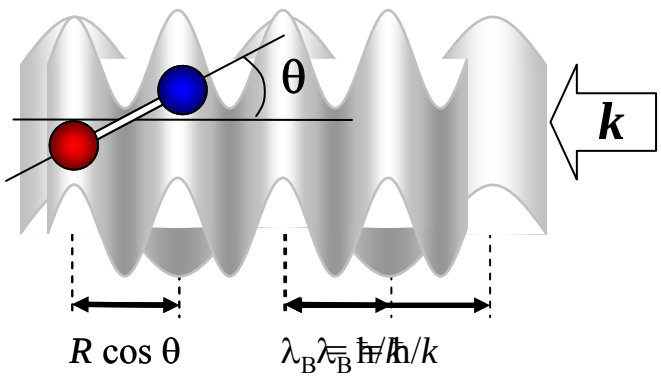


$I_{align} \sim 5\times10^{13}$ W/cm^2
$\tau_{align} \sim 60$ fs

$I_{HHG} \sim 2\times10^{14}$ W/cm^2
$\tau_{HHG} \sim 30$ fs

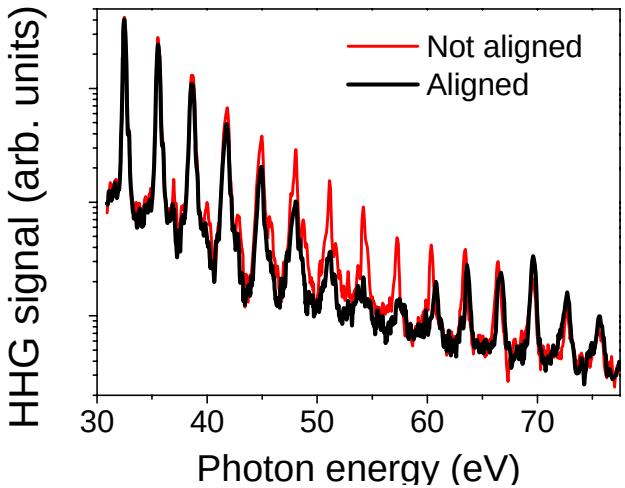


Two-center interference



$R\cos\theta = (m+1/2)\,\lambda_B$

Constructive interference



M. Lein *et al.,* Phys. Rev. Lett. 88, 183903 (2002)

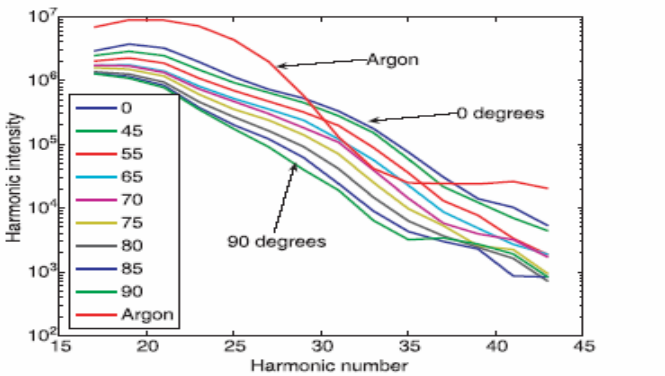
C. Vozzi *et al.,* Phys. Rev. Lett. **95**, 153902 (2005)

Tomographic reconstruction of orbitals

The dependence of HHG on molecular orientation also carries information about the electronic orbital structure.

Tomographic reconstruction

N_2



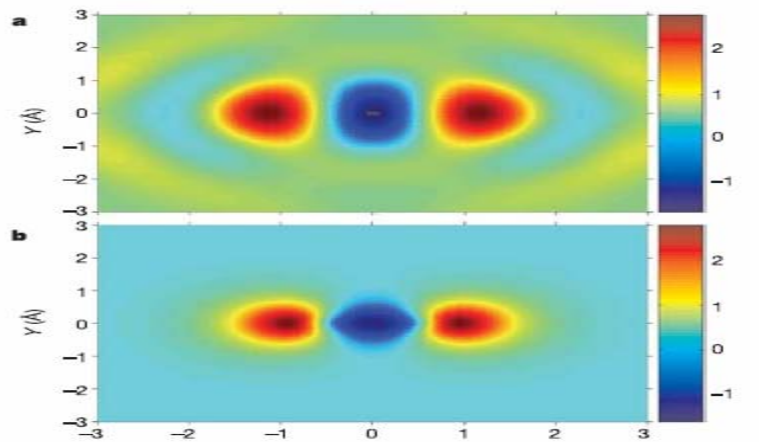


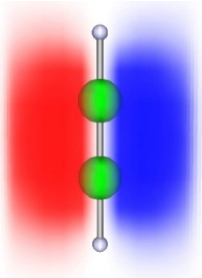
Figure 3 High harmonic spectra were recorded for N_2 molecules aligned at 19 different angles between 0 and 90° relative to the polarization axis of the laser. For clarity, only some of the angles have been plotted above. The high harmonic spectrum from argon is also shown; argon is used as the reference atom. Clearly the spectra depend on both the alignment angle and shape of the molecular orbital.

- Reconstructed orbital is HOMO + contribution from lower lying orbitals.
- Tomographic retrieval relies on validity of SFA – this must be checked!
- Only been demonstrated in N_2 so far.

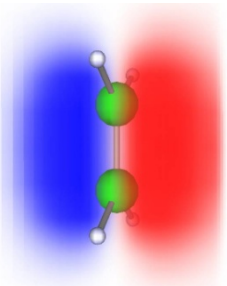
J. Itatani *et al.,* Nature 432, 867 (2004)
S. Patchkovskii *et al*., Phys. Rev. Lett. 97, 123003 (2006)

HHG in aligned polyatomics

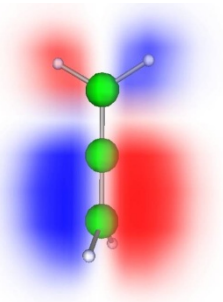
C_2H_2 (Acetylene)

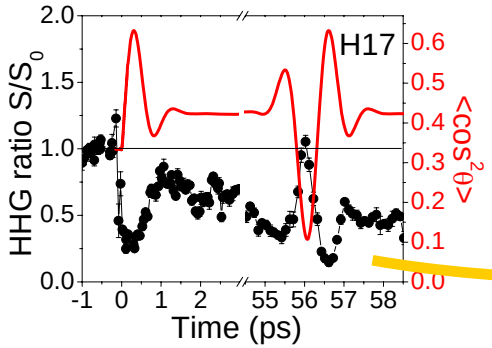


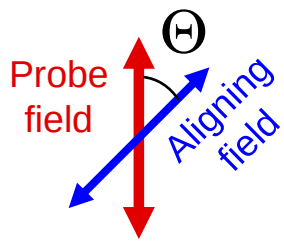
C_2H_4 (Ethylene)

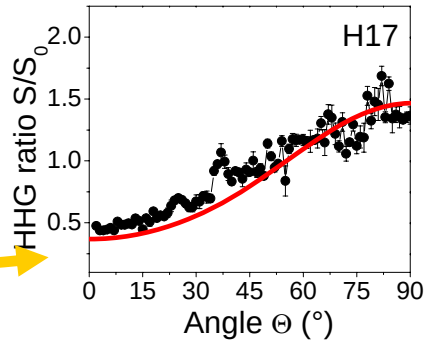


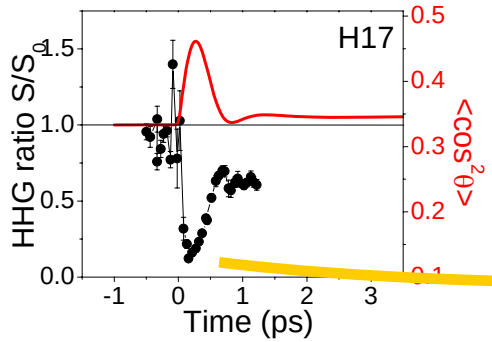
C_3H_4 (Allene)

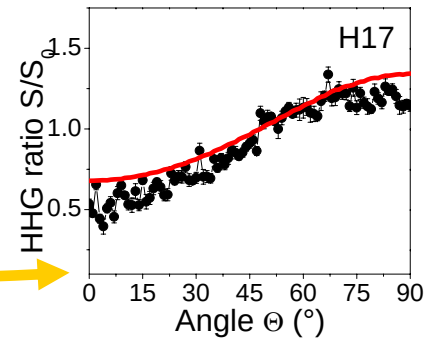


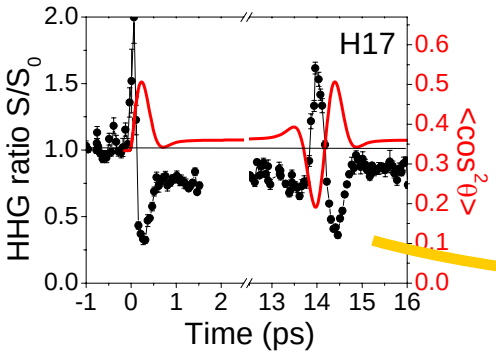


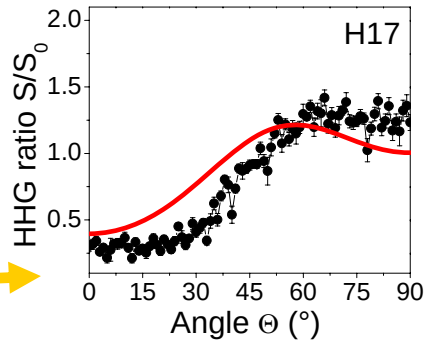








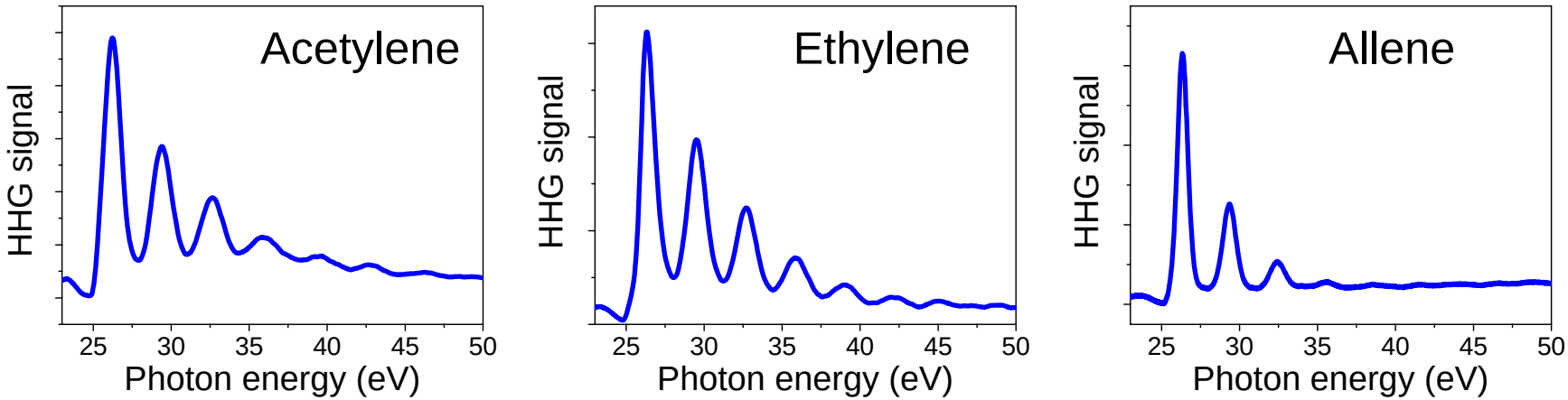




Harmonic signal maps out the HOMO structure

R. Torres *et al.*,
Phys. Rev. Lett. 98, 203007 (2007)

Some limitations



Limited harmonic range due to the low I_P (~ 10 eV) of the molecules.

Cutoff: $E_{\text{fotón}} = I_P + 3.17\, U_P$

Ionization saturates at relatively low intensities, but…

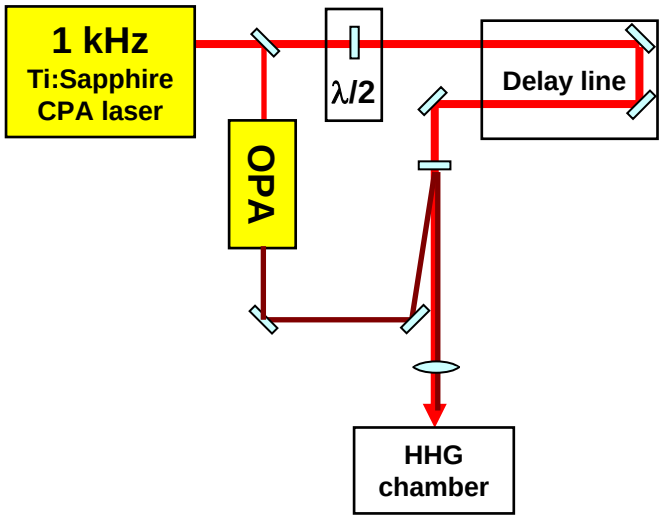
$U_P \sim I\,\lambda^2$

We can extend the range of harmonics increasing the laser wavelength while keeping the intensity below the saturation threshold.

Drawback: HHG efficiency drops as $< \lambda^{-5}$ due to wavepacket dispersion in the continuum

Mid-IR HHG in aligned molecules (I)

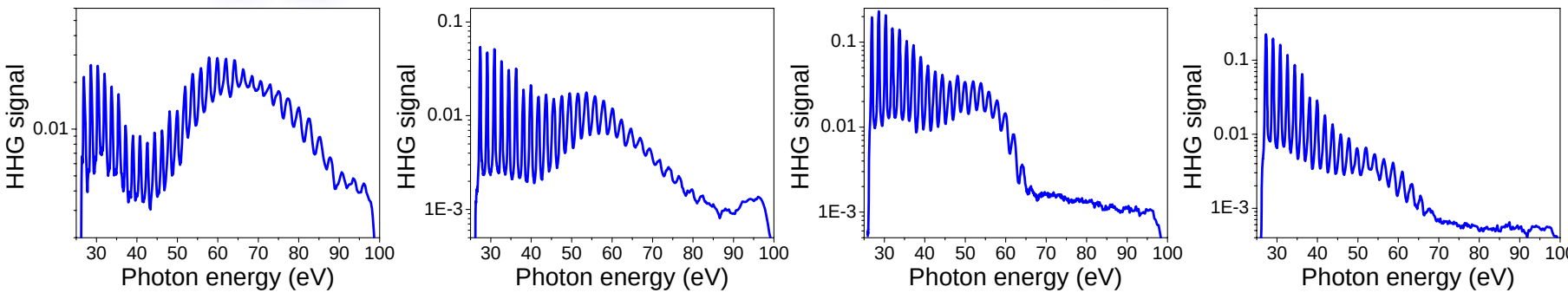
Experimental setup



$\lambda_{align} = 800$ nm { $I_{align} \sim 5\times10^{13}$ W/cm^2, $\tau_{align} \sim 80$ fs

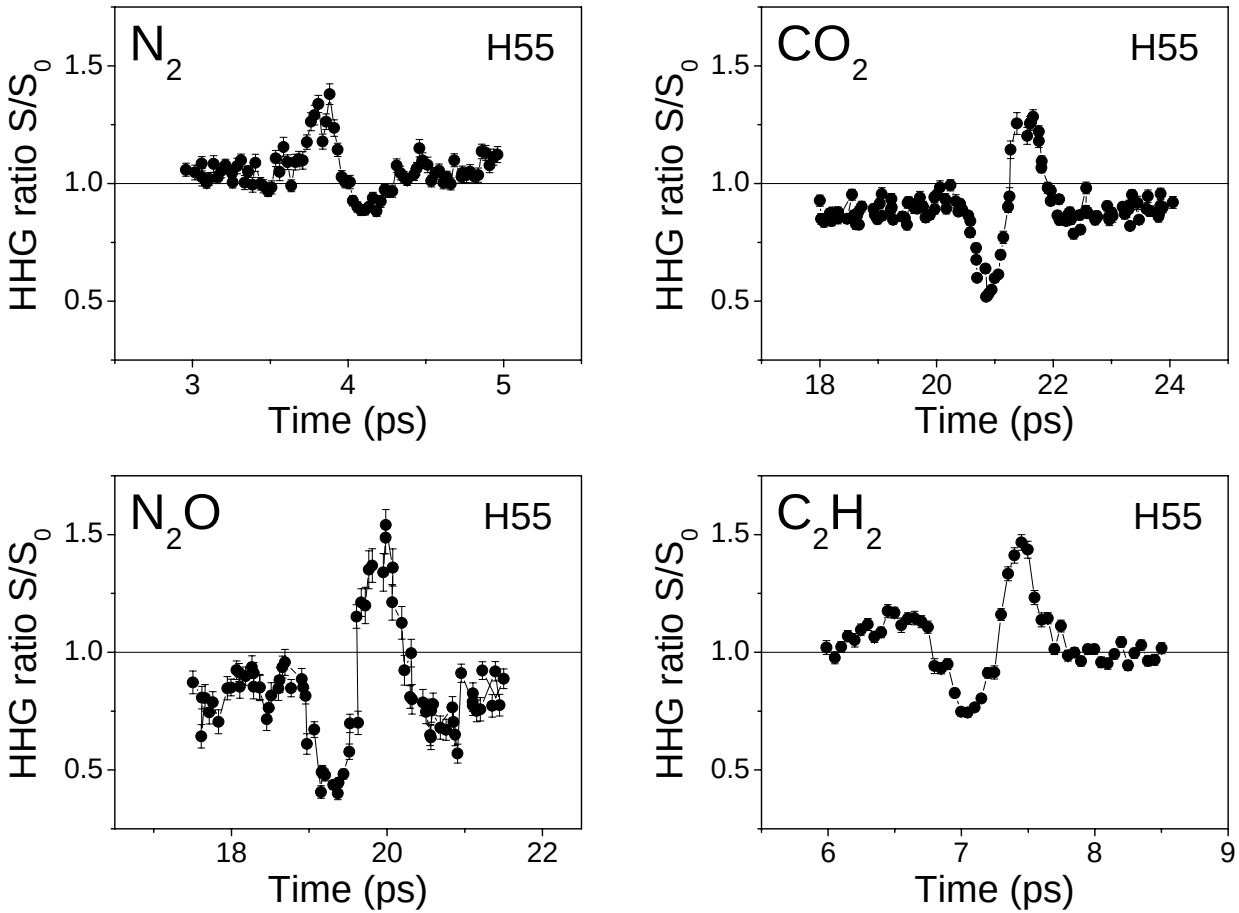
$\lambda_{HHG} = 1300$ nm { $I_{HHG} \sim 2\times10^{14}$ W/cm^2, $\tau_{HHG} \sim 50$ fs

N_2 CO_2 N_2O C_2H_2



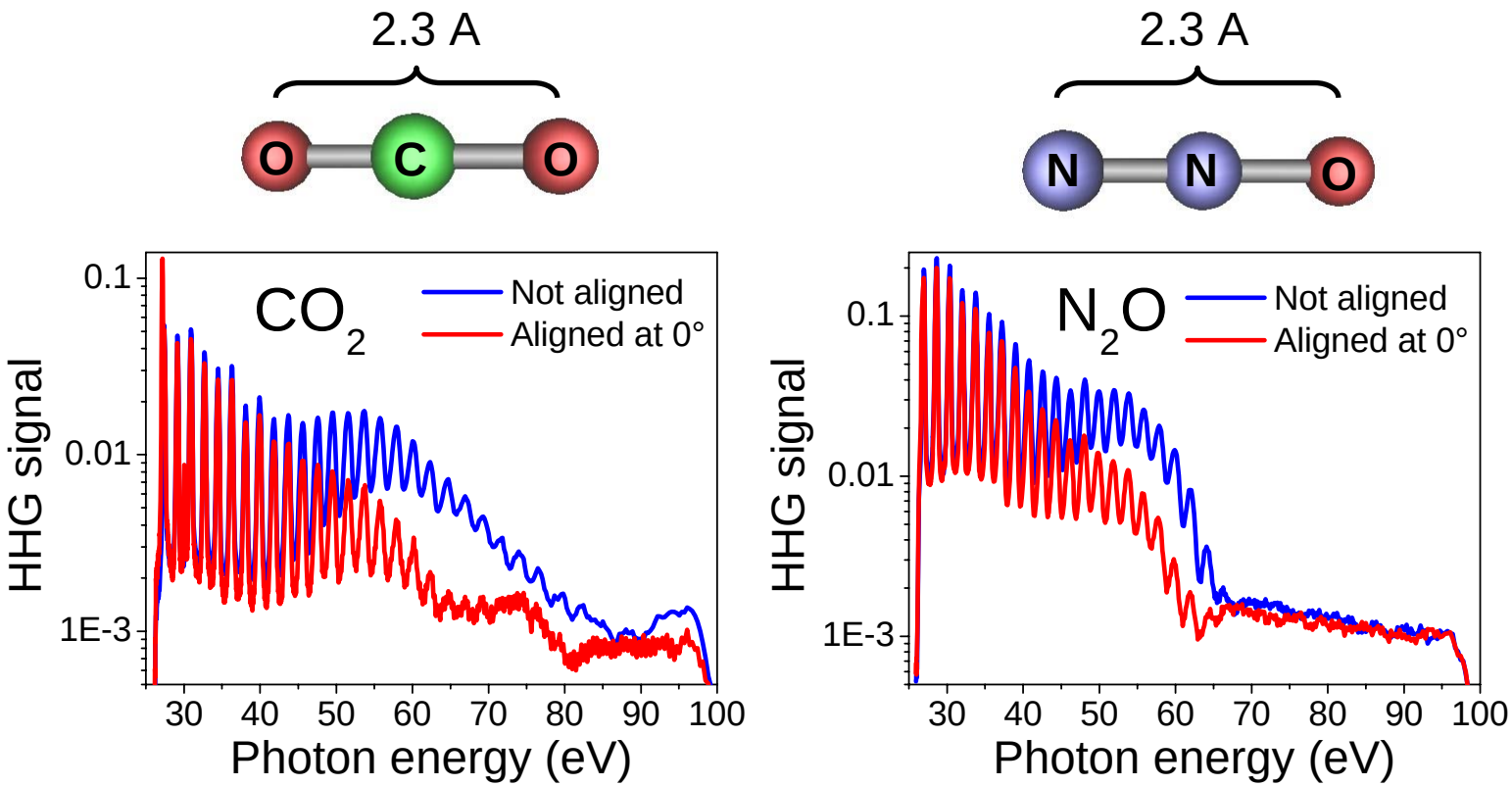
1 kHz mid-IR laser source provides high energy harmonics with a good signal/noise ratio

Mid-IR HHG in aligned molecules (II)



Large modulation in HHG signal at the half revival observed in high energy harmonics

Mid-IR HHG in aligned molecules (III)



New evidence of harmonic suppression in aligned CO_2.

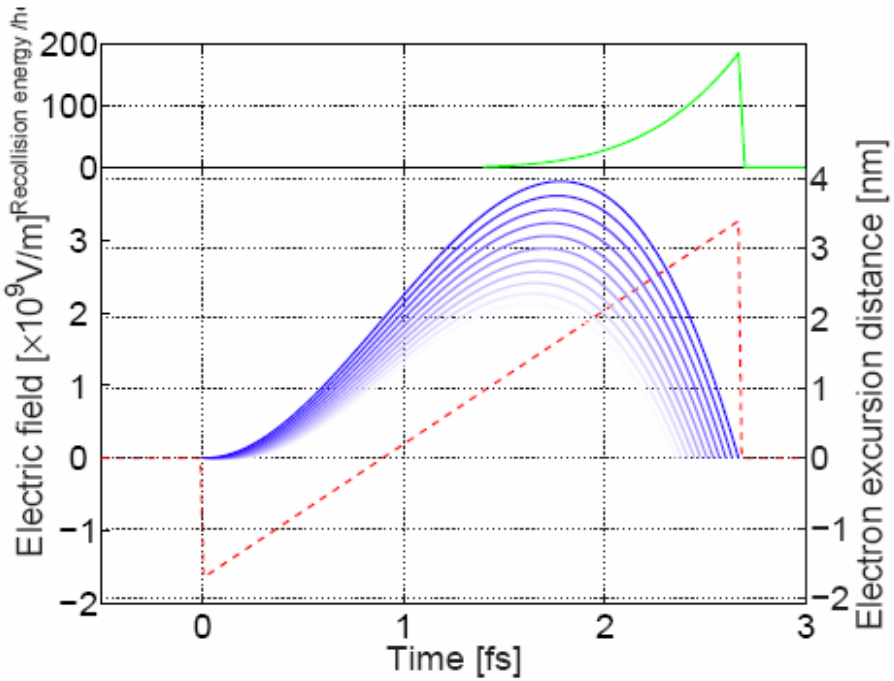
Evidence of harmonic suppression in aligned N_2O, not observed before, compatible with two-center interference.

The perfect wave

Is it possible to increase the electron recollision energy while keeping a high recollision probability?

What is the optimum electric field waveform that achieves this for a given total energy and periodicity?

A ramp with a DC offset maximises recollision energy: **The perfect wave.**



$$E(t) = \pm\sqrt{\frac{F}{T}\frac{2}{\pi\epsilon_0 c}}\left(\frac{3t}{T} - 1\right)$$

Proven analytically

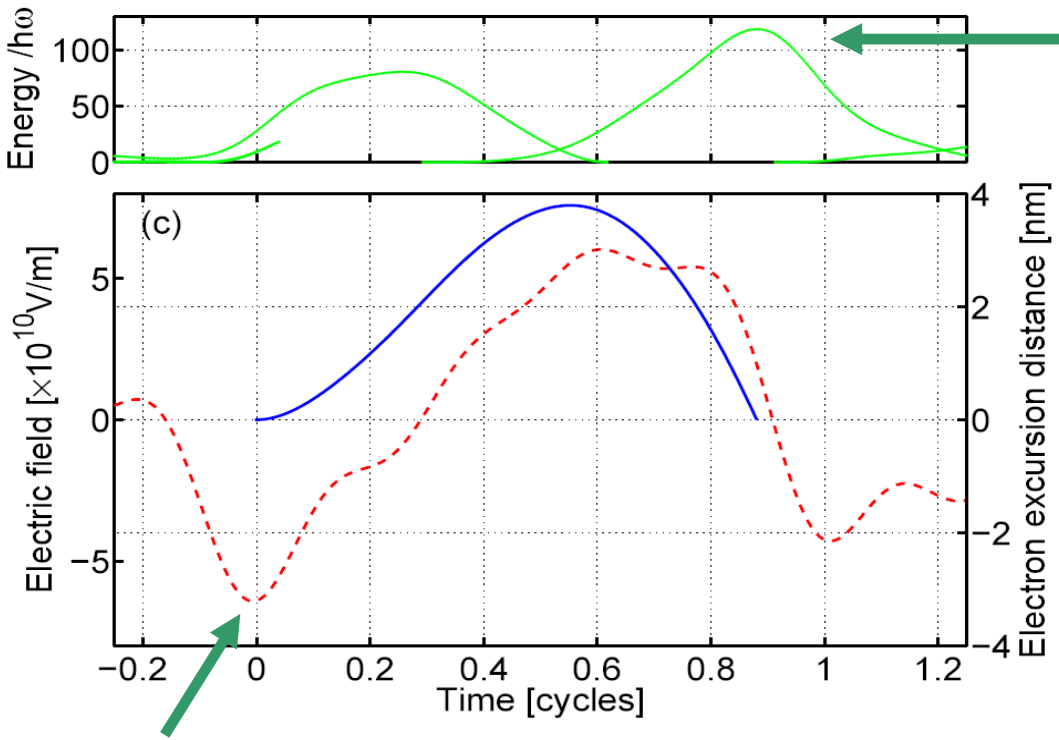
L.Chipperfield *et al.*,
Phys. Rev. Lett. 102, 063003 (2009)

This is clearly an impractical waveform (!)
How might we approximate this in the lab?

The perfect wave

An approximation to the sawtooth can be synthesised using a finite number of fields.

Waveform synthesized from 800nm + 400nm + 267nm + 200nm + 1600nm
$\omega + 2\omega + 3\omega + 4\omega + 0.5\omega$



Peak recollision ~ $7U_P$

High field here increases ionisation probability

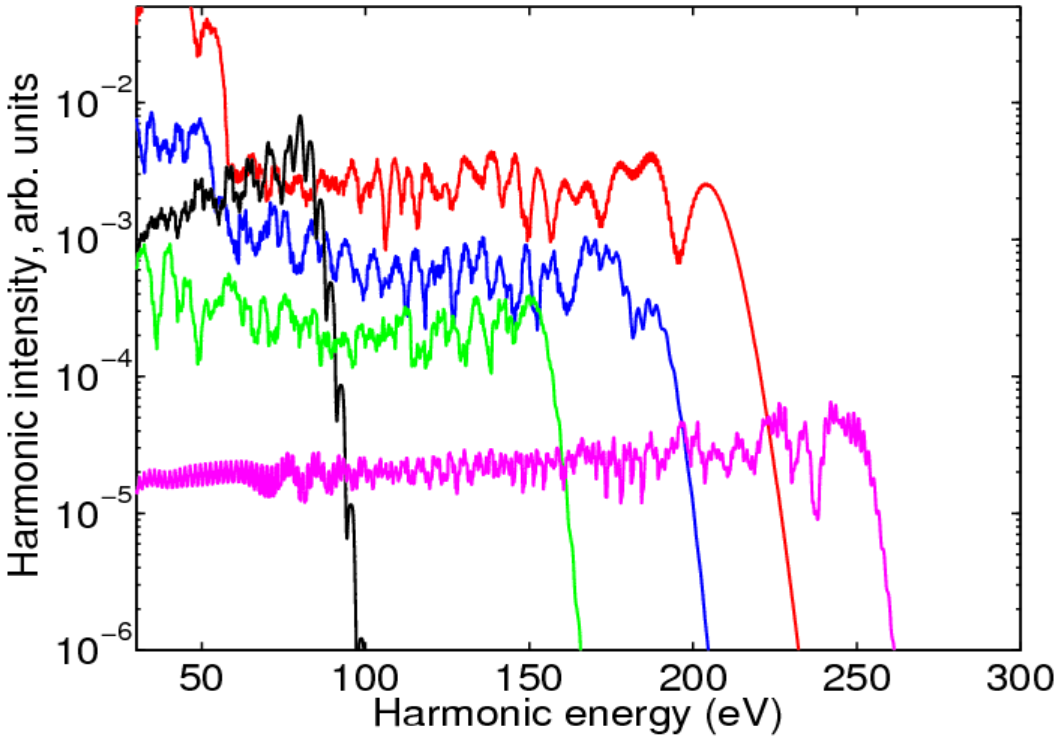
Genetic algorithm used to find optimum amplitudes and phases of fields

λ (nm)	Rel. Energy
1600	0.5
800	1
400	0.08
267	0.05
200	0.03

L. Chipperfield *et al.*, Phys. Rev. Lett. **102**, 063003 (2009)

The perfect wave

This waveform overcomes the efficiency reduction of using a long wavelength field



800nm

1200nm

1600nm

800 nm+1600 nm

Optimised:
800nm + 1600nm
+400nm + 267nm
+200nm

It works because the electron returns sooner, but still gains the high acceleration, compared to a longer wavelength.

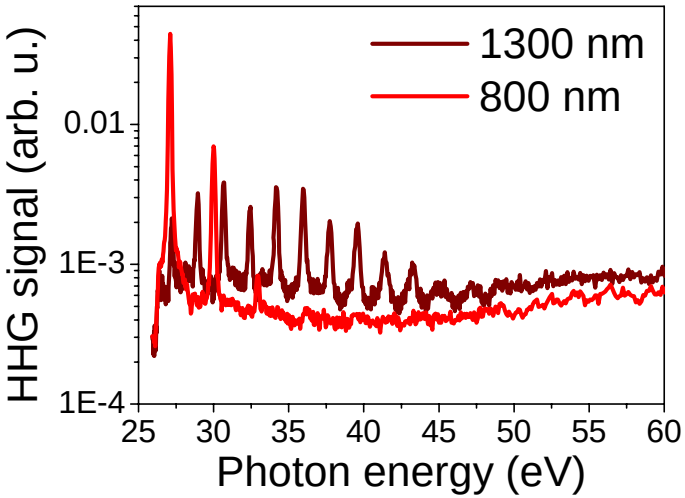
The results of this waveform are robust to propagation in a realistic experimental conditions.

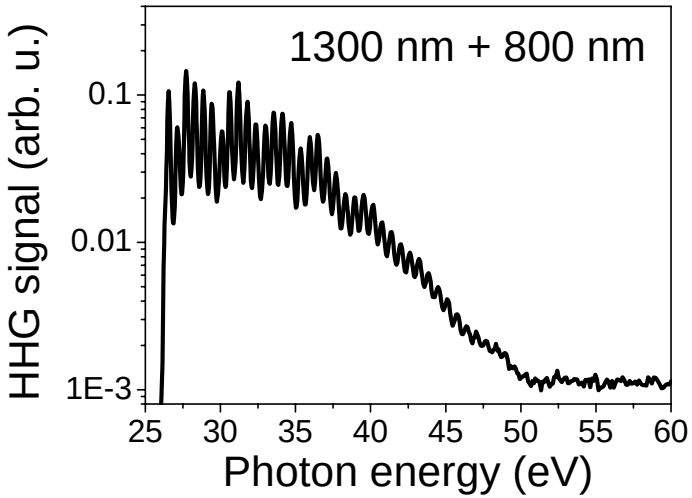
L. Chipperfield *et al.*, Phys. Rev. Lett. 102, 063003 (2009)

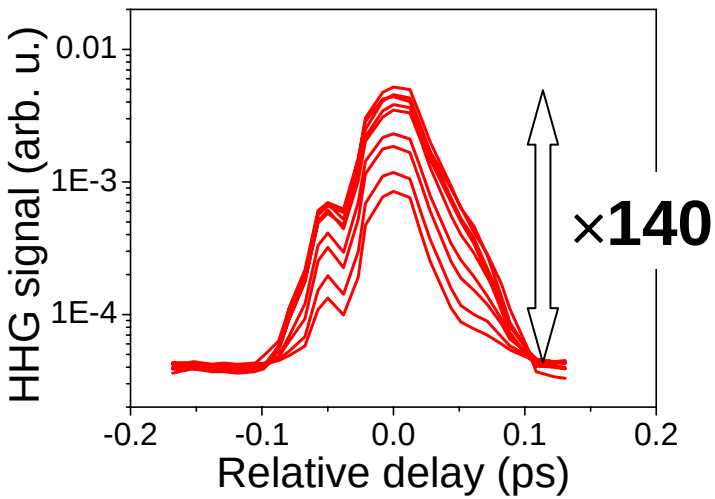
Two-colour HHG

HHG in Argon with **1300 nm** + **800 nm** (ω,1.6 ω)

$I_{1300nm} = I_{800nm} = 5\times10^{13}$ W/cm^2







Together with the appearance of intermediate harmonics we observe an enhancement of more than **two orders of magnitude** in harmonic intensity when the two pulses ω and 1.6 ω are overlapped.

Conclusions

- High harmonic generation has an enormous potential as an **ultrafast** probe of molecular systems.
- Part of the potential is due to our capability to **control** de measurements by controlling the target (**molecular alignment**) and the probe (**electron trajectories**).
- The use of high repetition rate (1 kHz) **mid-IR** laser sources is ideal to extend the number of harmonics available for imaging.
- A combination of pulses of **different wavelengths** can compensate the drop in efficiency of HHG in the mid-IR.
- The control of electron trajectories is essential to address some of the issues raised by the new ultrafast molecular imaging techniques.

Credits

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