



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

Probing Molecular Proton Dynamics with Chirp Encoded Electron Recollisions

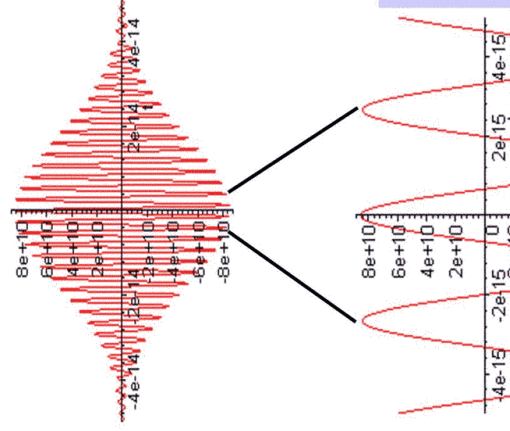
1. Review of sub-cycle electron dynamics and HHG
2. CEP (Carrier-Envelope Phase) determination directly from the HHG spectrum
3. Probing of proton dynamics in molecules using chirp encoded recollision.

S.Baker, J.Robinson, M. Lein (Heidelberg/Kassel), C.Chirila, C.Haworth, L.Chipperfield, P. L. Knight, J.W.G.Tisch and J. P. Marangos (Imperial College)

Attosecond Conference, Santa Barbara, 1st August 2006

Intense laser pulses provide high frequency electromagnetic waves of large amplitude.

~1 TW pulses are typically focused by a lens to a spot of area $1/1000^{\text{th}}$ cm^2 to give a peak intensity of 10^{15}Wcm^{-2}



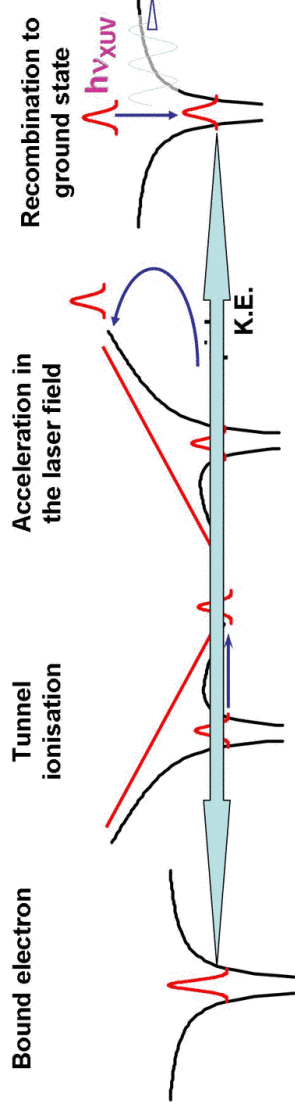
Huge electric fields
 $8 \times 10^{10} \text{V/m}$ (800 million Volts per cm) are generated in a pulse of peak intensity 10^{15}Wcm^{-2}

An electromagnetic wave oscillating at an optical frequency has a cycle period of a few femtoseconds (800nm period 2.66fs)

It is the objective of this work to use the carrier-wave frequency rather than the pulse envelope duration to provide the temporal resolution.

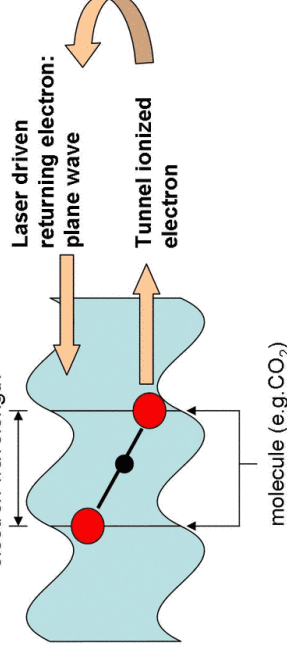
High harmonic generation occurs on a sub-optical cycle timescale

- Recollisional model of HHG: e.g. Corkum PRL 1993



HHG signal arises from coherent addition of contributions from atoms/molecules in the sample. For these contributions to add constructively initial and final states must be the same, giving the process a unique specificity.

The HHG process can be transparently formulated in the strong field approximation



Amplitude of HHG process determined by (c.f. Lewenstein et al 1994) :

$$D_x(t) = 2i \int_0^t dt' E(t') C(t-t') \int \frac{d^3 p}{(2\pi)^3} \bar{d}_x^*[\mathbf{p} + \mathbf{A}(t)] \times \bar{d}_x(\mathbf{p} + \mathbf{A}(t')) e^{-i \int_{t'}^t dt'' \{[\mathbf{p} + \mathbf{A}(t'')]^2 / 2 - E_0\}} + \text{c.c.},$$

Tunnel ionization from the molecular bound-state;

Propagation in the laser field;

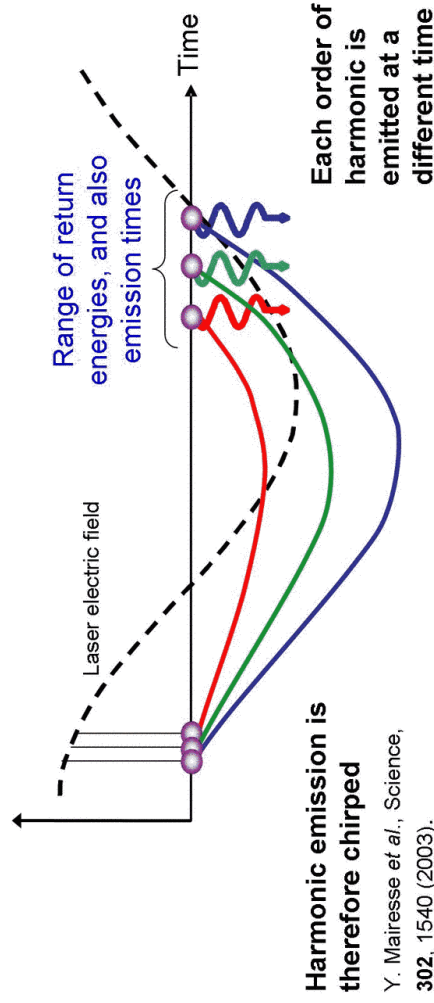
Recombination back into molecular bound-state.

The last factor plays a critical role in new methods to use HHG to image molecular structure in aligned molecular samples e.g. Tomographic reconstruction (Itatani et al Nature (2004)) or recombination step interference signatures studied by our group (Lein et al PRL (2002), Vozzi et al PRL (2005)) and Kanai et al Nature (2005).

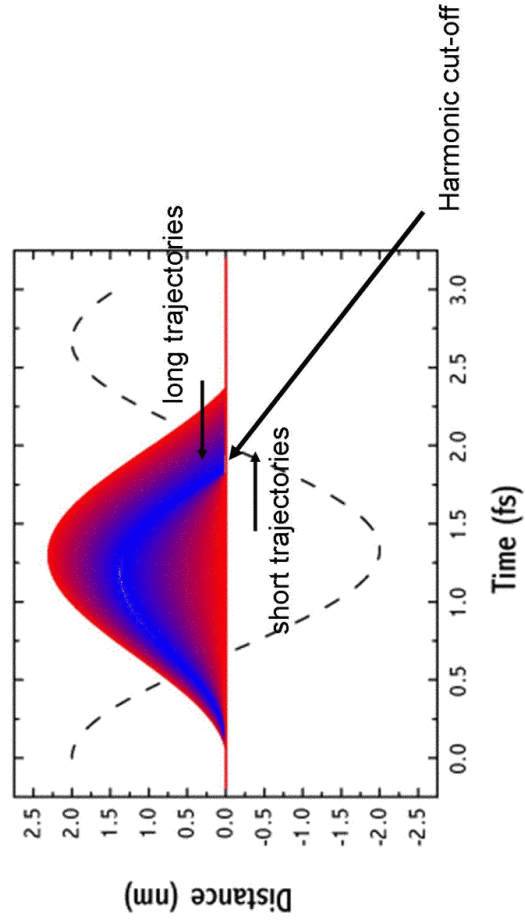
Temporal chirp of harmonic spectrum

Ionisation can occur for a range of times around the peak of the electric field.

Parts of the electron wavepacket born at different times follow different trajectories, and gain varying amounts of energy from the field.

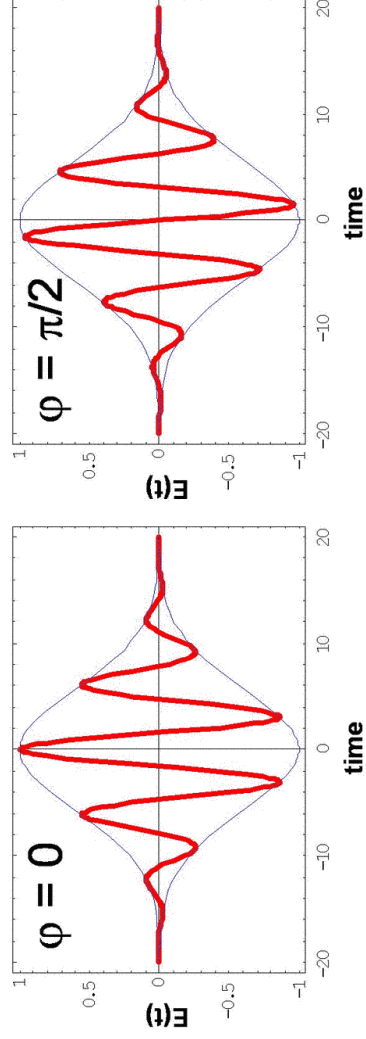


Temporal chirp of electron wavepacket



The E-field waveform of a few-cycle pulse is sensitive to the carrier-envelope phase

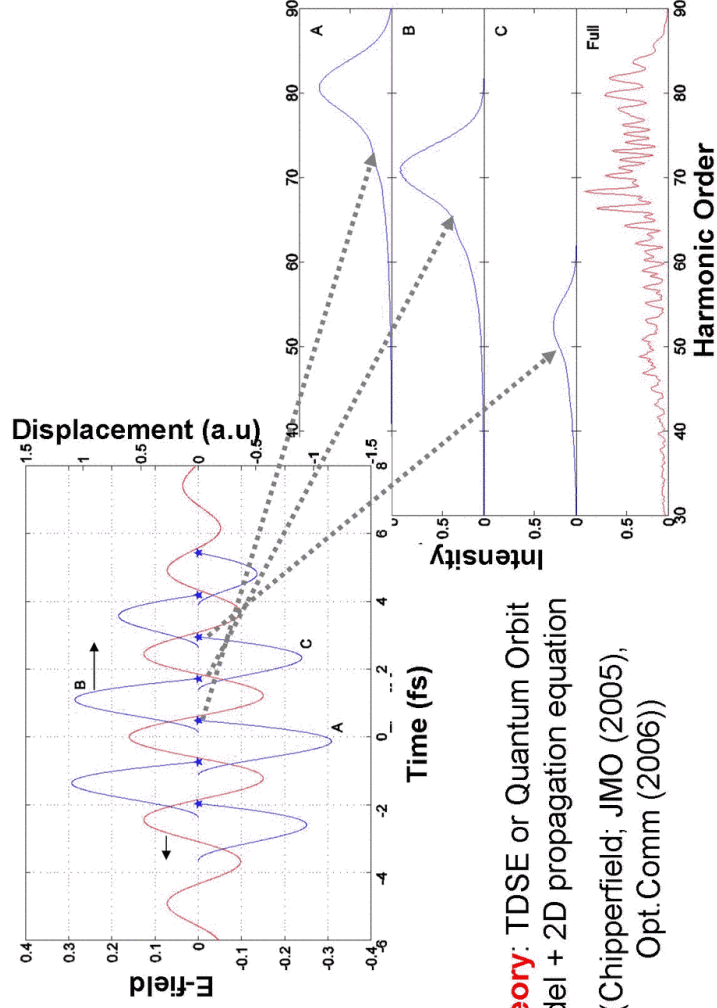
$$E(t) = E_o(t) \cos(\omega t + \varphi) \quad \text{CEP}$$



The CEP is an important parameter for many strong-field processes, e.g. attosecond pulse generation.

Determination of the value of CEP is a challenging problem

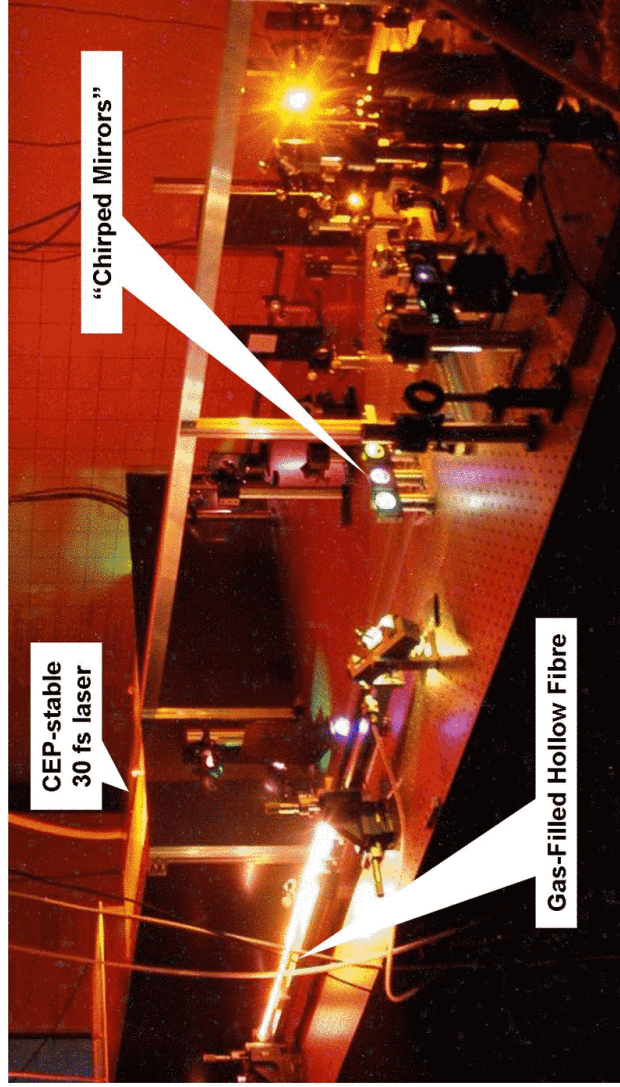
Our modelling showed that “half-cycle cut-offs” (HCO’s) can be used to measure CEP



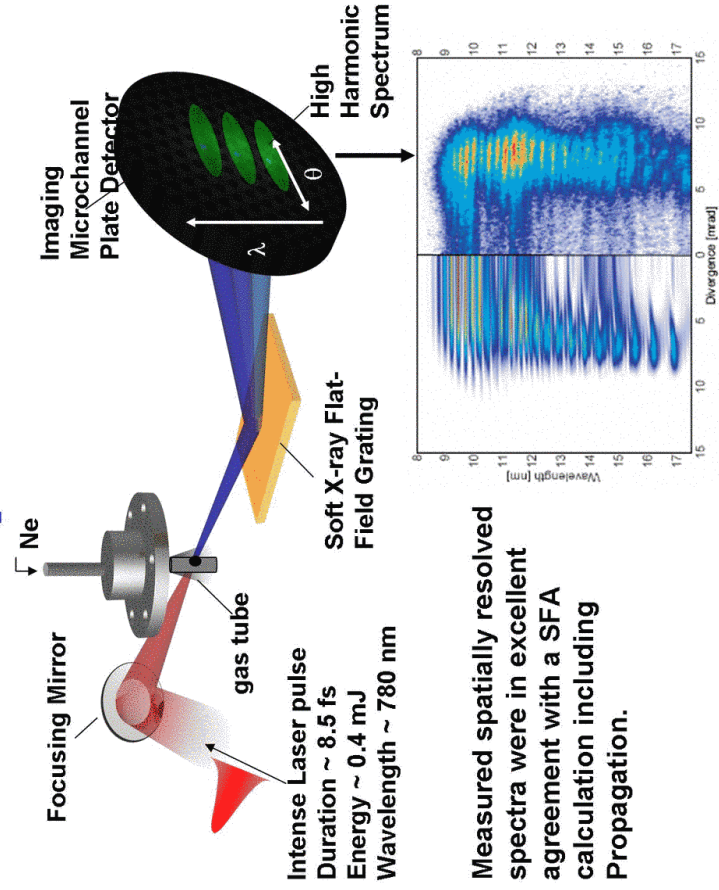
Theory: TDSE or Quantum Orbit model + 2D propagation equation

(Chipperfield; JMO (2005),
Opt.Comm (2006))

Imperial College few-cycle source 0.4mJ/6.5fs min. CEP-stable

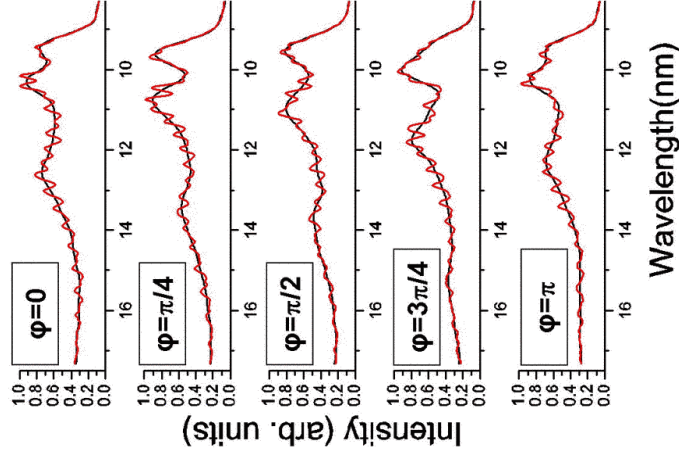


Harmonic spectra were measured with spatial resolution

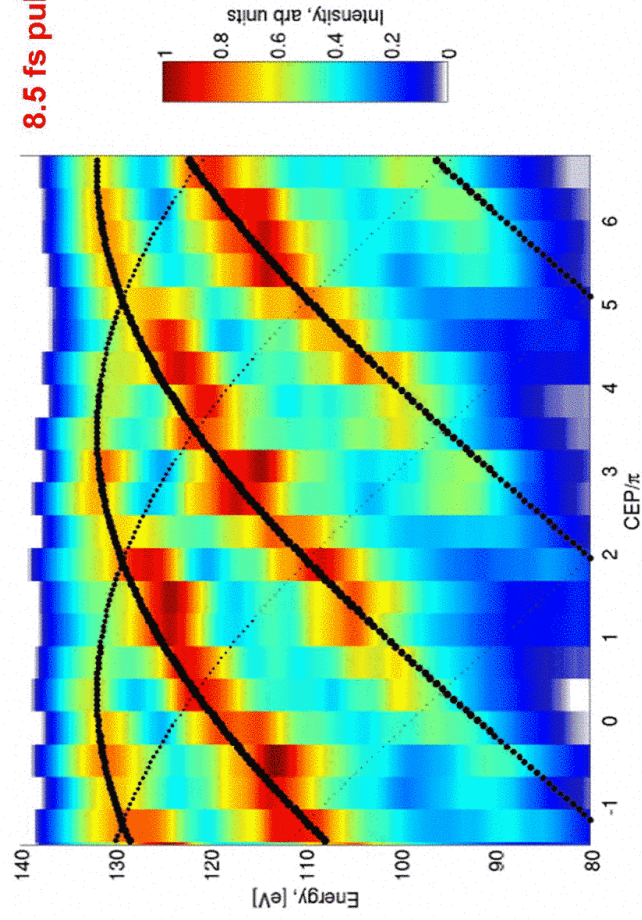


The HCOs are clear in the spatially-resolved lineouts and move as CEP varied.

8.5 fs pulse

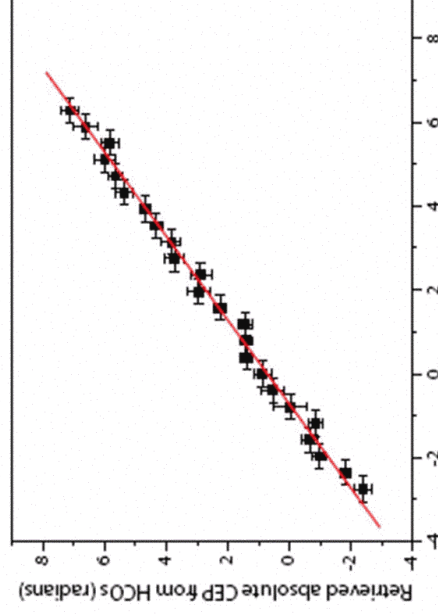


Excellent match between theory and experiment for HCO shifts as function of CEP



This provides basis for new CEP measurement technique !

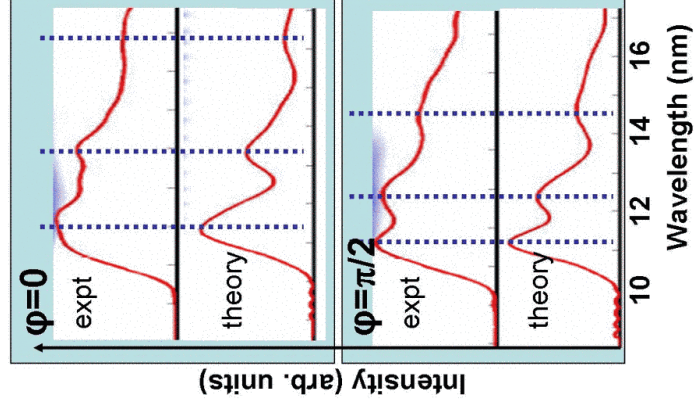
An algorithm for accurate CEP retrieval has been implemented



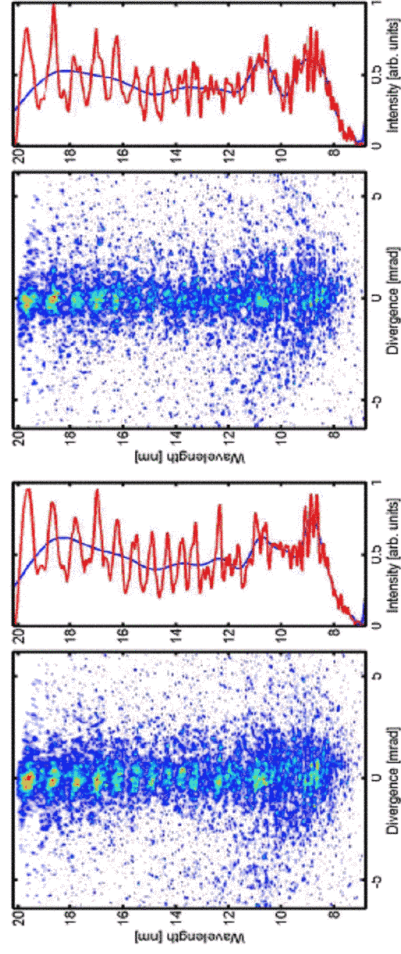
Relative CEP from phase stabilisation system (radians)

Retrieval of absolute CEP. Graph shows the absolute CEP retrieved with our fitting algorithm given the pulse from our FROG measurement, against relative CEP change from our phase stabilisation system. The y-errors are generated from the accuracy of fit given by the retrieval algorithm. The x-error is the RMS error in the phase stabilisation system lock. The red line is a linear fit to the data where the gradient has been fixed to 1. The CEP offset between the lock point and the absolute value is given by the y-intercept which is 0.72 ± 0.05 radians. This shows that we can measure the CEP to an accuracy of 50 mrad which corresponds to 20 attoseconds.

We can even measure the CEP for a 13 fs pulse (5 cycles)

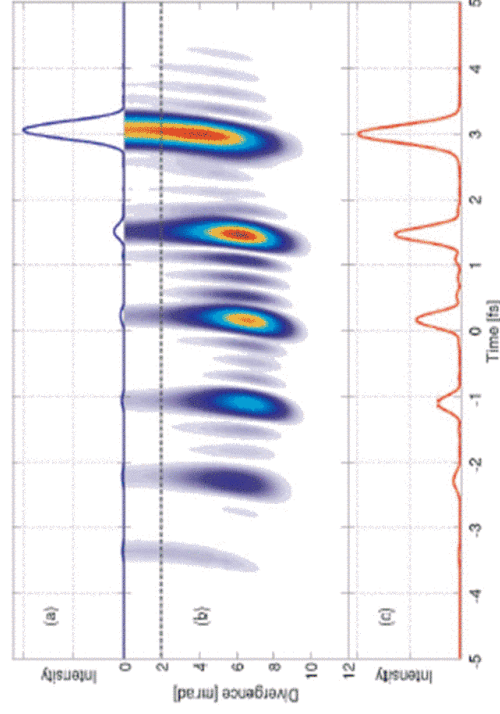


We can obtain sufficient signal for the retrieval of CEP from a single shot

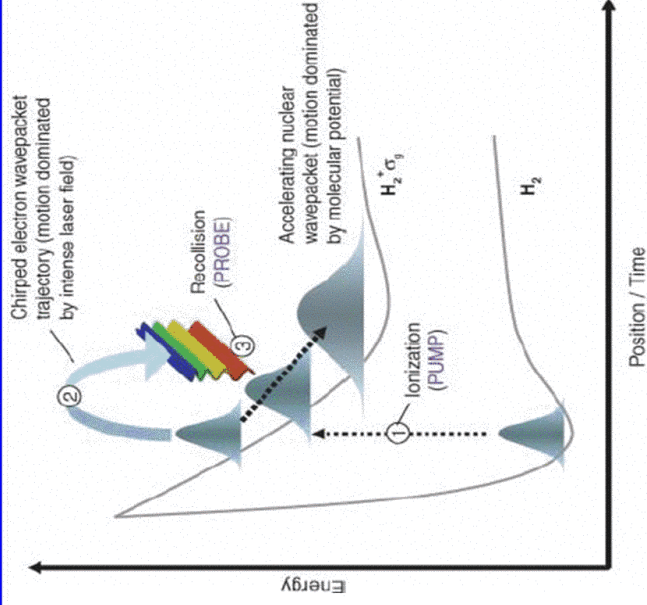


Single shot experimental high harmonic spectra generated with 8.5fs pulses, half-cycle cut-offs visible in smoothed line-out

Calculation shows that by appropriate spatial and spectral filtering tunable attosecond pulses can be produced



HHG from molecules can also be used to see fast nuclear dynamics in the molecular ion



Using HHG to probe ultrafast nuclear dynamics

Intensity of harmonic of frequency ω proportional to:

$$\omega^2 |a(k)v(k)|^2$$

$v(k)$ is the recombination amplitude: for a molecule

$$v(k) = \int \chi_0(R) \langle \Psi_0(R) | k | e^{i k x} \Psi_0^+(R) \rangle \chi(R, \tau(k)) dR$$

Vibrational wavefunctions (nuclear contribution) Electron travel time Electronic ground states

Overlap evolves in time because ionisation simultaneously launches a vibrational wavepacket on the ionic PES.

[Phys. Rev. Lett., **94**, 053004 (2005).]

Exploiting the temporal chirp of an harmonic spectrum

Lein showed [Phys. Rev. Lett., **94**, 053004 (2005)] that harmonic signal includes contribution from nuclear part of wavefunction:

Dipole moment responsible for HHG given by

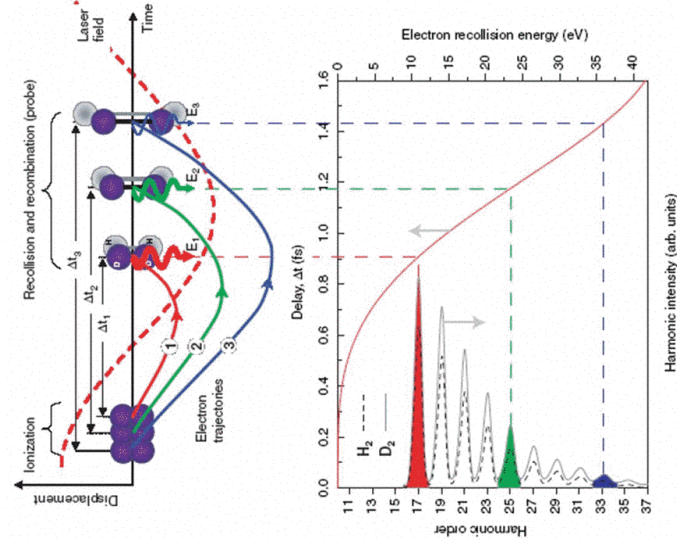
$$D_x(t) = 2i \int_0^t dt' E(t') C(t-t') \int \frac{d^3 p}{(2\pi)^3} \bar{d}_x^*[\mathbf{p} + \mathbf{A}(t)] \\ \times \bar{d}_x(\mathbf{p} + \mathbf{A}(t')) e^{-i \int_{t'}^t dt'' \{[\mathbf{p} + \mathbf{A}(t'')]^2 / 2 - E_0\}} + \text{c.c.},$$

where $C(t)$ is the “nuclear autocorrelation function”

$$C(\tau) = \int dR \chi^*(R, 0) \chi(R, \tau)$$

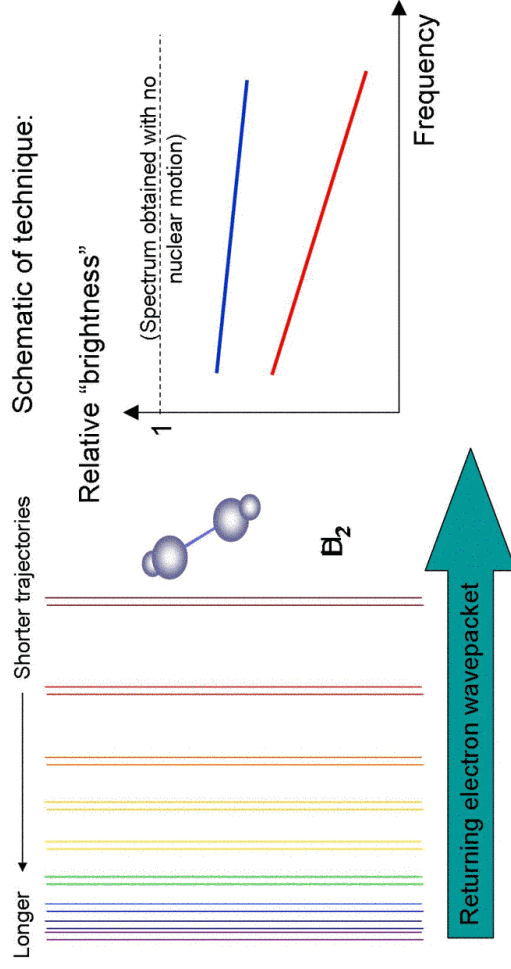
Wavefunction describing nuclear wavepacket

For the short trajectories selected in this experiment there is a well defined time to frequency encoding during the 0.6-1.6fs recollision interval



Exploiting the temporal chirp of an harmonic spectrum

To reveal effect of nuclear motion, need to “calibrate” for $a(k)$ factor
 – Lein suggests isotope comparison



Exploiting the temporal chirp of an harmonic spectrum

2 predictions:

1. Stronger harmonic signal in a heavy isotope
2. Ratio between signals $D_2:H_2$ increases with harmonic order

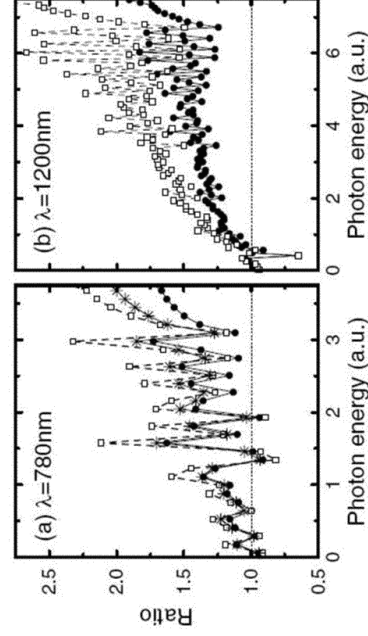


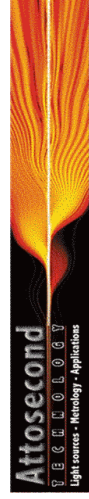
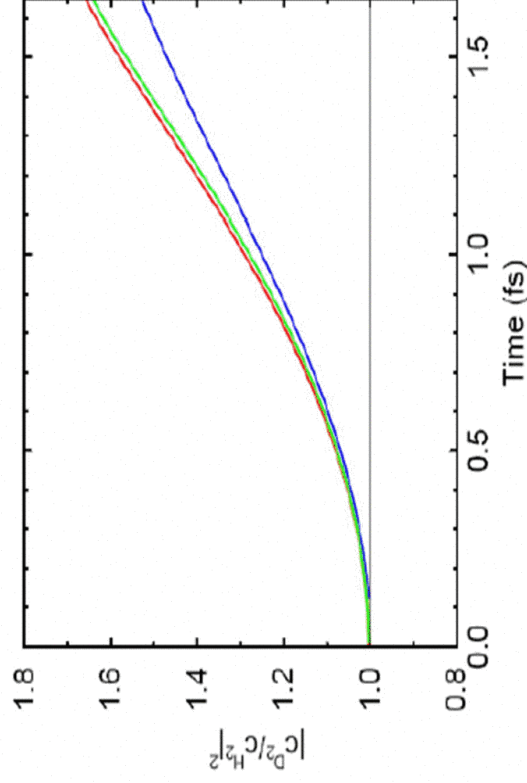
FIG. 2. Ratio between harmonic intensities in different isotopes (aligned perpendicular to the field): D_2 vs H_2 (circles connected by solid lines), T_2 vs H_2 (squares connected by dashed lines). Shown are the ratios for odd harmonics at 780 nm wavelength [panel (a)] and 1200 nm wavelength [panel (b)]. Panel (a) includes also the ratio D_2 vs H_2 for randomly oriented molecules (stars). The laser intensity is $4 \times 10^{14} \text{ W/cm}^2$.

Phys. Rev. Lett., **94**,
053004 (2005)

Strong order-to-order
variation due to interference
between short and long
trajectories.

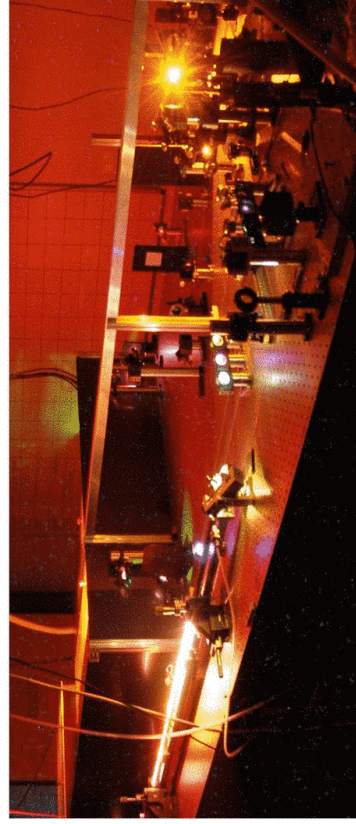
Modelling has included two-centre interference and Stark shifts

Figure S1. Ratio of the nuclear correlation functions in D_2 and H_2 as a function of time using different approximations: no interference and no Stark shift included (blue); with interference but no Stark shift included (green); with interference and Stark shift approximately included (red).



This measurement uses our high intensity few-cycle laser system to drive HHG in the molecules

Requires short (<~10fs) pulses to avoid “disturbance” of molecule prior to ionisation. In particular ionization occurs only in the few-cycles $\sim 2 \times 10^{14} \text{ Wcm}^{-2}$.



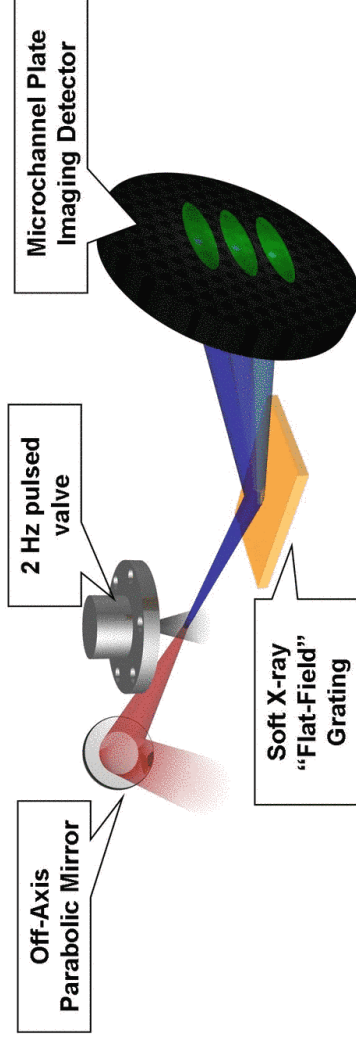
1 kHz, 7-8 fs, 0.25 mJ.

Experimental approach

Focus 9 mm before jet to isolate short trajectories.

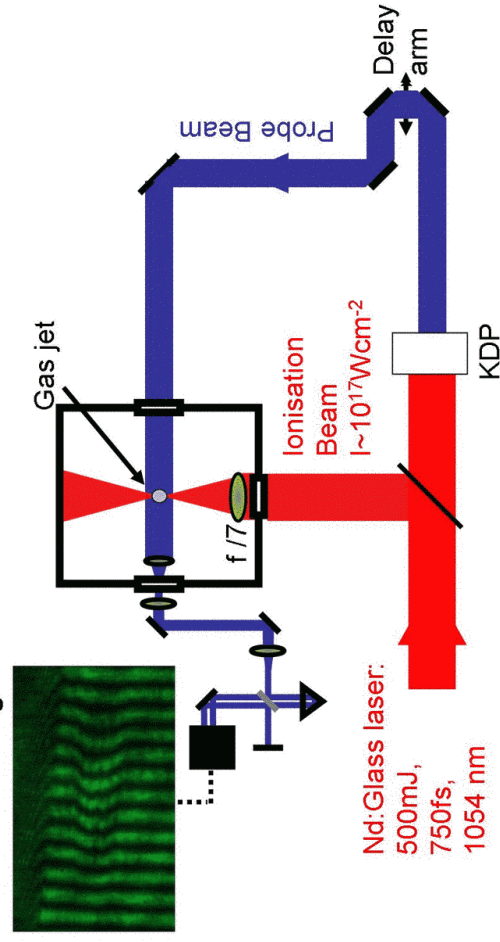
Intensity delivered at interaction region: $2 \times 10^{14} \text{ Wcm}^{-2}$: shot-to-shot fluctuation <3%, **monitored between data runs.**

Apply correct gas jet backing pressures to ensure equal gas densities at the interaction region.

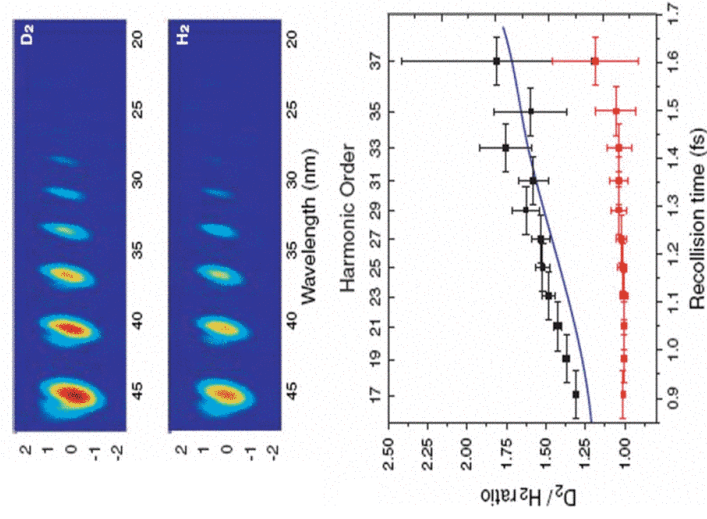


Experimental approach

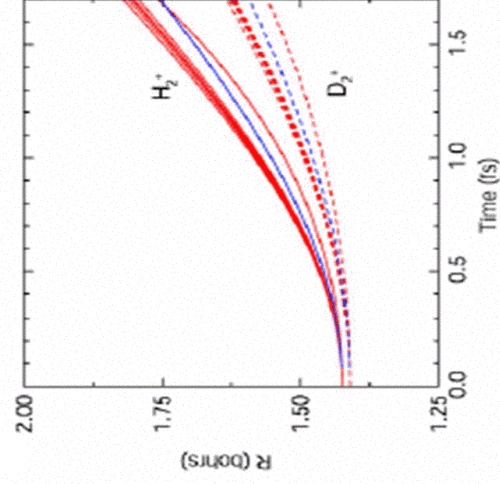
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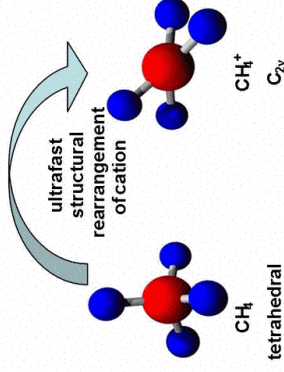
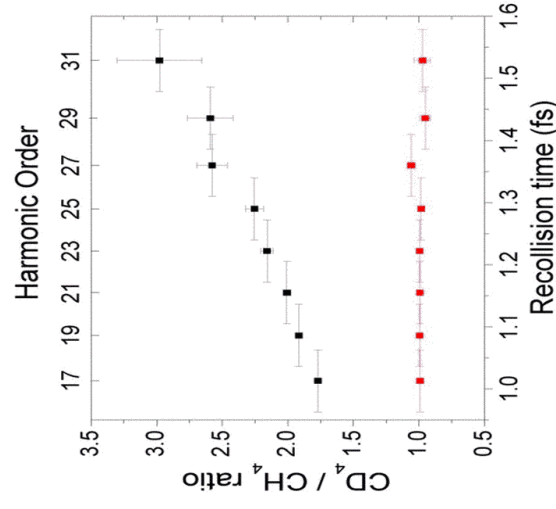
Experiment Confirms These Predictions



And the proton dynamics can be reconstructed from the H_2/D_2 ratio



The nuclear autocorrelation function ratio between CH_4 and CD_4 provides the first evidence of an ultra-fast rearrangement of methane upon ionisation



Baker *et al* Science **312**, 424 (2006)

Conclusions and further work

- Carrier envelope phase can be directly determined from HHG spectra.
- Proton dynamics can be imaged using inherent chirp within the harmonic emission process
- Experiments are underway to track proton dynamics over a longer timescale using longer wavelengths (using IR OPA at ALLS facility in Montreal)
- This technique is applicable in principle to measurement of electronic dynamics also.

