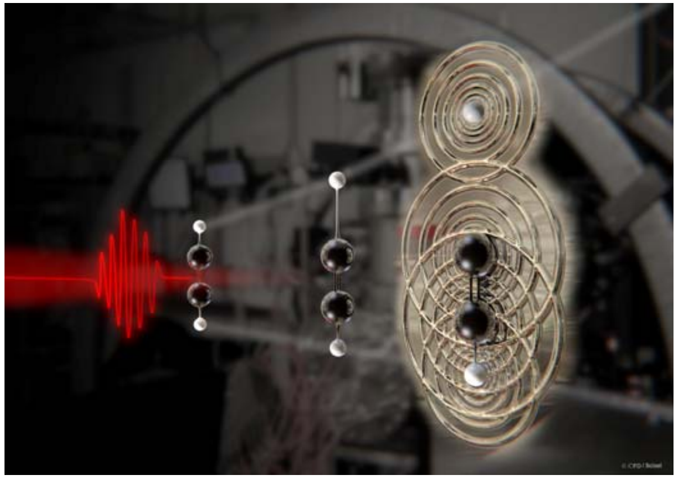
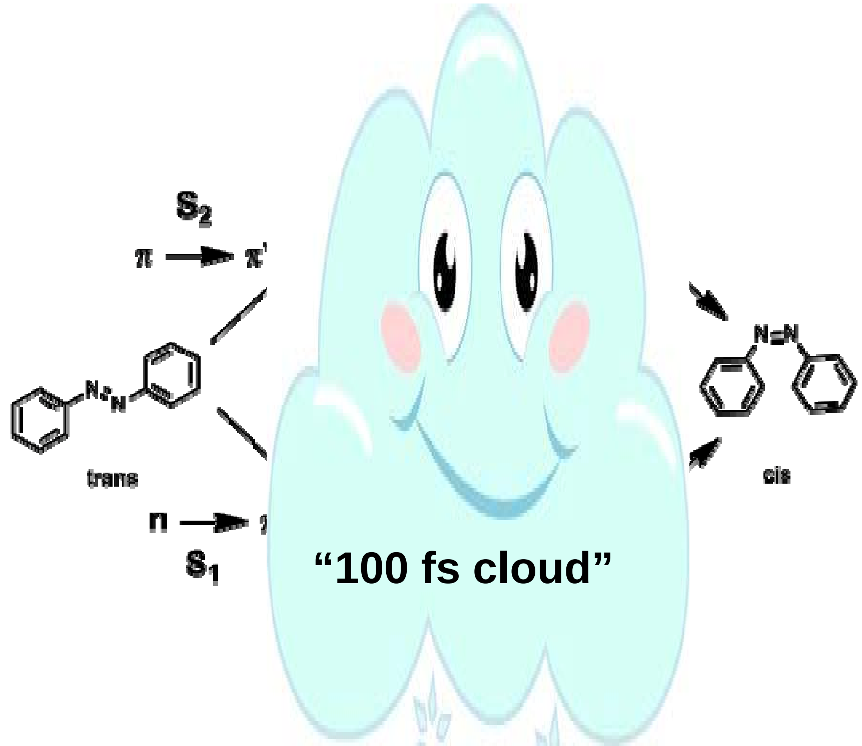
Imaging molecular bond breaking with one electron



B. Wolter, M. G. Pullen, A.-T. Le, M. Baudisch, K. Doblhoff-Dier, A. Senftleben, M. Hemmer, C. D. Schröter, J. Ullrich, T. Pfeifer, R. Moshammer, S. Gräfe, O. Vendrell, C. D. Lin, J. Biegert

ICFO - The Institute of Photonic Sciences
The Barcelona Institute of Science and Technology
08860 Castelldefels (Barcelona), Spain
atto.icfo.eu

Motivation for our research



How does this work?

Probing some electronic transitions wil tand structural change

Image transformation of the entire s !

A.A. Beharry, G.A. Woolley Chem. Soc. Rev. 40, 4422 (2011)

Atomic-scale imaging with photons

Tools are needed to scrutinize electronic dynamics on its native length and timescale.

- **Ultrafast X-Ray Diffraction (UXD)**

  C.W. Siders et al. Science 86, 1340(1999)

  - X-Ray Synchrotron / FEL: 100 fs -10 fs, 1.9Å

    M-B€
    synchronization / random pulses
    radiation doses

  - keV High Harmonic Generation: as - fs

    Ch. Spielmann et al. Science 278, 661 (1997)
    T. Popmintchev et al. Science 336, 1287 (2012)

    low yield wavelengths long
    broadband imaging problem

Atomic-scale imaging with electrons

Ultrafast Electron Diffraction/Microscopy (UED/UEM)

M. Dantus et al. J. Phys. Chem. 98, 2782 (1994) B.J. Siwick et al. Science 302, 1382 (2003)

W.E. King et al. J. Appl. Phys. 97, 111101 (2005) V.A. Lobastov et al. PNAS 102, 7069 (2005) **and many others…**

Challenges: **Coulomb repulsion (temporal resolution)**

Incoherent scattering (S/N - single molecule)

Solids

C. Gerbig et al. New J. Phys. 17, 043050 (2015)

M. Müller et al. ACS Photonics, 3, 611 (2016)

A. Ryabov et al. Science 353, 374 (2016)

B. Schröder et al. Appl. Phys. Lett. 107, 231105 (2016)

~10 fs, pm

Molecules (ensamble avg'ed)

C.J. Hensley et al. Phys. Rev. Lett. 109, 133202 (2012)

J. Yang et al. Nature Commun. 7, 11232 (2016)

J. Yang et al. Phys. Rev. Lett. 117, 153002 (2016)

Y. Ito et al. Struct. Dyn. 3, 034303 (2016)

~100 fs, pm

Diatomics

M. Meckel et al., Science 320, 1478–1482 (2008)

C. Blaga et al. Nature 483, 7388 (2012)

<10 fs, pm

Single molecules

M. Pullen et al., Nature Commun. 6, 7262 (2015)

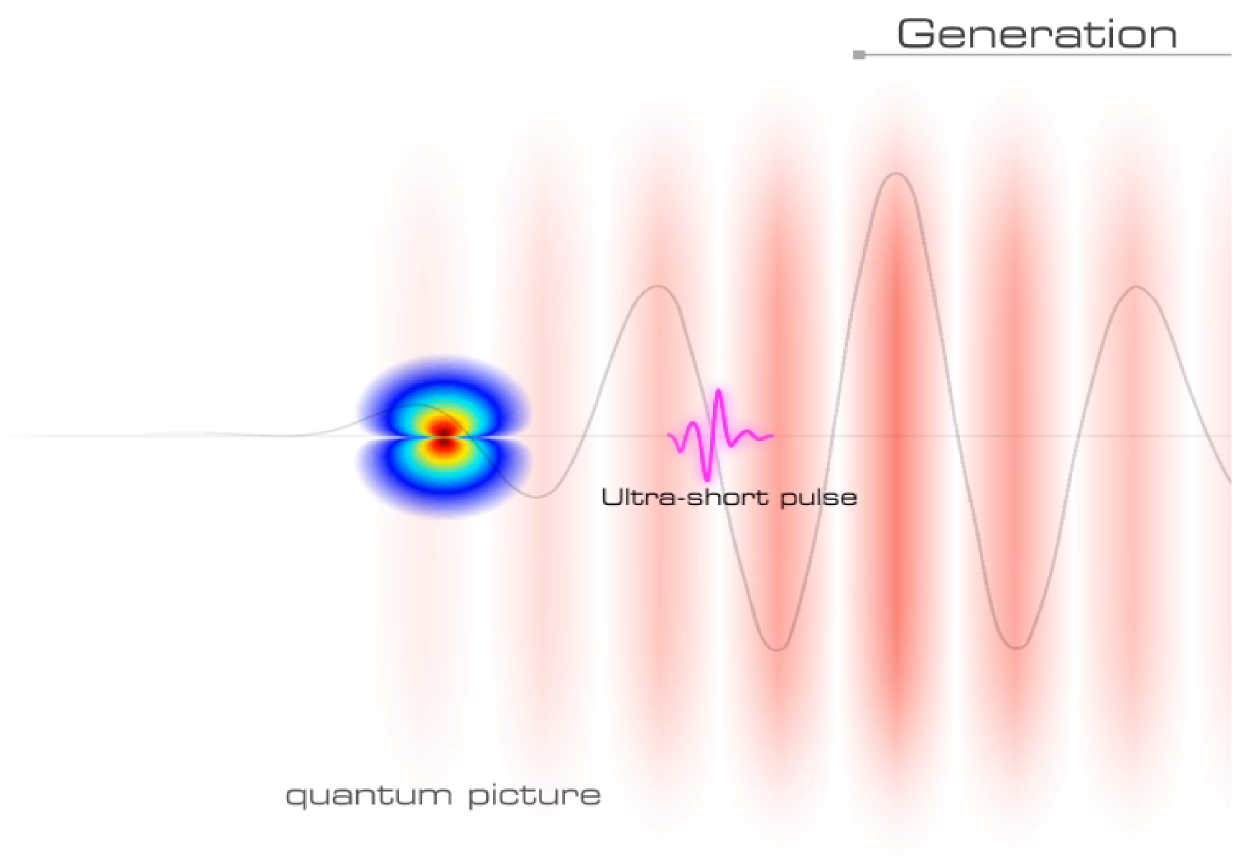
M. Pullen et al. Nature Commun. 7, 11922 (2016)

B. Wolter et al. Science 354, 308 (2016)

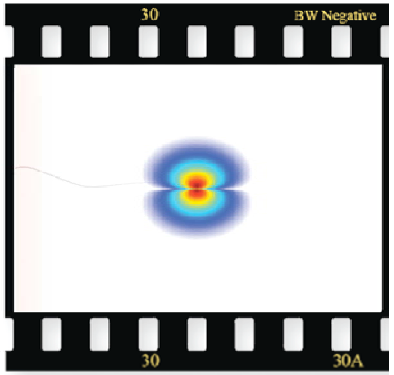
<1 fs, pm

R.J.D. Miller Faraday Discuss.194, 777 (201

Laser-driven recollision



Field Driven Recollision



"Field free"

... calculated with Qprop - thanks to D. Bauer, Rostock

Ponderomotive energy: $U_P \propto I \cdot \lambda^2$ Photons: $3.2 U_P$ Electrons: $10 U_P$

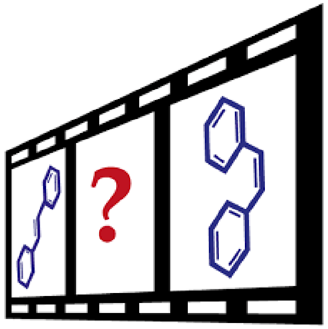
Why it is interesting:
- **Sub-cycle electron / photon pulses**

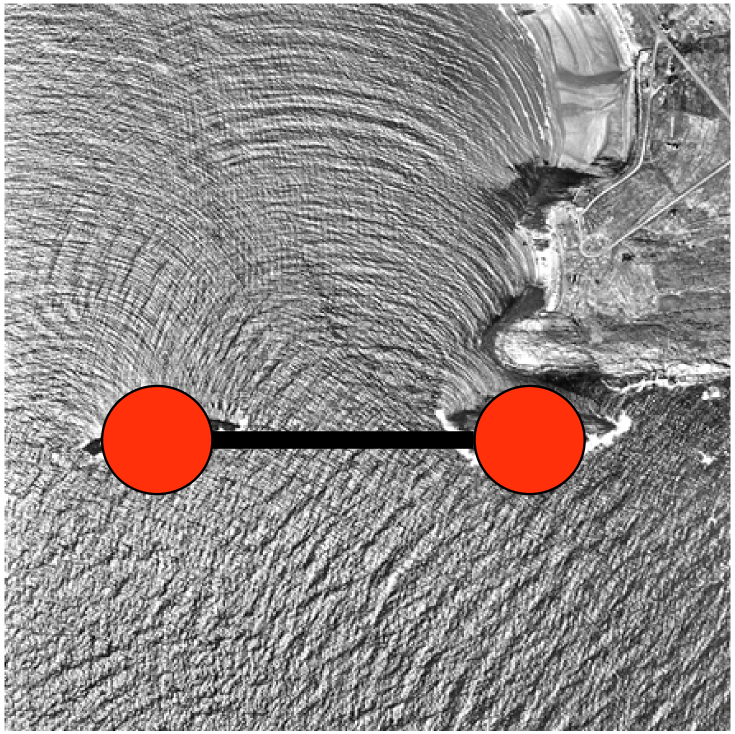
Why it is challenging:
- **Full control over the electric field of a laser pulse** (stability, CEP, few-cycle)
- **Low cross sections require high avg. power sources** (rep. rate)

Space-time imaging of molecules

How does a chemical bond break or form?

When and why does a molecule change its shape (function)?



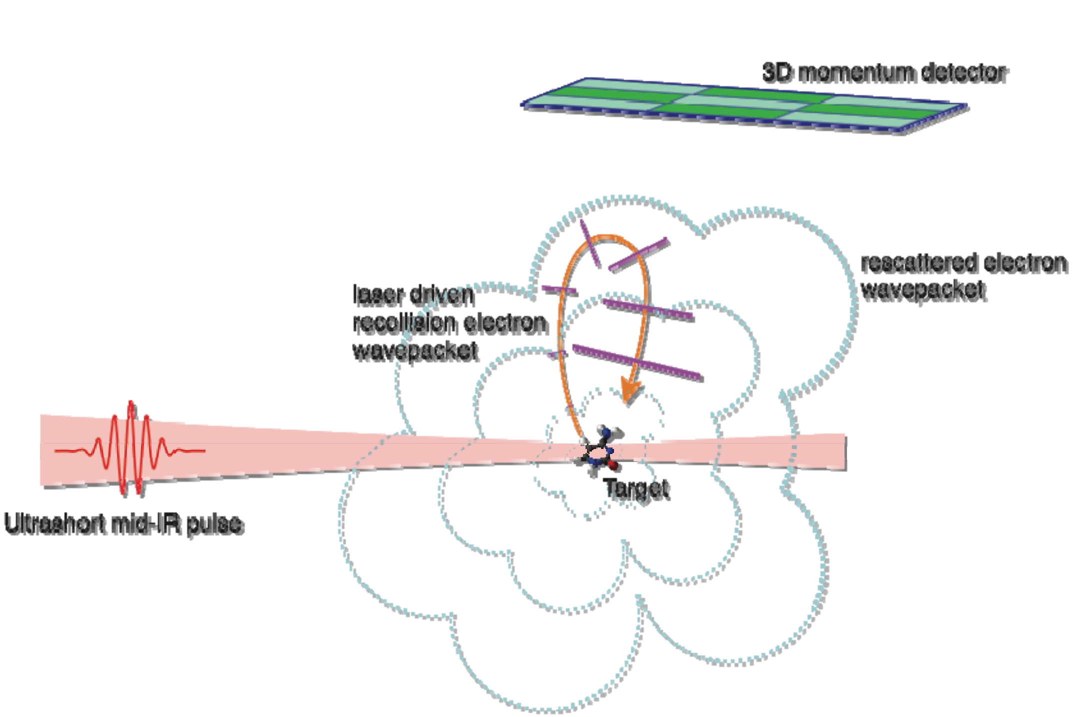


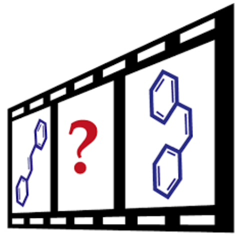
1. spatial resolution: ~ pm

2. temporal resolution: “a few” fs

- **Interference to image**
- **Electron waves**
- **Attosecond wave packets**

Space-time imaging of molecular structure





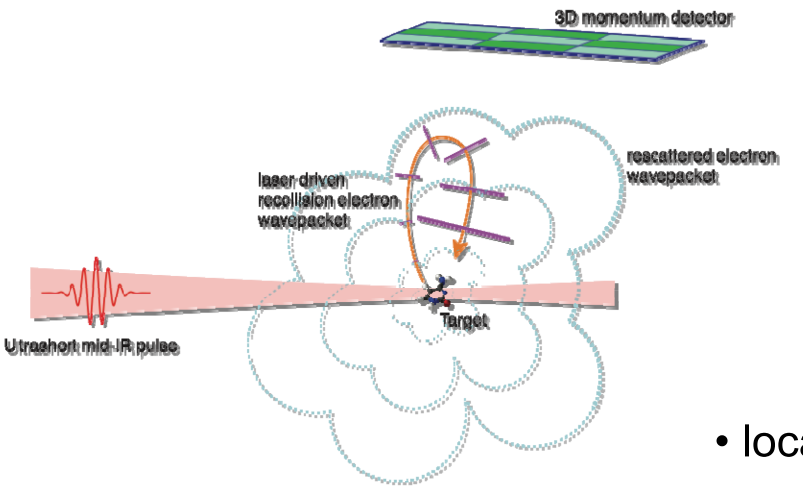
- No space charge issue - ~1 electron imaging
- Sub-cycle timing - attosecond resolution
- σ~5 orders higher than x-rays
- Coherent electron scattering
- UED: J~10^7 A/cm^2 versus LIED: J~10^{11} A/cm^2

T. Zuo et al. Chem. Phys. Lett. 259, 313 (1996)

M. Lein et al. Phys. Rev. A 66, 051404 (2002)

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

Space-time imaging of molecules



Why ~~is~~ was this difficult to do?

- locating cores with high impact energy (Cb shielding)

  recollision (10 U_p)

- discriminate from direct ionisation

  measure in 3D

- plane wave scattering

  mid-IR recollision

- correct for laser field for field free DCS

  mid-IR recollision

M. Pullen et al., Nature Commun. 6, 7262 (2015)

M. Pullen et al. Nature Commun. 7, 11922 (2016)

160 kHz

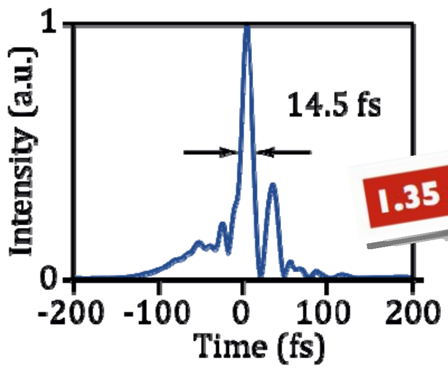
2.9 - 9 cycles (32 - 98 fs) - up to 21 W

3200 nm

CEP stable

power 0.9% rms, 2% PP, 44h **(293d @ 1 kHz)**

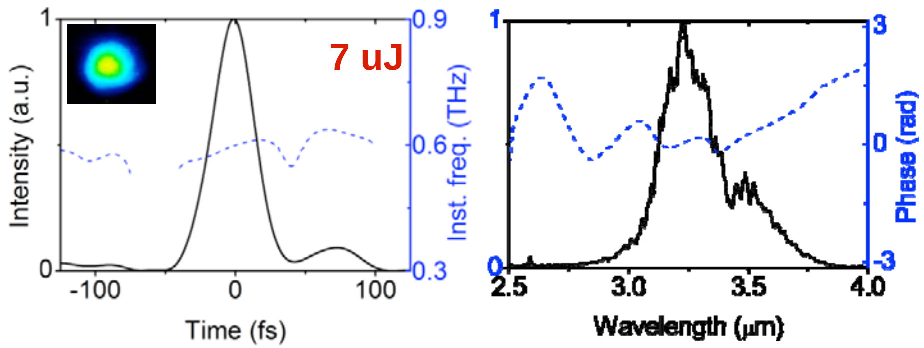
3300 nm, 1600 nm, 800 nm, 400-180 nm



60 uJ

1.35 cycles at 9.6 W

U. Elu et al. Optica in press

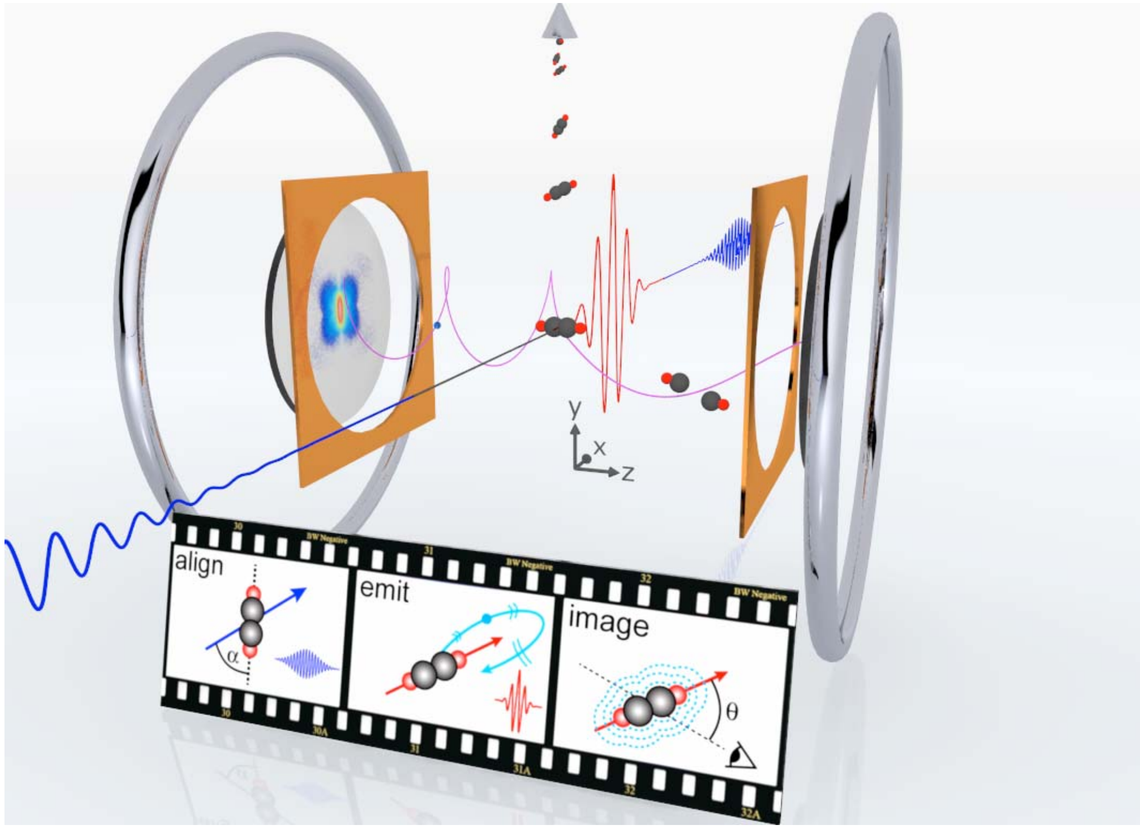


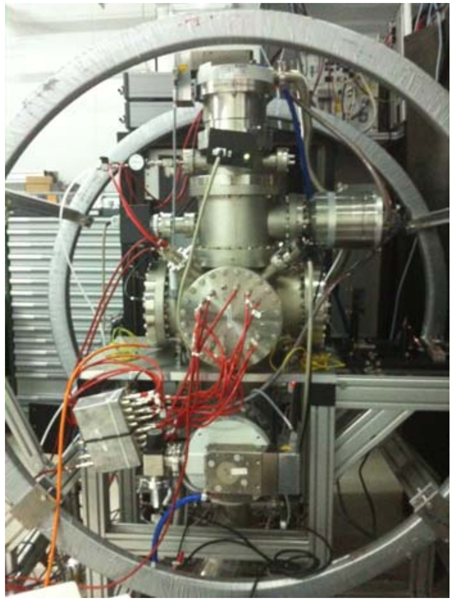
32 fs (2.9 cycles)

O. Chalus et al. Opt. Exp.16, 21297 (2008)
F. Silva et al. Nature Commun. 3, 807 (2012)

M. Hemmer et al. Opt. Exp. 22, 028095 (2013)
M. Baudisch et al. J. Optics 17, 094002 (2015)

3D coincidence detection





$\Delta P_{parallel}$ = 0.012 a.u. (2 meV)
ΔP_{trans} = 0.025 a.u. (8.5 meV)
10^{-11} mbar

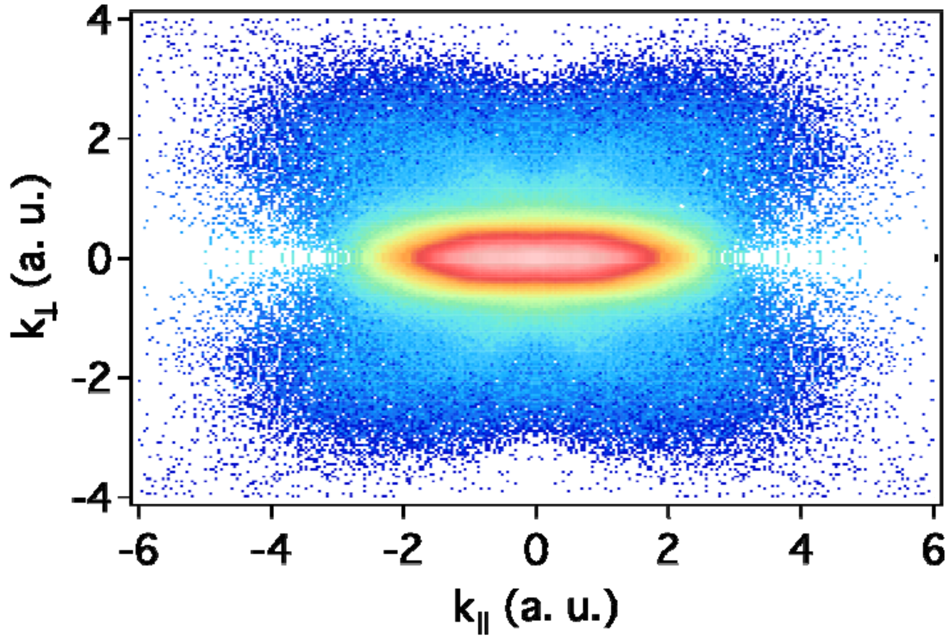
R. Moshammer, T. Pfeifer,
J. Ullrich, A. Senftleben

J. Ullrich et al. Nucl. Instrum. Meth. 108, 425 (1996)

B. Wolter et al. Phys. Rev. X 5, 021034 (2015)

Space-time imaging of acetylene

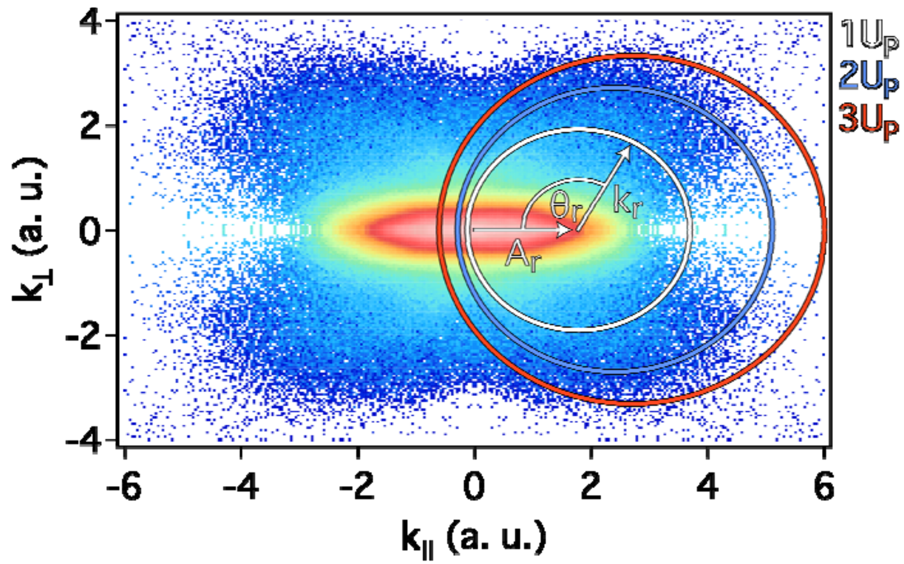
A.-T. Le, X. Wang, C.D. Lin
K. Doblhoff-Dier, S. Gräfe
O. Vendrell



M. Pullen et al., Nature Commun. 6, 7262 (2015)

B. Wolter et al. Phys. Rev. X 5, 021034 (2015)

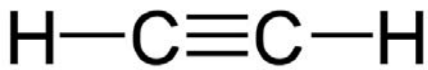
Data Extraction - Bond Length

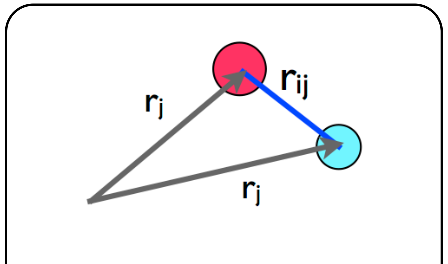


A.-T. Le, X. Wang, C.D. Lin

K. Doblhoff-Dier, S. Gräfe

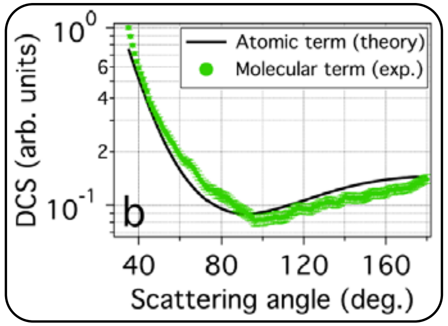
O. Vendrell



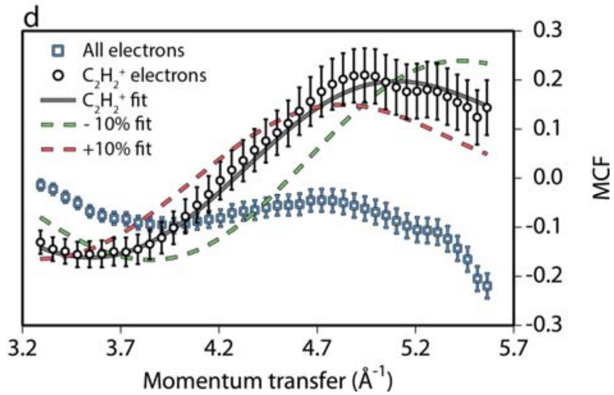


$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = 2\pi/q_{ij}$

$\frac{d\sigma}{d\Omega}(p_r,\theta) \propto \left| \int \rho(\mathbf{r}) e^{-iq(p_r,\theta)\mathbf{r}} d\mathbf{r} \right|^2$



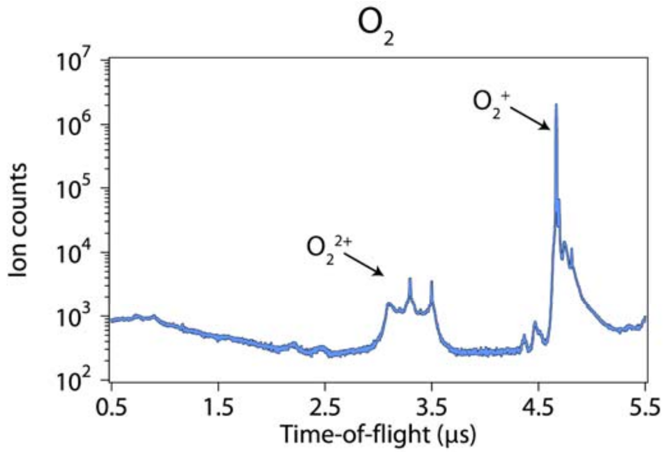
$D_{\text{QRS}}(\mathbf{p}_{\text{det}}) = \frac{d\sigma}{d\Omega}(\mathbf{p}_r) W(p_r)$

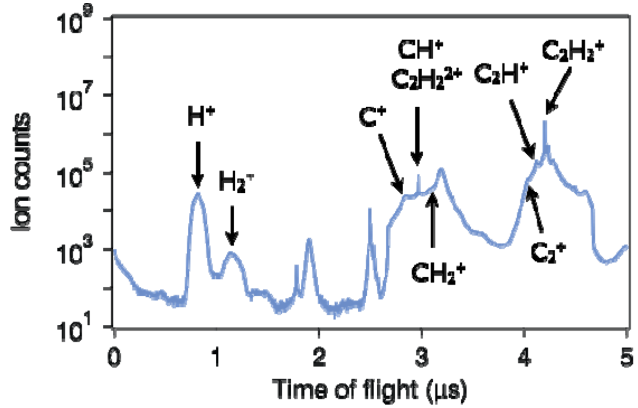


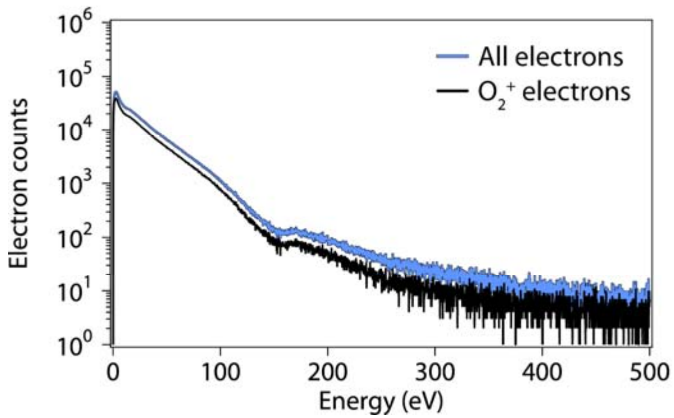
C. Blaga et al. Nature 483, 7388 (2012) M. Pullen et al. Nature Commun. 6, 7262 (2015) B. Wolter et al. Phys. Rev. X 5, 021034 (2015)

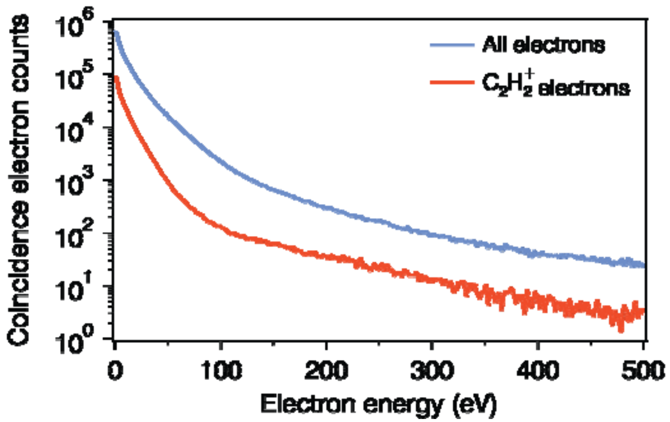
An additional challenge

C. I. Blaga et al. Nature. 483, 194 (2012)





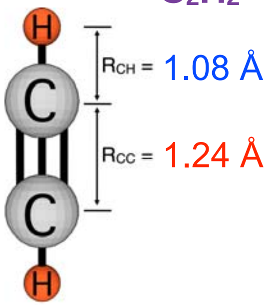




M. Pullen et al. Nature Commun. 6, 7262 (2015) M. Pullen et al. Nature Commun. 7, 11922 (2016)

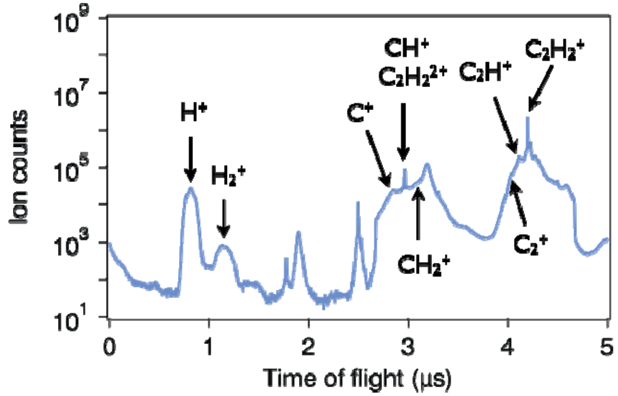
An additional challenge

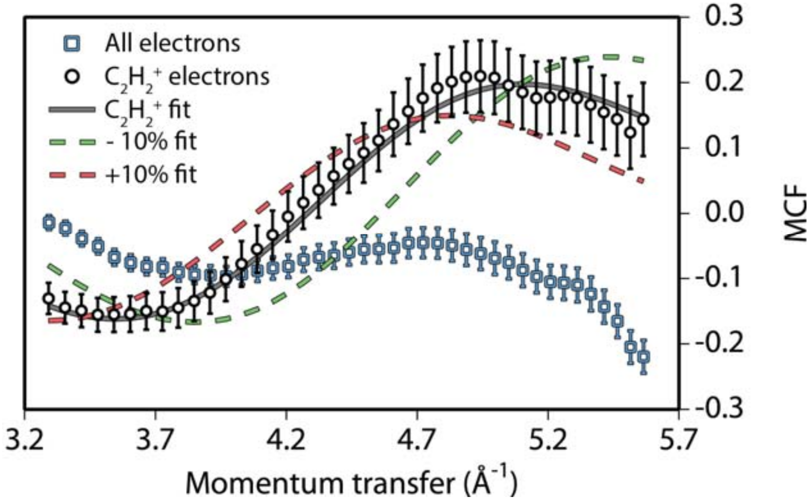
$C_2H_2^+$



$$D_{CH}^{AA} = (1.10 \pm 0.02)\text{Å}$$

$$D_{CC}^{AA} = (1.22 \pm 0.01)\text{Å}$$



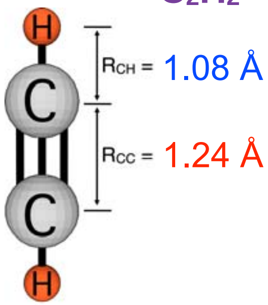


Data tagging permits isolating different pathways

M. Pullen et al. Nature Commun. 6, 7262 (2015) M. Pullen et al. Nature Commun. 7, 11922 (2016)

Space-time imaging of molecular structure

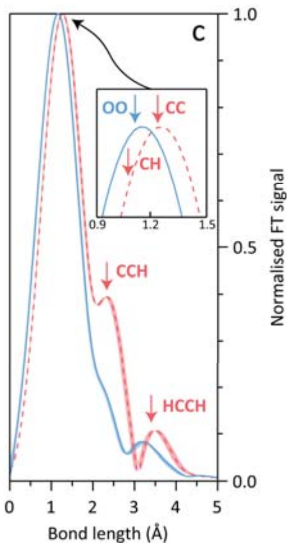
$C_2H_2^+$



$$D^{AA}_{CH} = (1.10 \pm 0.02)\text{Å}$$

$$D^{AA}_{CC} = (1.22 \pm 0.01)\text{Å}$$

- ❖ **First MIR-LIED imaging of a polyatomic molecule**
- ❖ **Retrieval of the entire molecular structure**
- ❖ **Bond length errors ~5% (LCLS 15% but photons)**



- ❖ **FT-LIED/FABLES imaging of C_2H_2 and O_2**

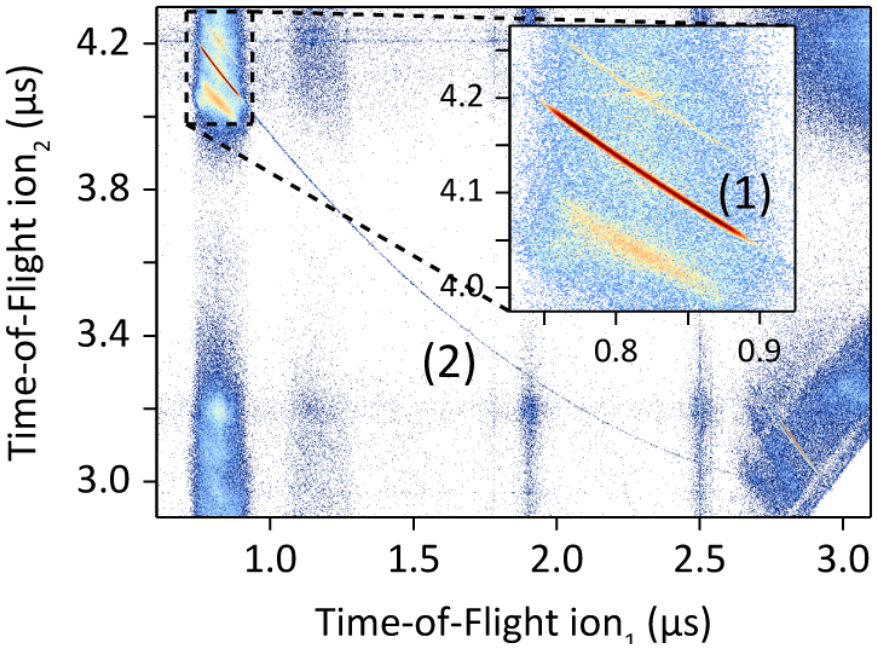
J. Xu et al. Nature Commun. 5, 4635 (2014). M. Pullen et al. Nature Commun. 7, 11922 (2016)

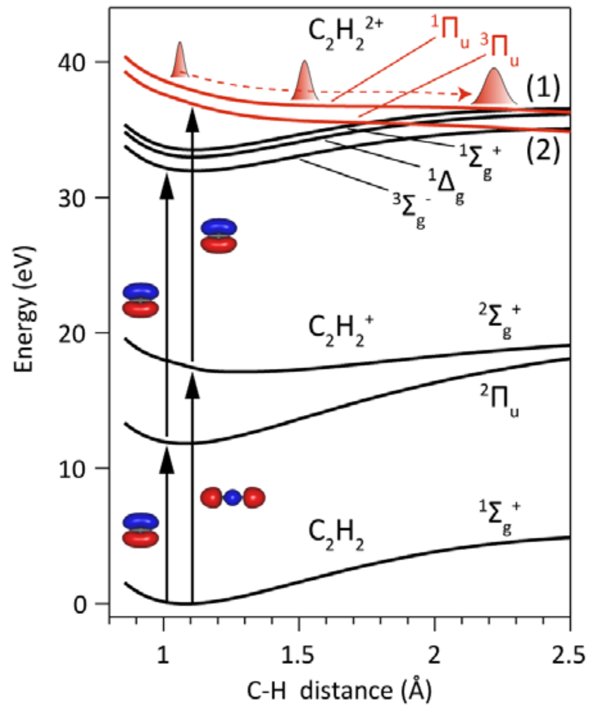
- ❖ **Dynamic imaging of C60**

collab. C. Blaga, L. DiMauro, M. Kling

B. Wolter et al. Phys. Rev. X 5, 021034 (2015) M. Pullen et al. Nature Commun. 6, 7262 (2015)

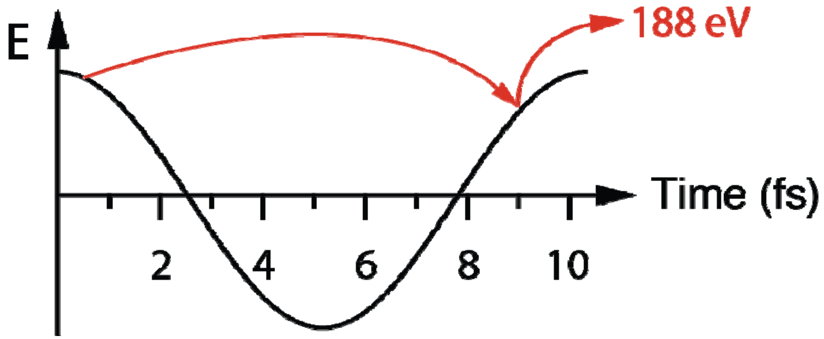
Photoion photoion coincidence (PiPiCo)





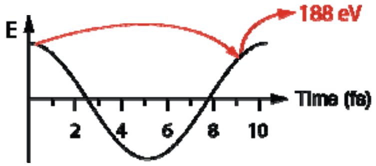
B. Wolter et al. Science 354, 308 (2016)

Space-time imaging of molecular structure



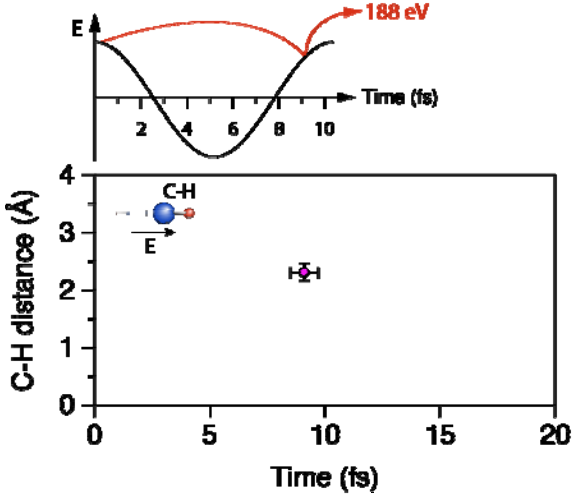
B. Wolter et al. Science 354, 308 (2016)

Space-time imaging of molecular structure



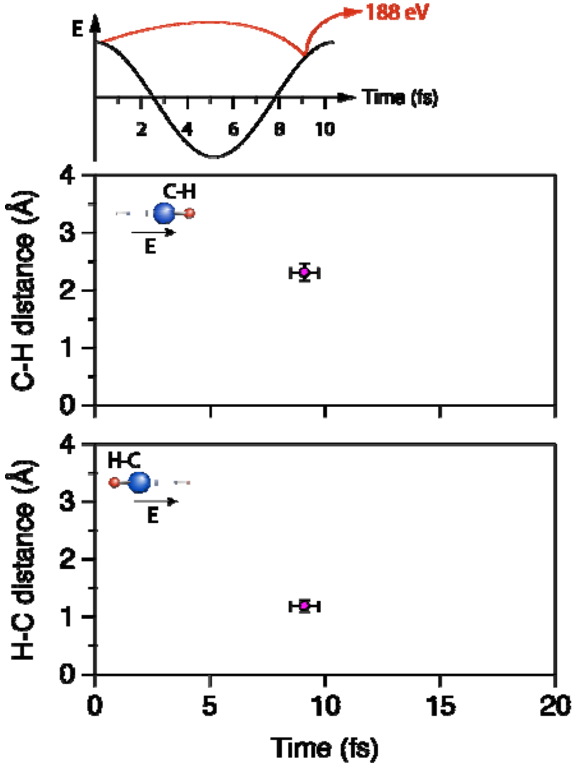
B. Wolter et al. Science 354, 308 (2016)

Space-time imaging of molecular structure



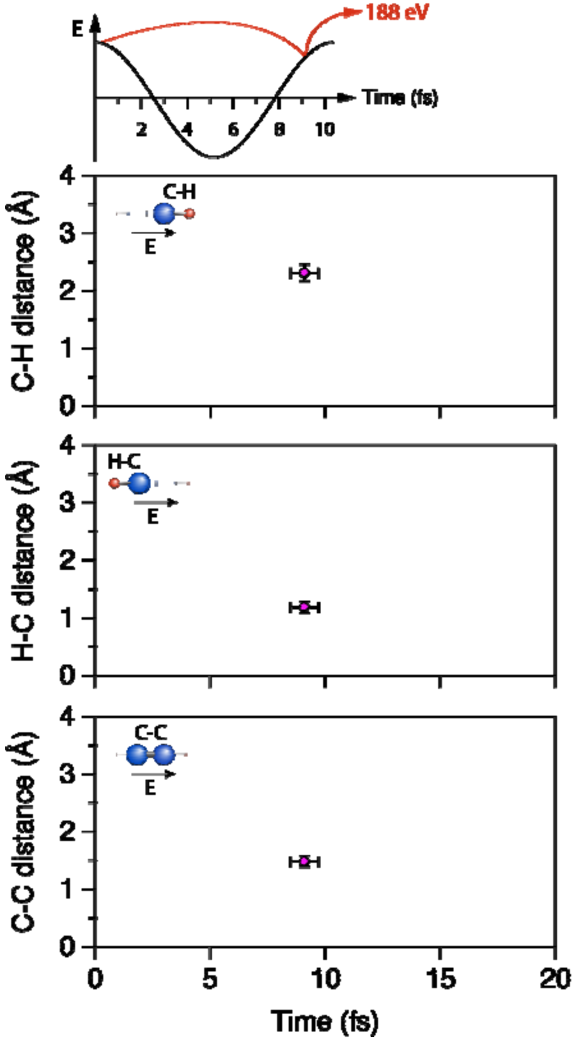
B. Wolter et al. Science 354, 308 (2016)

Space-time imaging of molecular structure



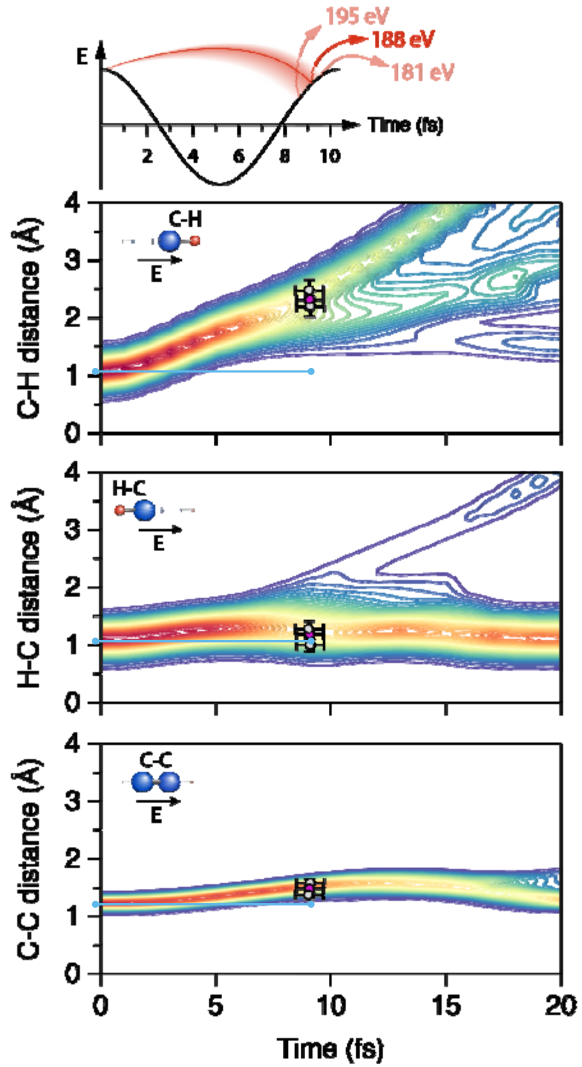
B. Wolter et al. Science 354, 308 (2016)

Space-time imaging of molecular structure



B. Wolter et al. Science 354, 308 (2016)

Space-time imaging of molecular structure



time of imaging: (9.15 ± 0.6) fs

+118%

1.06 Å ➔ (2.31 ± 0.15) Å

Bond is "broken", proton departs

+12%

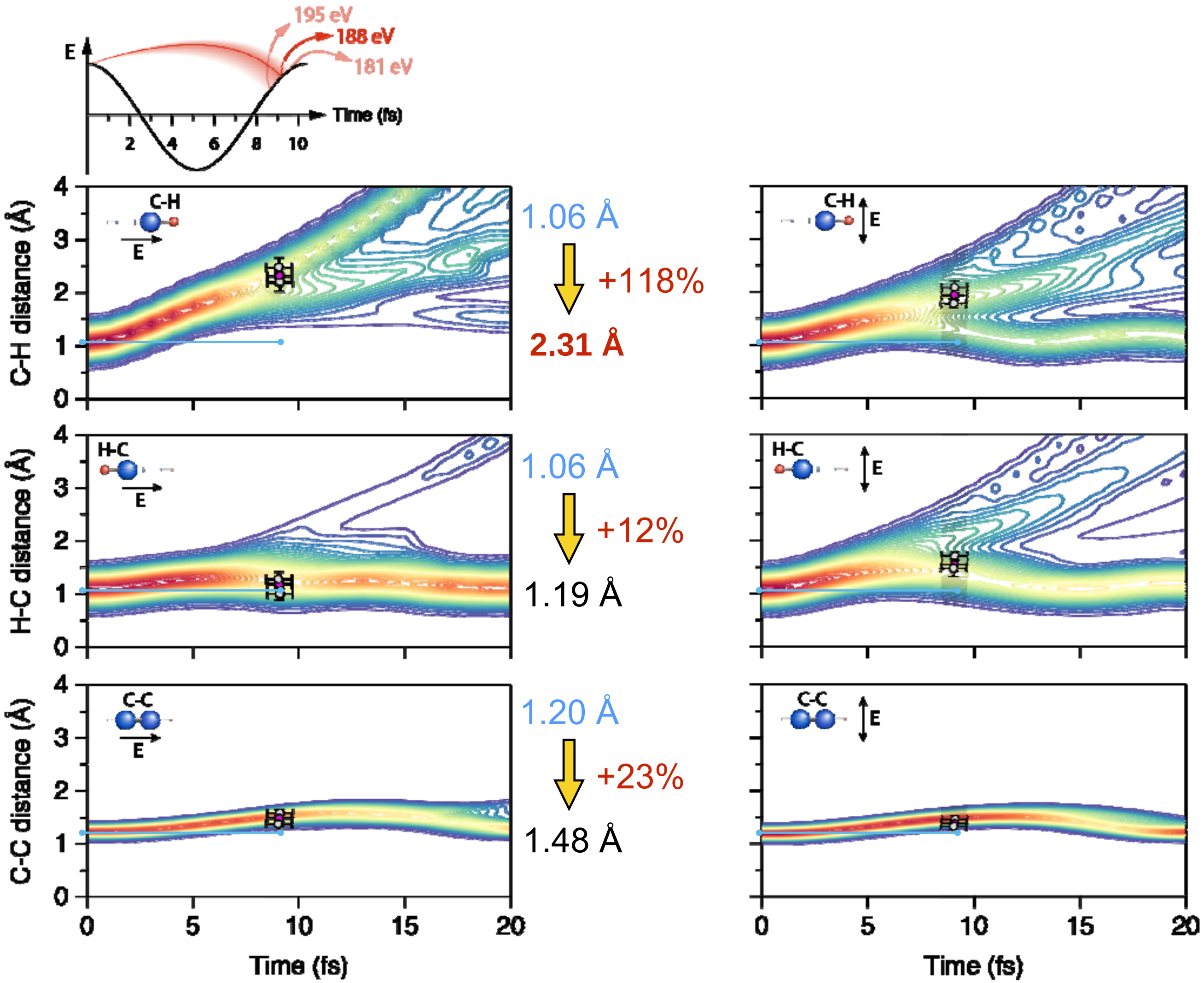
1.06 Å ➔ (1.19 ± 0.10) Å

+23%

1.20 Å ➔ (1.48 ± 0.11) Å

B. Wolter et al. Science 354, 308 (2016)

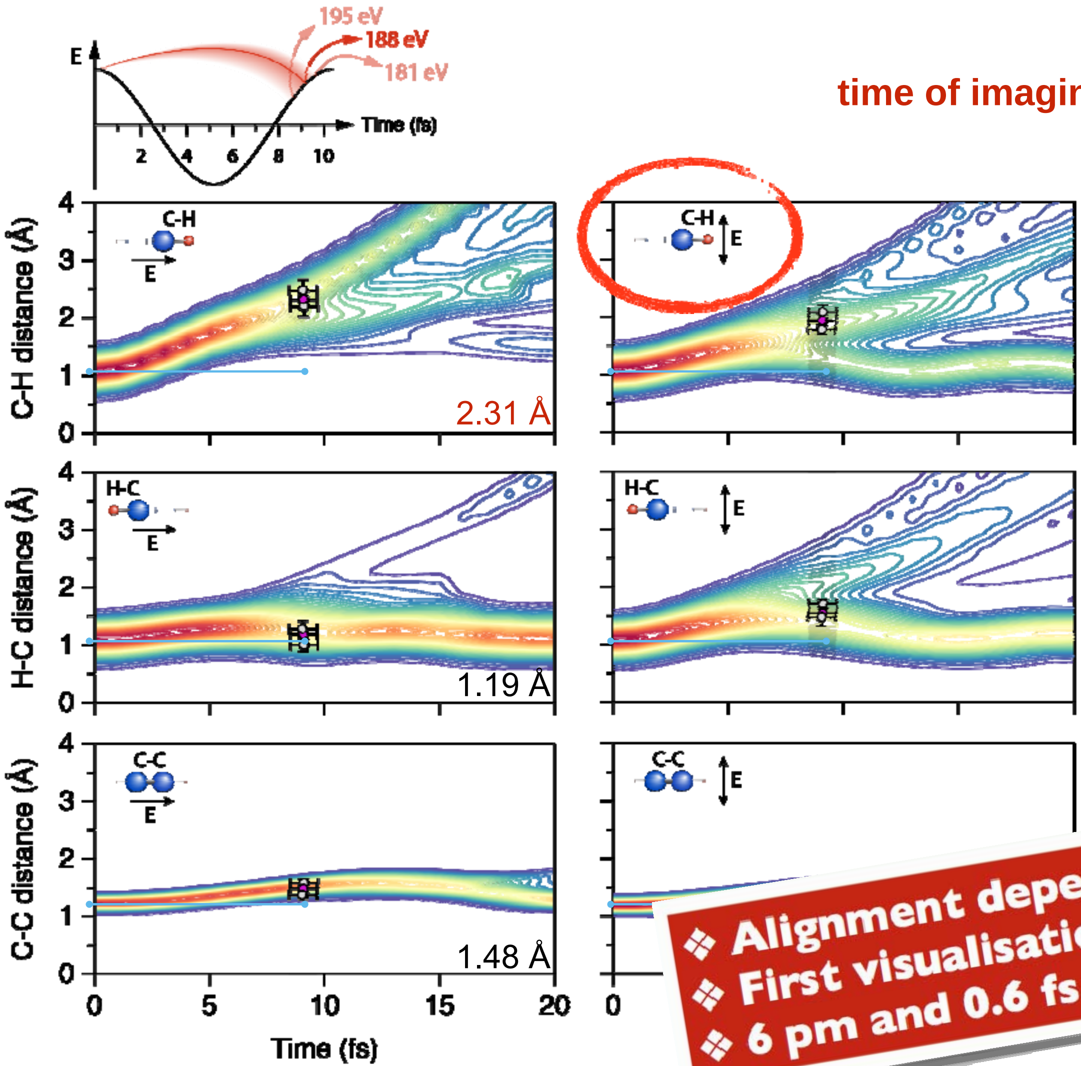
Space-time imaging of molecular structure



B. Wolter et al. Science 354, 308 (2016)

Space-time imaging of molecular structure

time of imaging: (9.15 ± 0.6) fs



1.06 Å → (1.94 ± 0.10) Å **+83%**

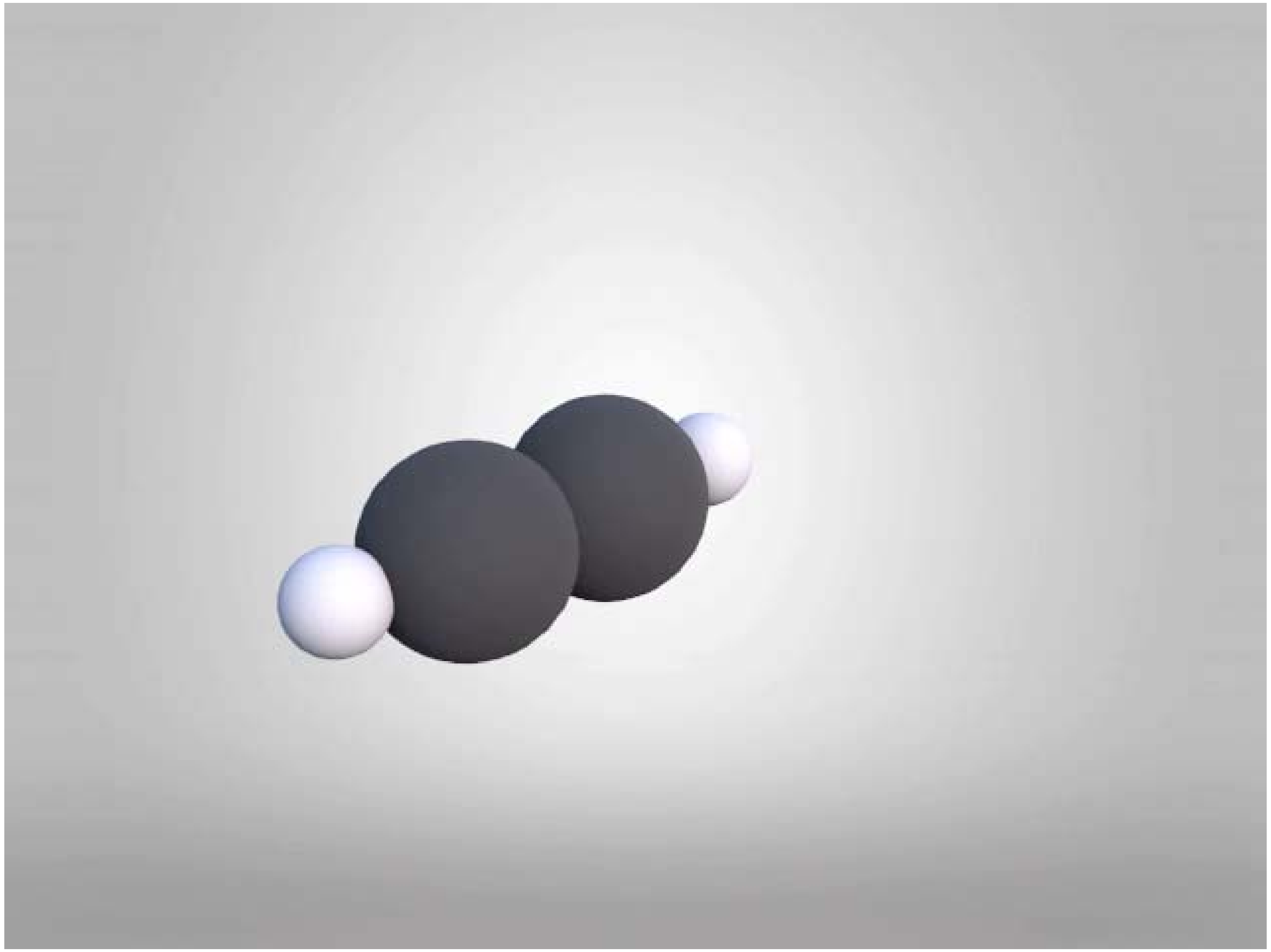
Bond elongation

1.06 Å → (1.54 ± 0.06) Å **+45%**

- **Alignment dependent deprotonation**
- **First visualisation of bond breaking**
- **6 pm and 0.6 fs resolution**

B. Wolter et al. Science 354, 308 (2016)

Movie from measurement

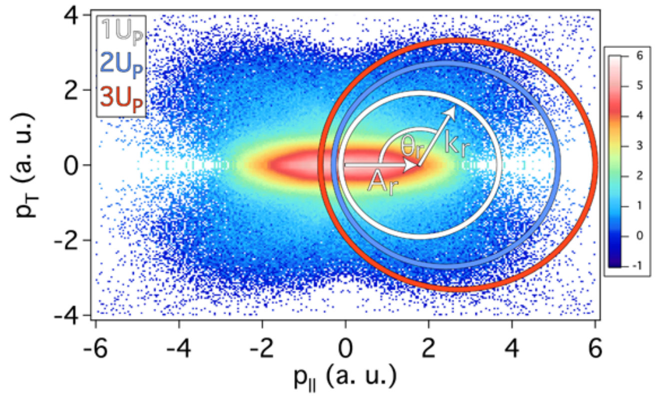


B. Wolter et al. Science 354, 308 (2016)

Summary and future

Mid-IR driven electron recollision & coherence/interference

❖ **picometer and attosecond resolution imaging**



- Atomic-scale imaging with one electron

M. Pullen et al. Nature Commun. 6, 7262 (2015)

- Imaging the onset of bond breaking and proton motion in 9 fs

M. Pullen et al. Nature Commun. 7, 11922 (2016) B. Wolter et al. Science 354, 308 (2016)

Future directions: Trigger dynamics (200 nm 10 fs)
Asymmetric and larger molecules
Understand the effects of the strong field better

Attoscience and Ultrafast Optics

A. Picon T. Steinle B. Wolter L. Vamos T. Kanai D. Rivas
T. Sidiropoulos N. Di Palo J. Huijts A. Sanchez
B. Nandy U. Elu B. Buades

M. Moshammer, A. Senftleben, T. Pfeifer, J. Ullrich A.-T. Le, X. Wang, C.D. Lin
K. Doblhoff-Dier, S. Gräfe
O. Vendrell


That's all Folks!