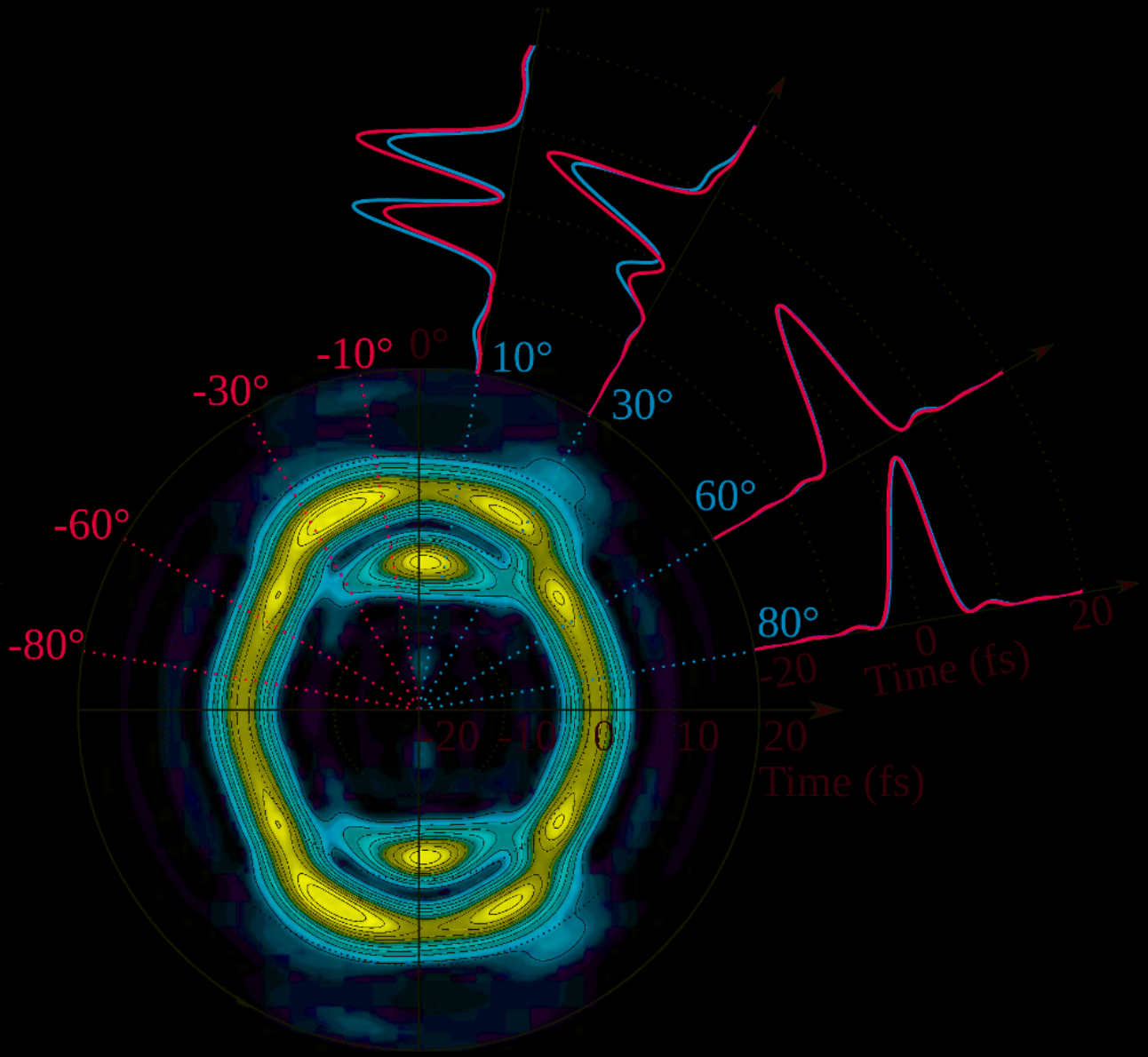
Measuring attosecond dynamics in molecules

Yann Mairesse, CELIA Bordeaux



What happens to a molecule on an attosecond timescale ?

Typical timescale of the oscillation of the electric field of visible light

Bound dynamics induced by an intense laser field :

Polarization of the molecule by the oscillating laser field

Electron dynamics in photoionization :

It takes a few hundreds attoseconds for an electron to escape from a molecular potential

The ionization dynamics can be more complex if resonances are involved
Autoionization, shape resonance

The electrons left in the molecular ion can rearrange in a few hundreds of attoseconds
Charge migration, electron correlation, electron-nuclear couplings

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics

Autoionization dynamics

Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
- Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse
- Charge migration
- Electron escape dynamics
- Autoionization dynamics

Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Time and spectrum

The spectral width of a source defines the **coherence time** $\tau_c = 1/\Delta\nu$

(coherence = ability to produce interferences)

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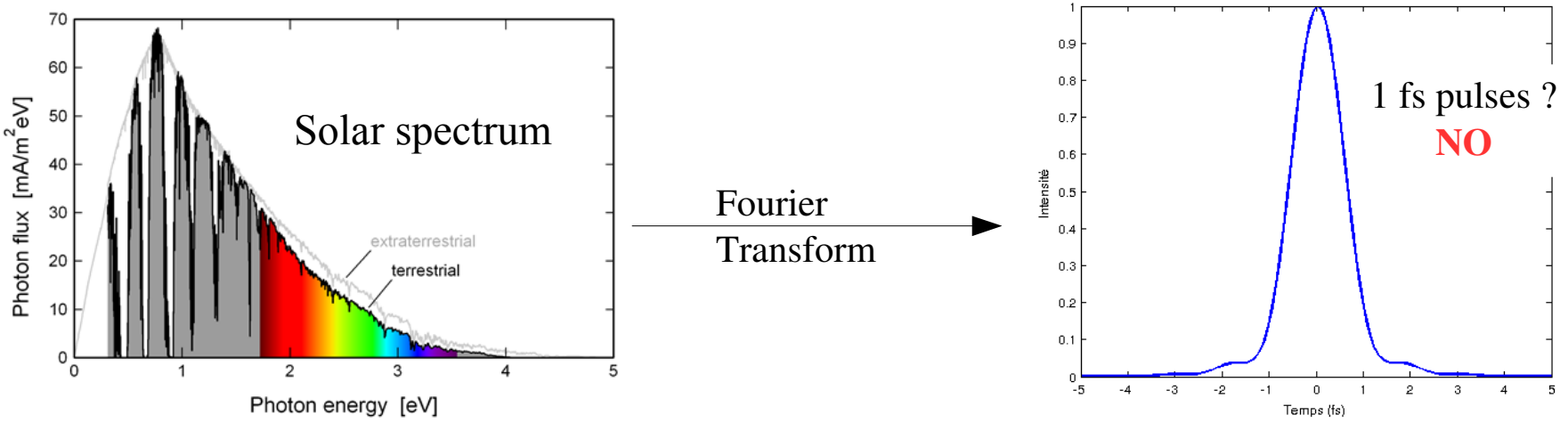
(coherence = ability to produce interferences)

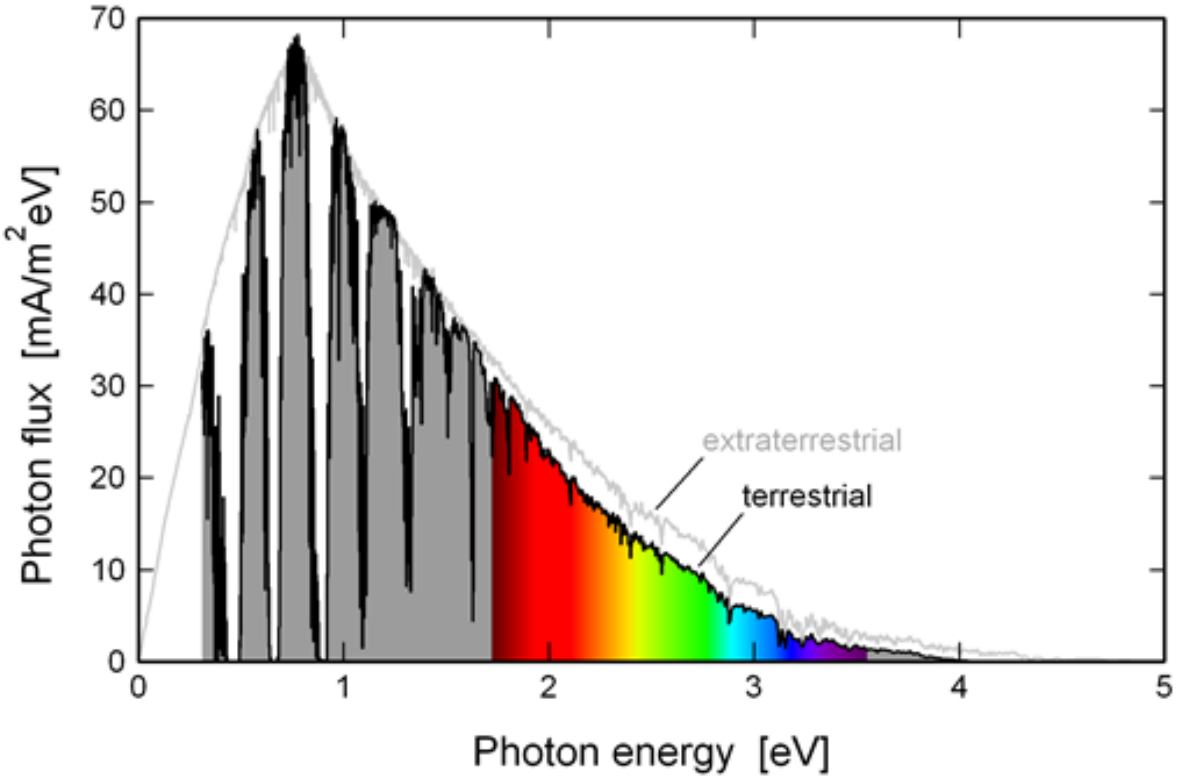
An ultrashort pulse has an ultrashort coherence time and thus a **broad spectrum**
This is a necessary condition, but not sufficient



The temporal profile is obtained by FT of the complex spectrum

Time and spectrum

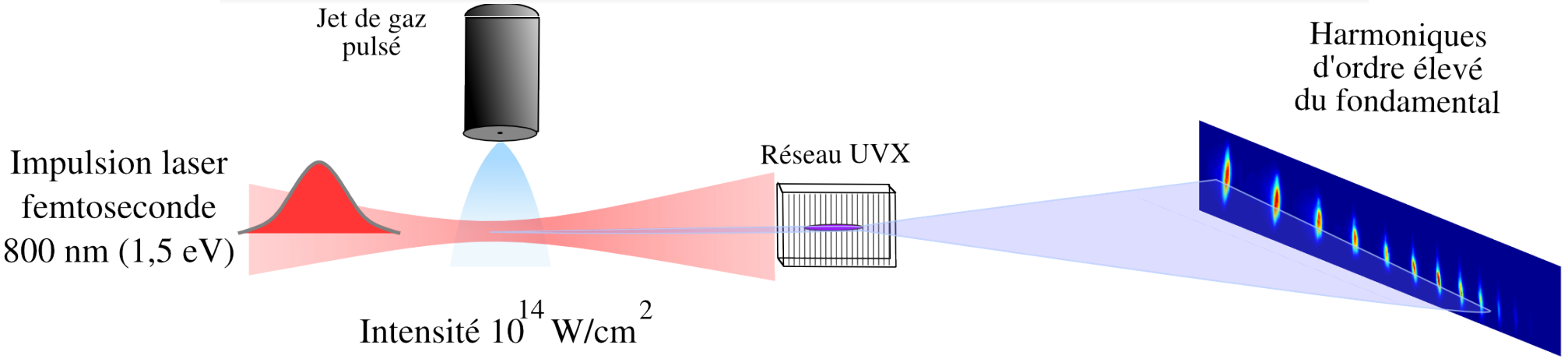
Solar spectrum :

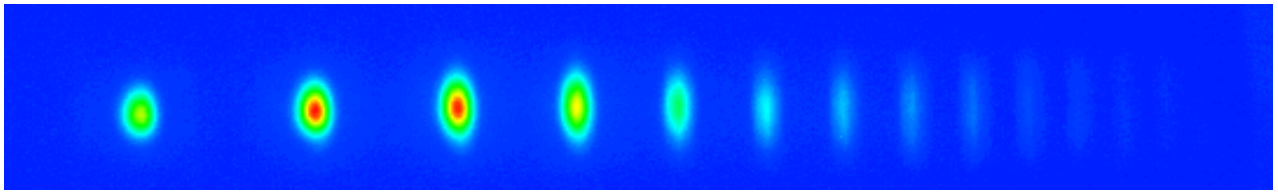


Producing attosecond pulses require a bandwidth of several eV
→ attosecond pulses extend in the UV-XUV spectral range

Need a broadband, coherent source in the XUV

High order harmonic generation in gases

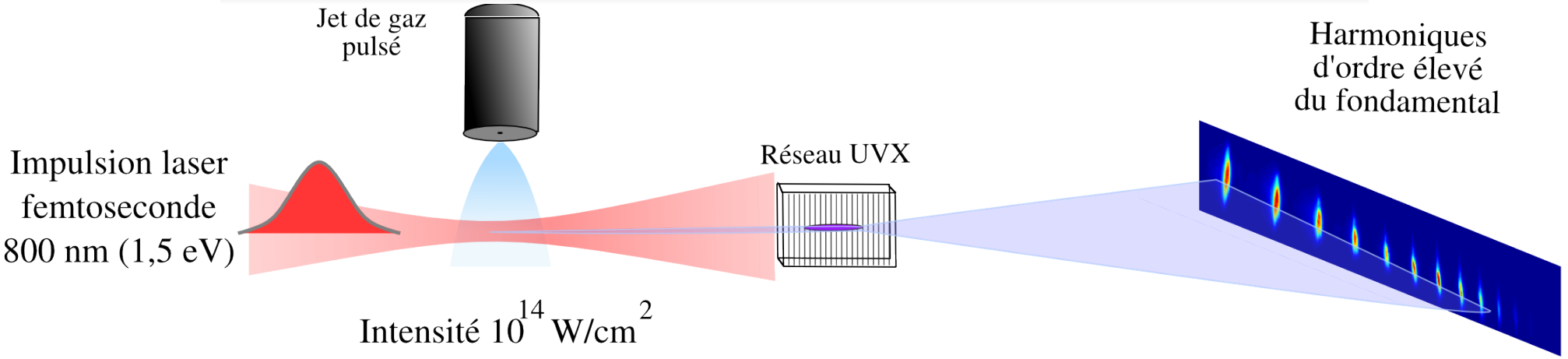




H15 23.3eV | H21 32.6eV | H27 41.9eV | H39 60.5eV

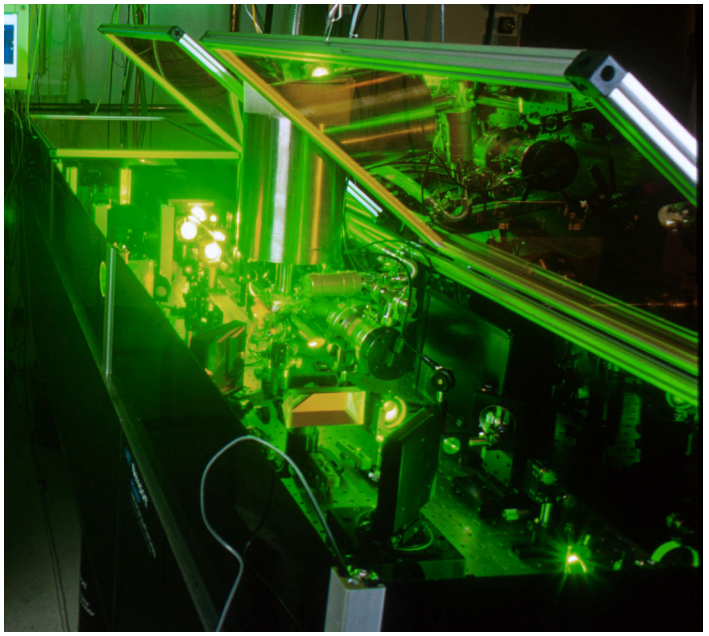
Discovered in 1988
Coherent emission (spatially and temporally)
Broadband radiation
Up to ~10^{10} photons per shot

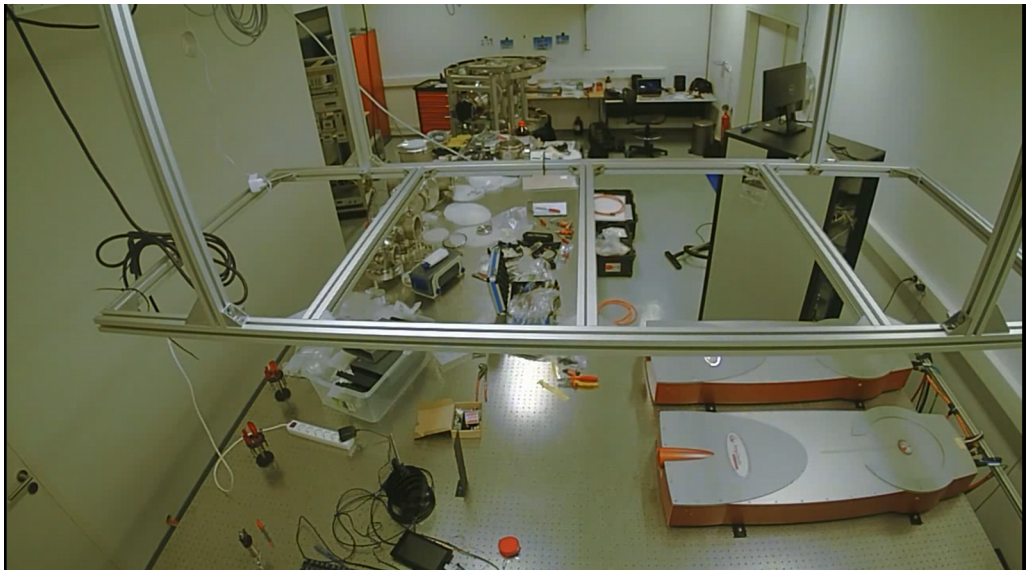
High order harmonic generation in gases



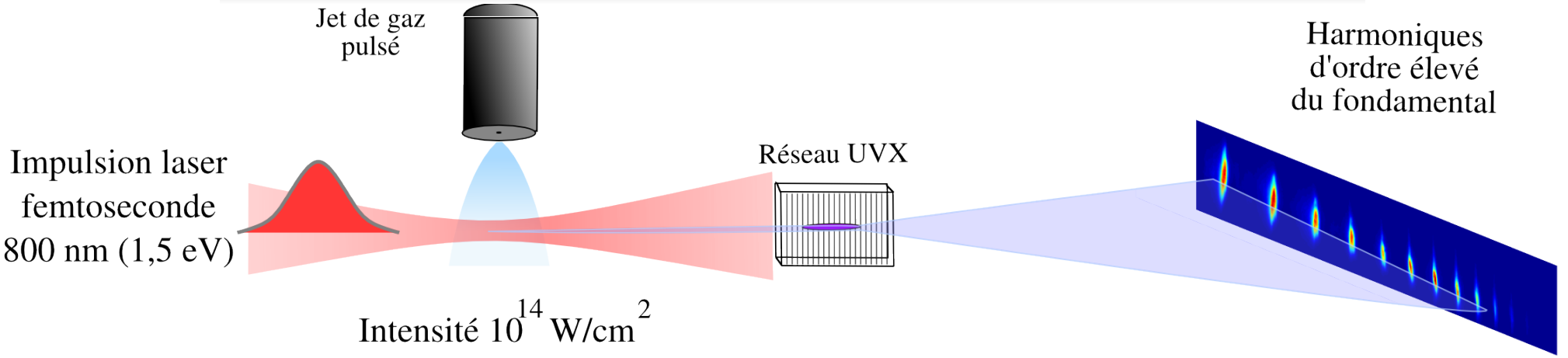
Typical experimental setup :

- Laser Chirped Pulse Amplification,
  Ti:Sa 1-10mJ, 5-50fs, <10kHz
  Yb Fiber 100µJ, 130-500fs, 100kHz-MHz





High order harmonic generation in gases



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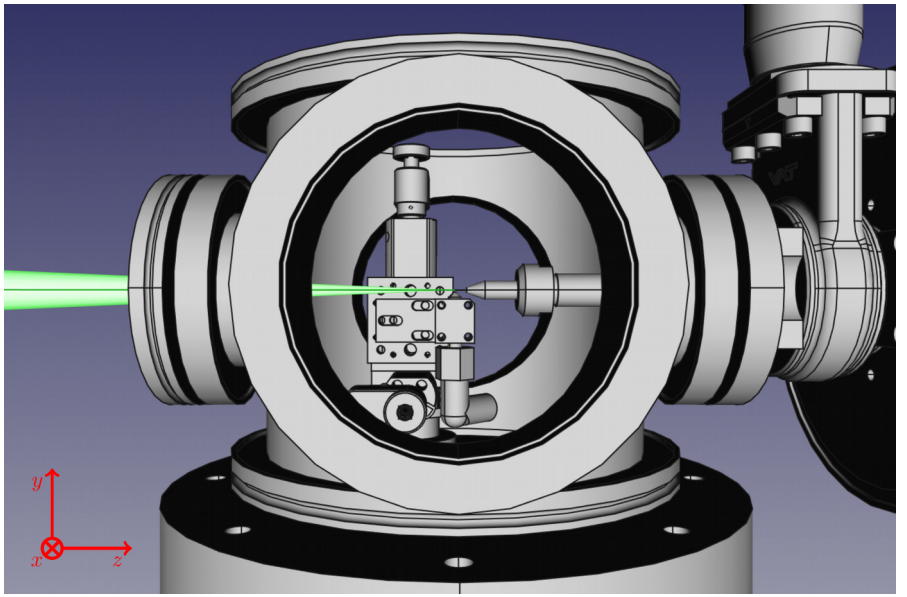
- Vacuum chambers and pumping:
  - Turbomolecular pumps : 1e-6 mbar range



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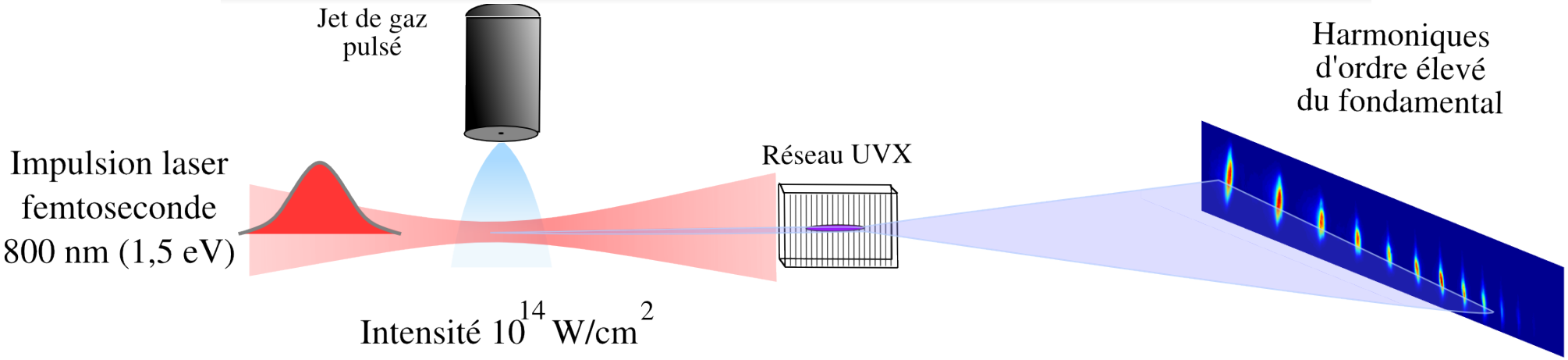

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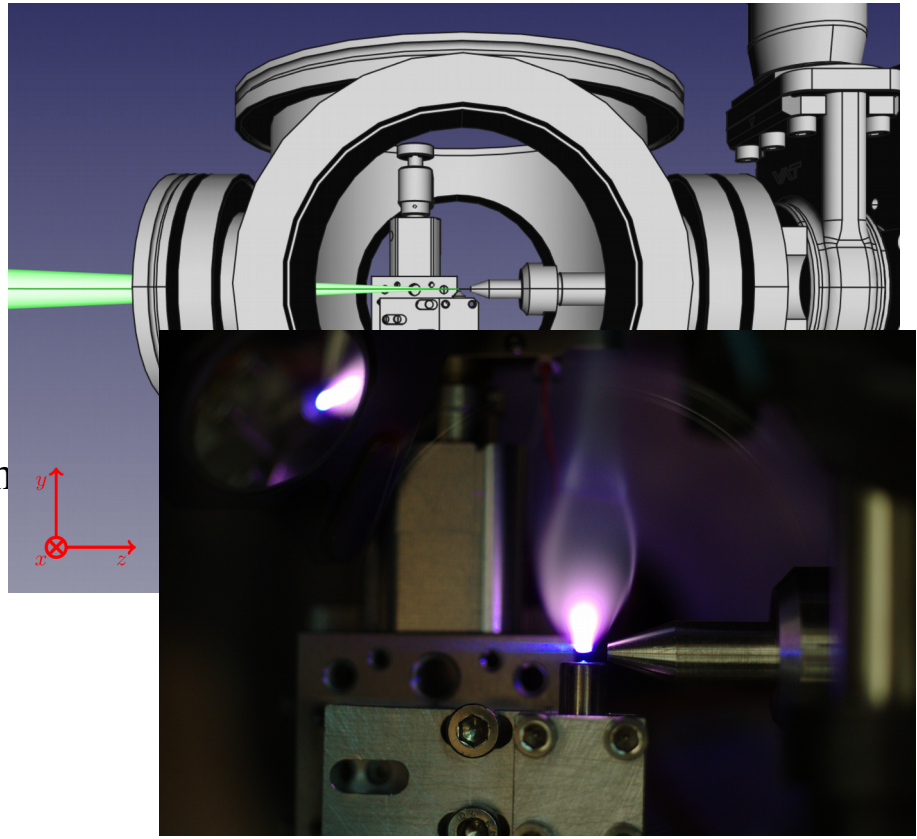
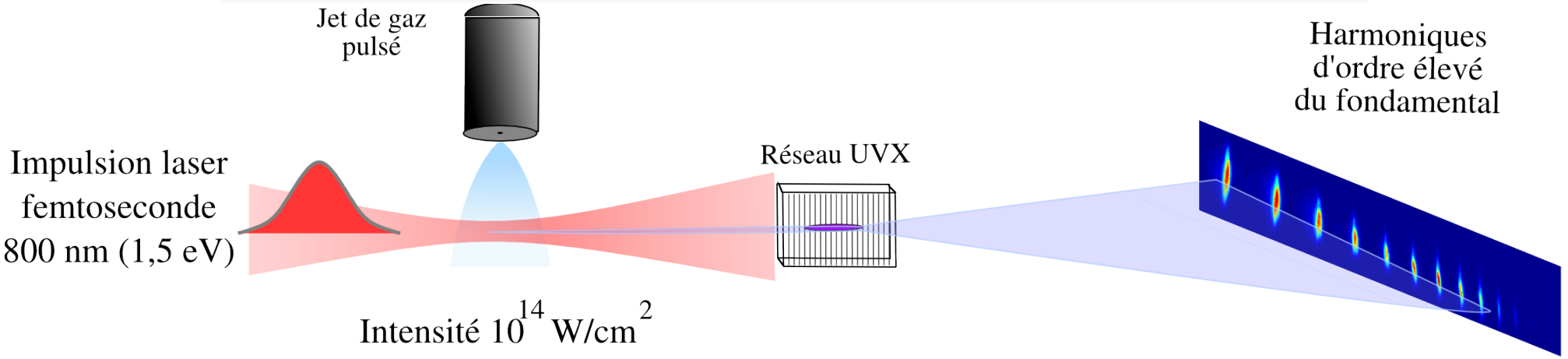
- Gas source :
  - Static cell, typically 1-10mm long
  - Effusive of supersonic jet: typically 200µm



High order harmonic generation in gases



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- Vacuum chambers and pumping:
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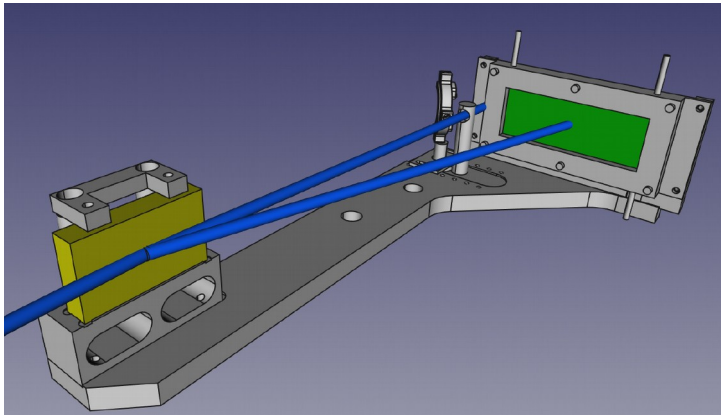
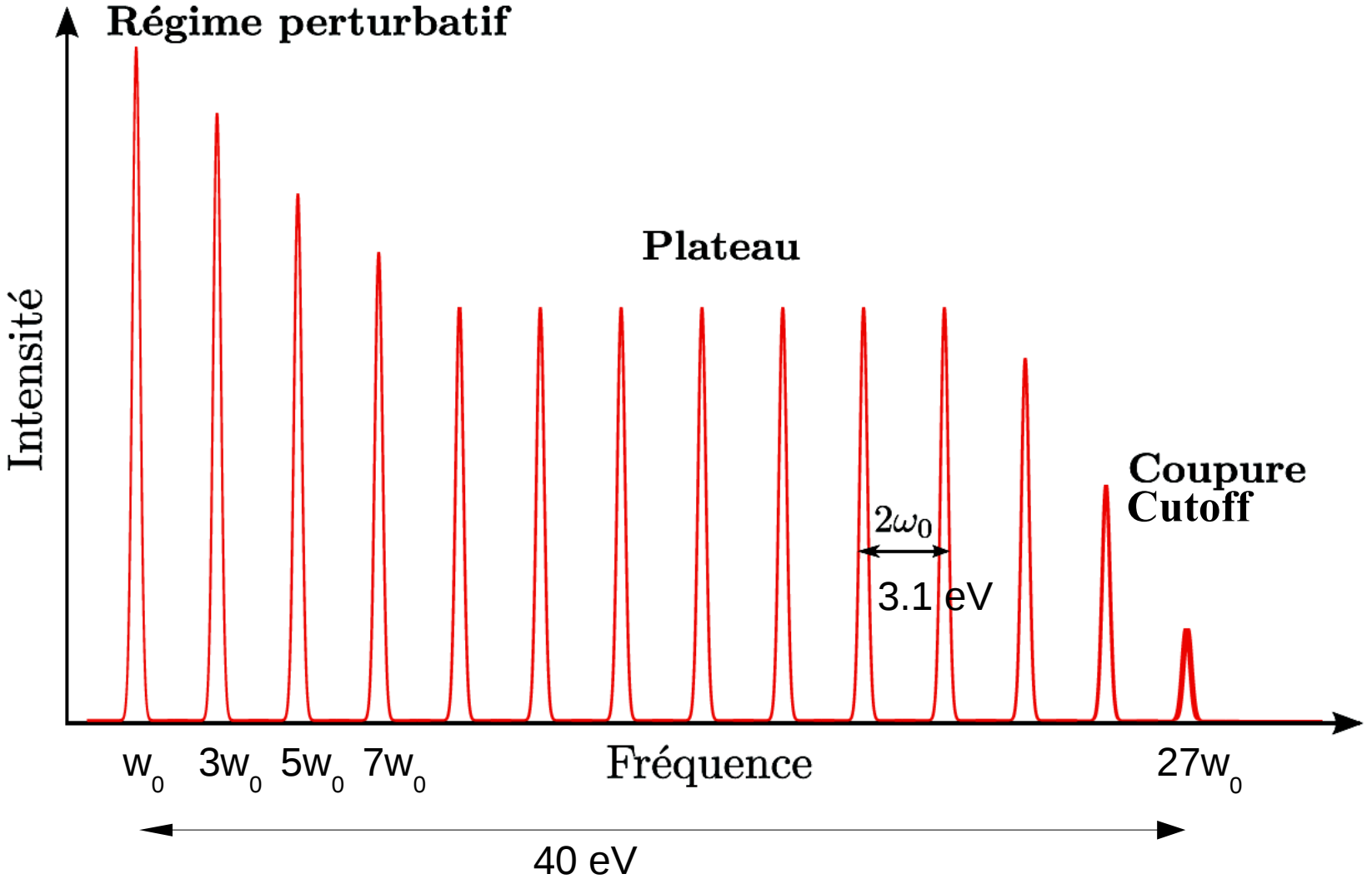
- Gas source :
  - Static cell, typically 1-10mm long
  - Effusive of supersonic jet: typically 200µm long
- Spectrum analyzer :
  - Transmission or reflection XUV grating
  - Photon detector : X CCD camera / Microchannel plates + visible camera



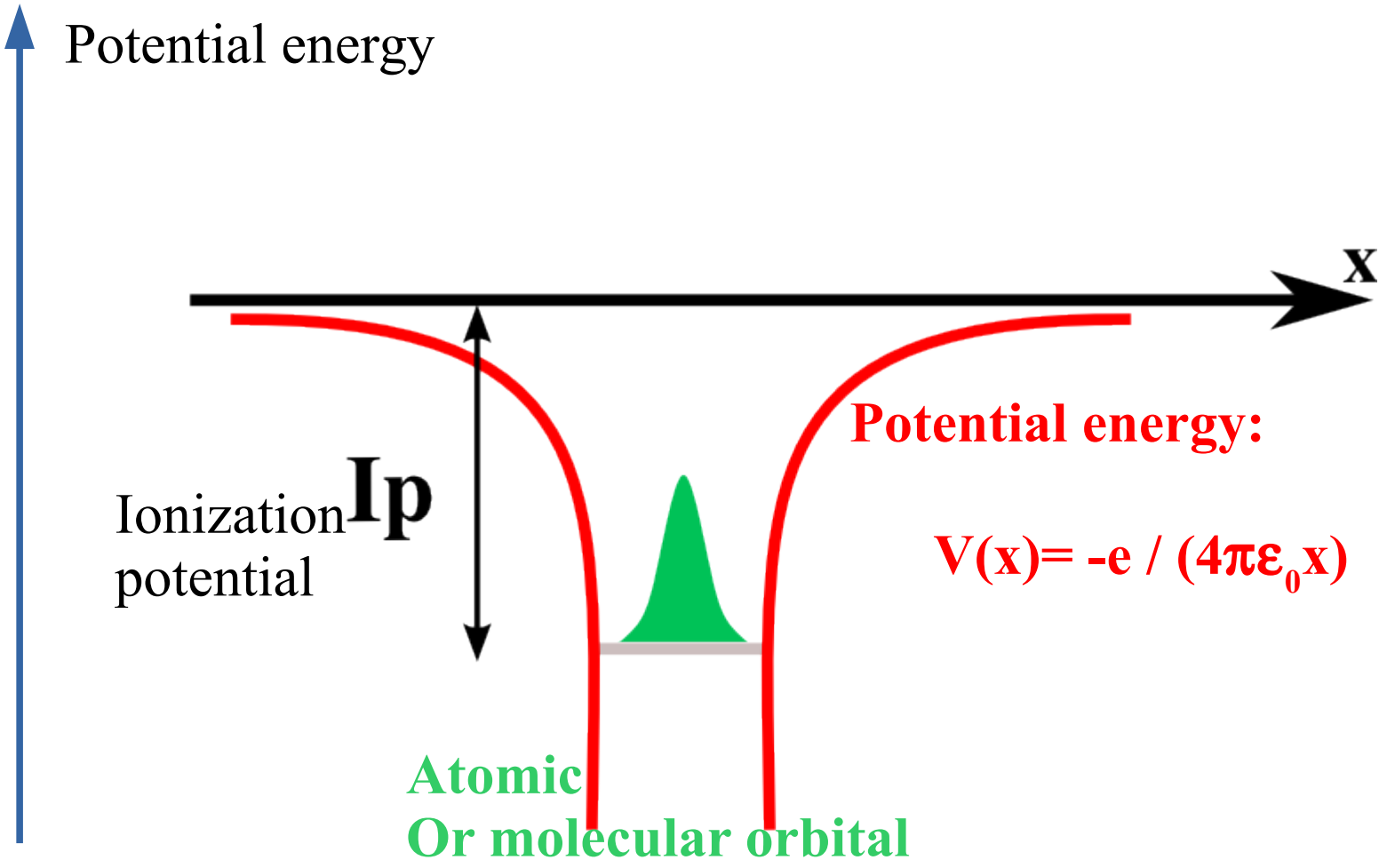
High order harmonic spectrum

w_0 =1.55 eV @ 800 nm

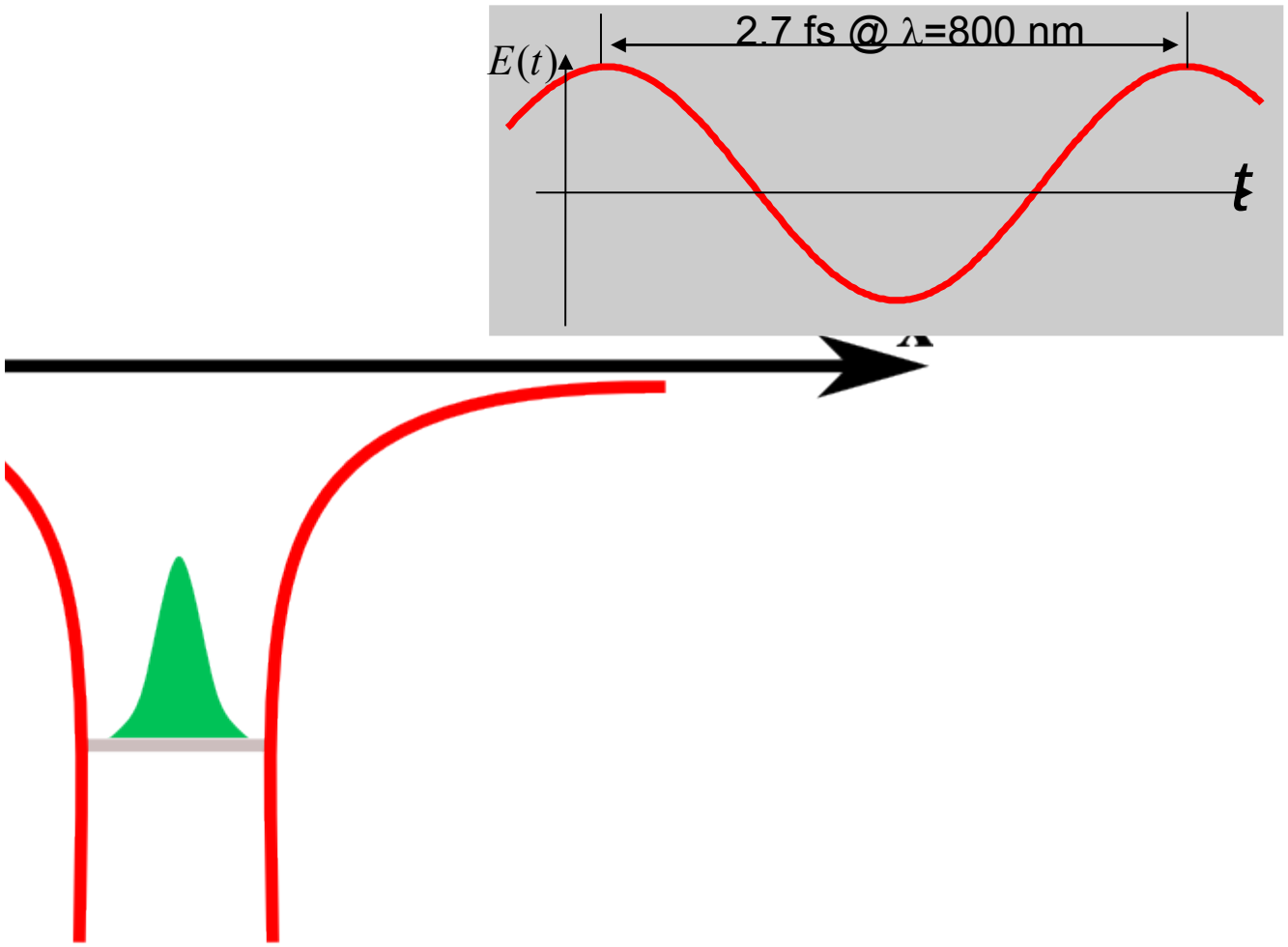


Source of attosecond pulses ?

High order harmonic generation mechanism

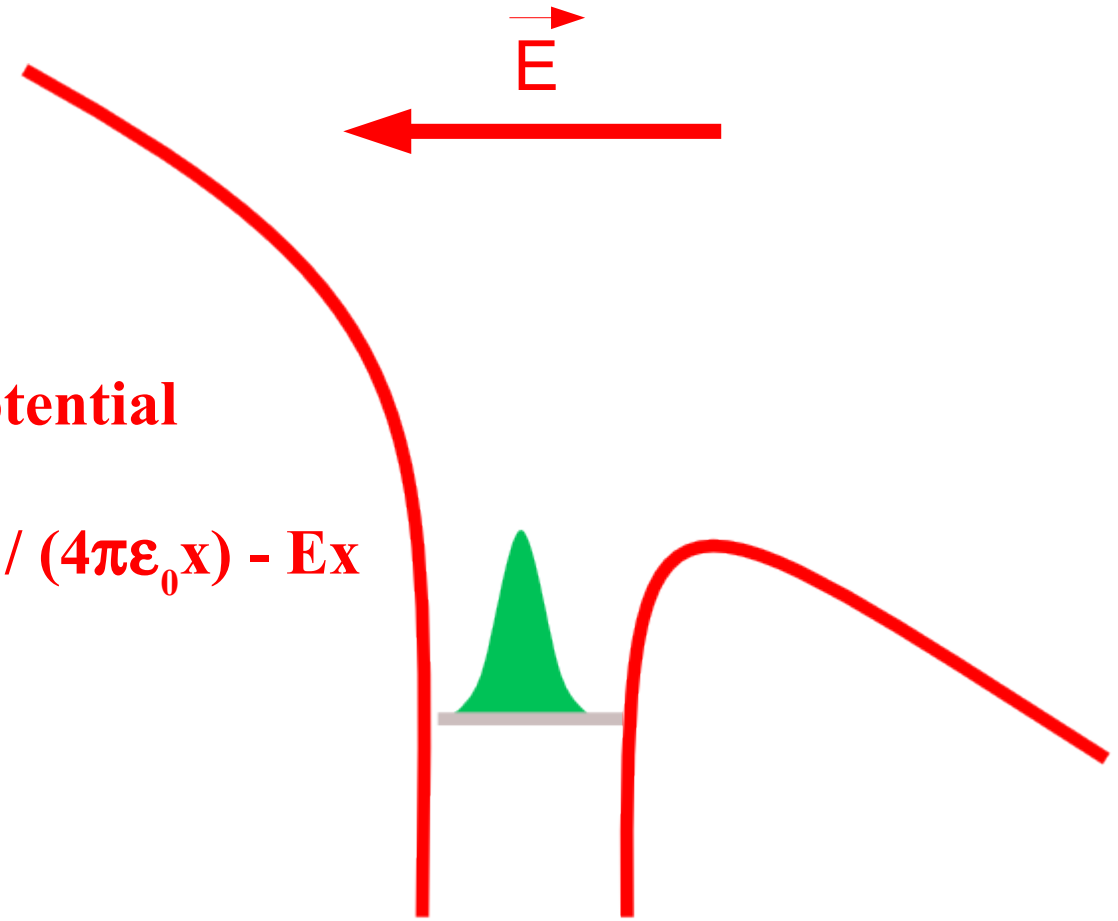


High order harmonic generation mechanism



Intense femtosecond laser pulse

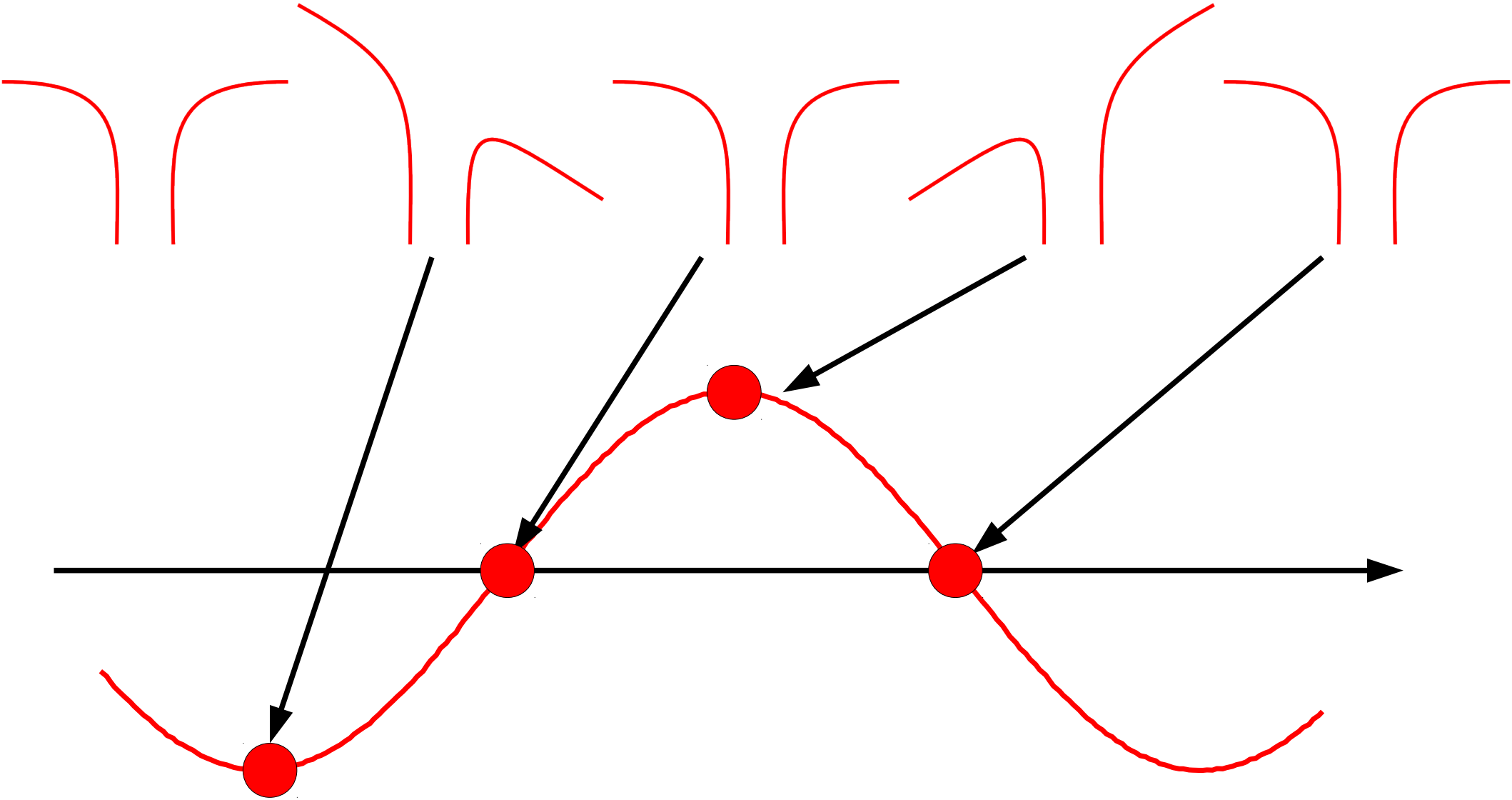
High order harmonic generation mechanism



Modified potential

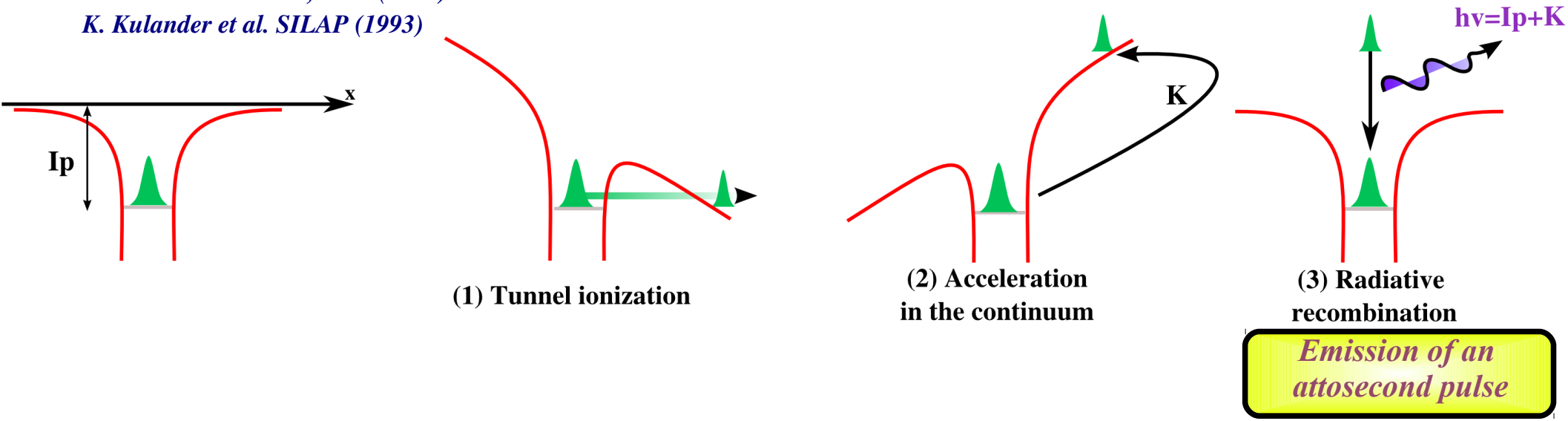
$$V(x) = -e / (4\pi\varepsilon_0 x) - Ex$$

High order harmonic generation mechanism



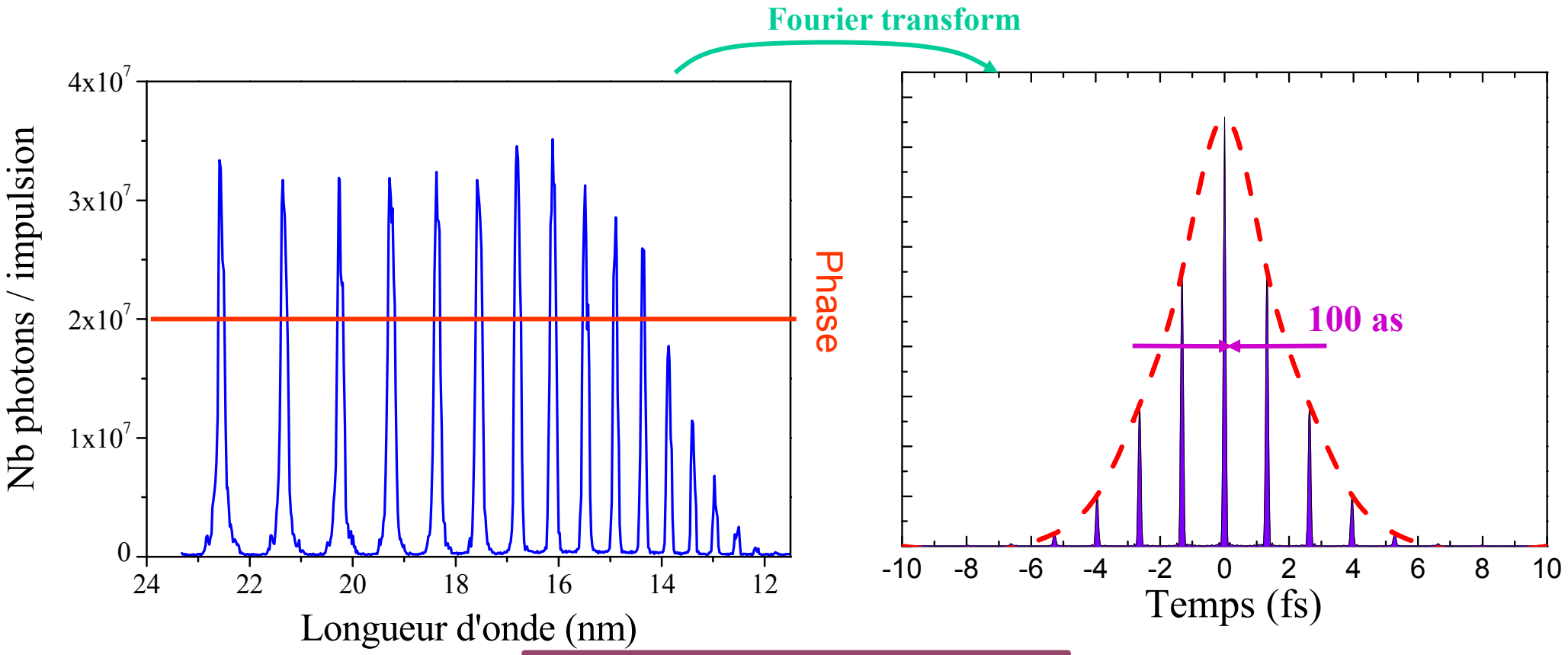
High order harmonic generation mechanism

P.B. Corkum PRL 71, 1994 (1993)
K. Kulander et al. SILAP (1993)



Periodicity $T_0/2$ → harmonics separated by $2\omega_0$, and attosecond pulse train

Superposition of several harmonics



Attosecond pulse train

Gy. Farkas & Cs. Toth, Phys Lett A 168 447 (1992)
S.E. Harris et al, Opt. Commun. 100 487 (1993)

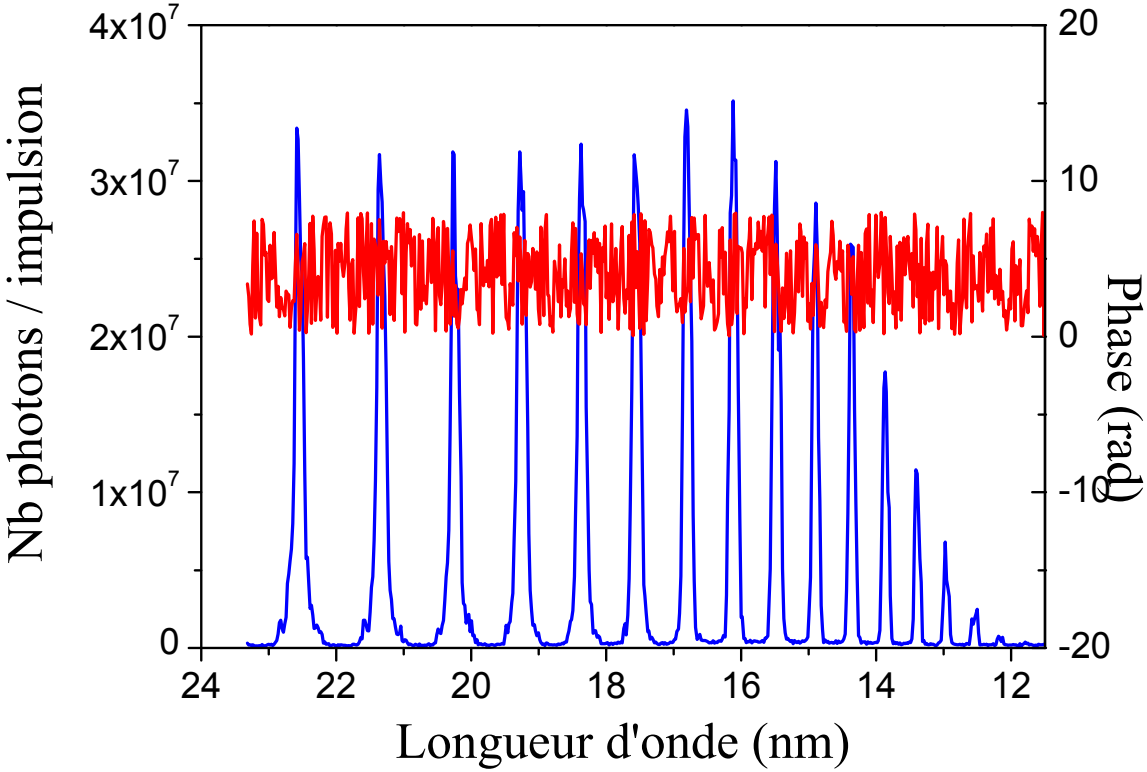
Superposition of N harmonics:

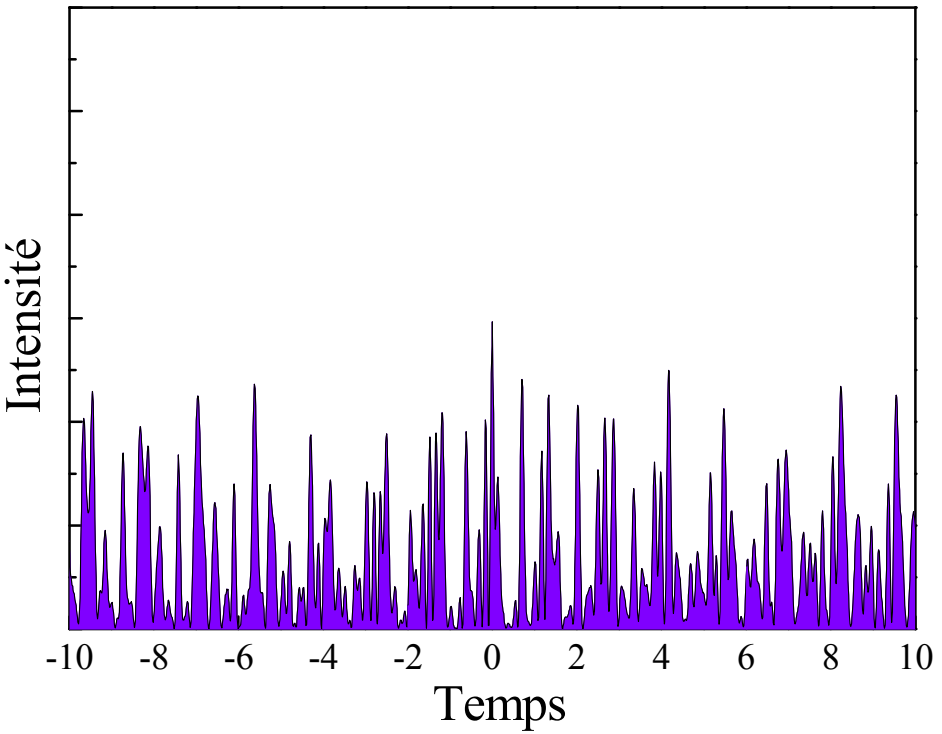
$$\tau \approx \frac{T_0}{2N}$$

→ τ < 10 as with 300 harmonics

Beware of spectral phase !

Effect of a random spectral phase





→ The temporal profile must be measured

Attosecond pulses were in fact produced in labs in 1988

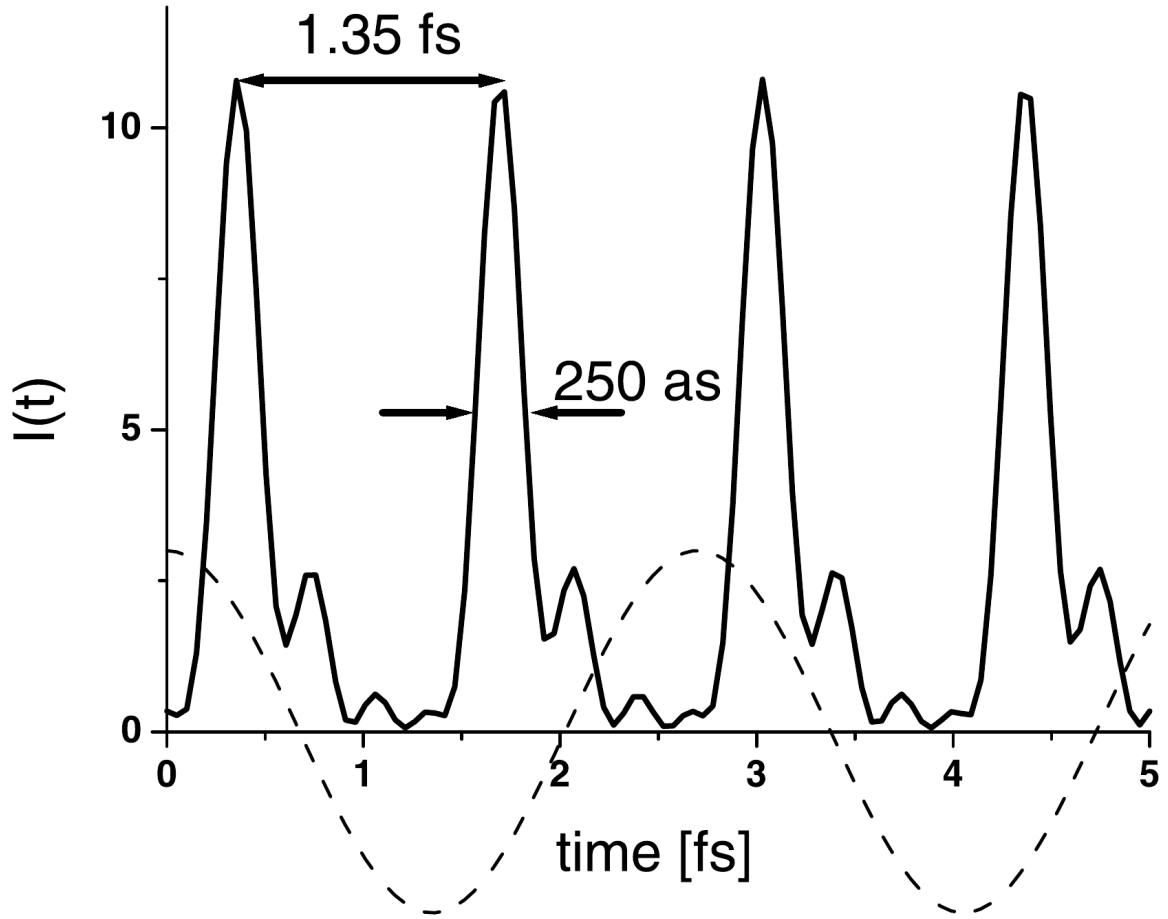
The issue was finding a way to measure them.

Attosecond pulse trains

Observation of a Train of Attosecond Pulses from High Harmonic Generation

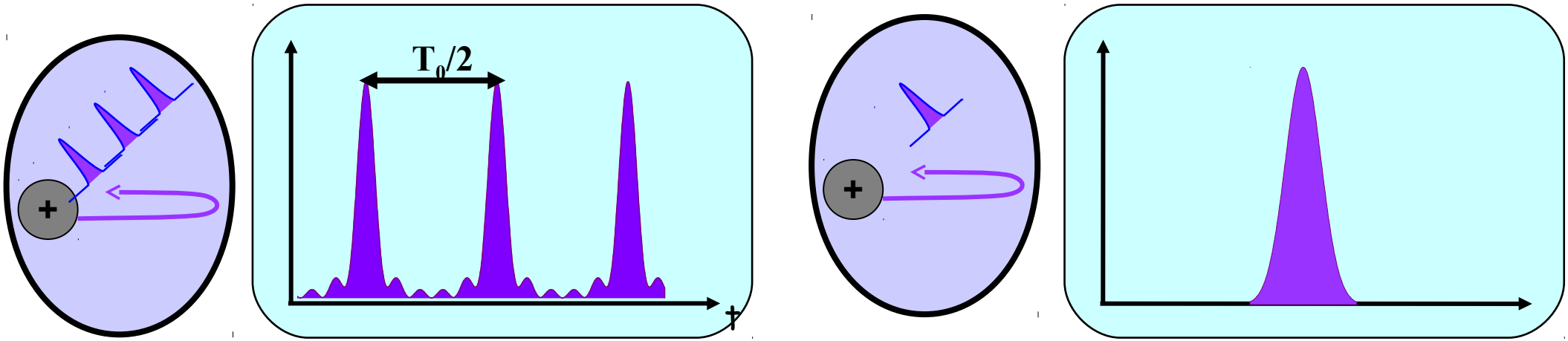
P. M. Paul,[1] E. S. Toma,[2] P. Breger,[1] G. Mullot,[3] F. Augé,[3]
Ph. Balcou,[3] H. G. Muller,[2*] P. Agostini[1]

SCIENCE VOL 292 1 JUNE 2001



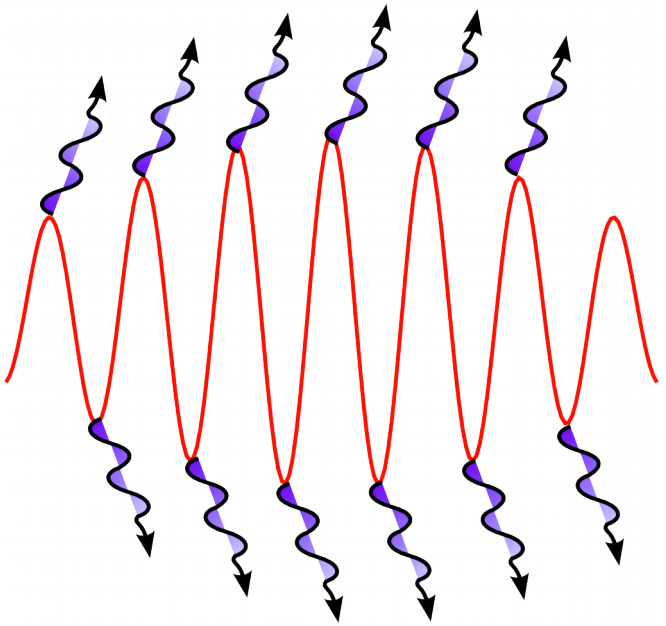
Attosecond pulse trains are routinely produced and well characterized

How to produce a single attosecond pulse ?



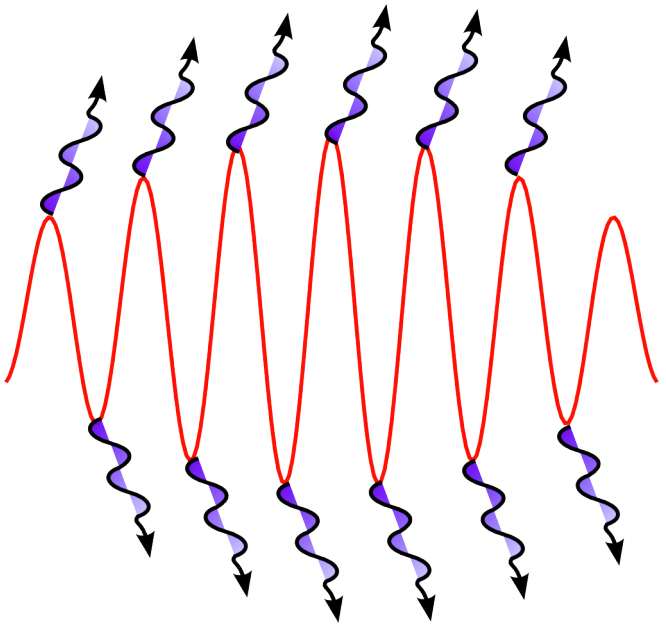
Need a single electronic recollision

Amplitude gating : few-cycle laser pulses



"Long" generating pulse
20 fs
Attosecond pulse train

Amplitude gating : few-cycle laser pulses



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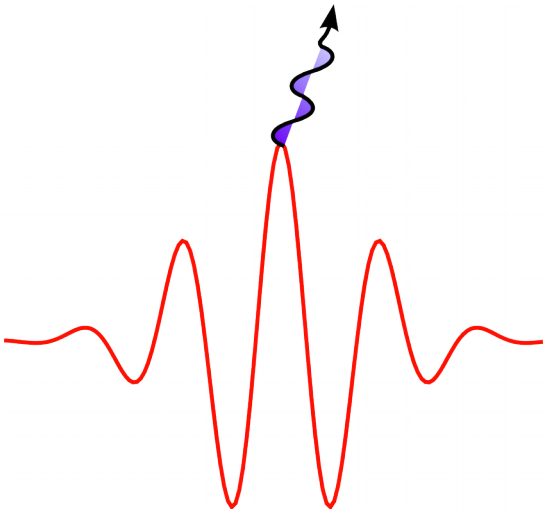


Monocycle generating pulse
5 fs
Single attosecond pulse

2001: **First measurement of single attosecond pulse**

Attosecond metrology

M. Hentschel*†, R. Kienberger*†, Ch. Spielmann*, G. A. Reider*, N. Milosevic*, T. Brabec*, P. Corkum‡, U. Heinzmann§, M. Drescher§ & F. Krausz*

NATURE | VOL 414 | 29 NOVEMBER 2001 | www.nature.com

State of the art

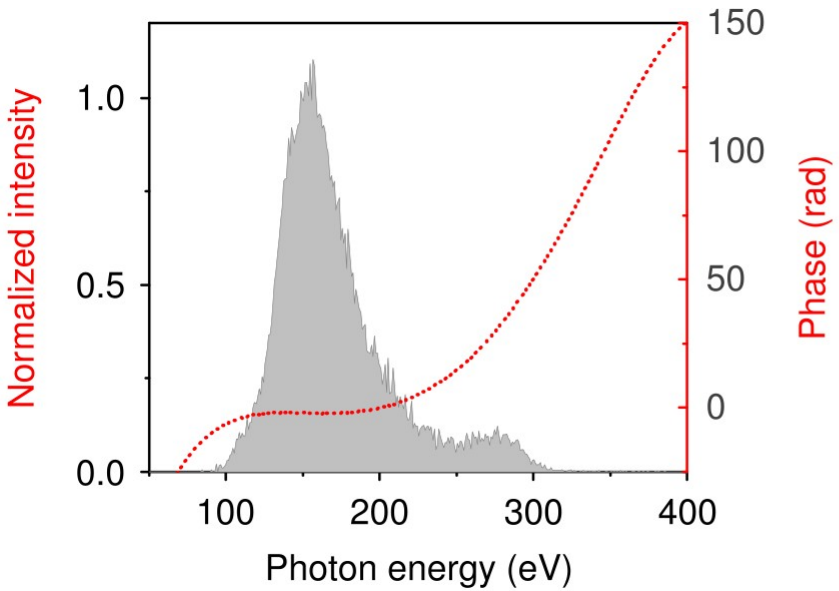
ARTICLE

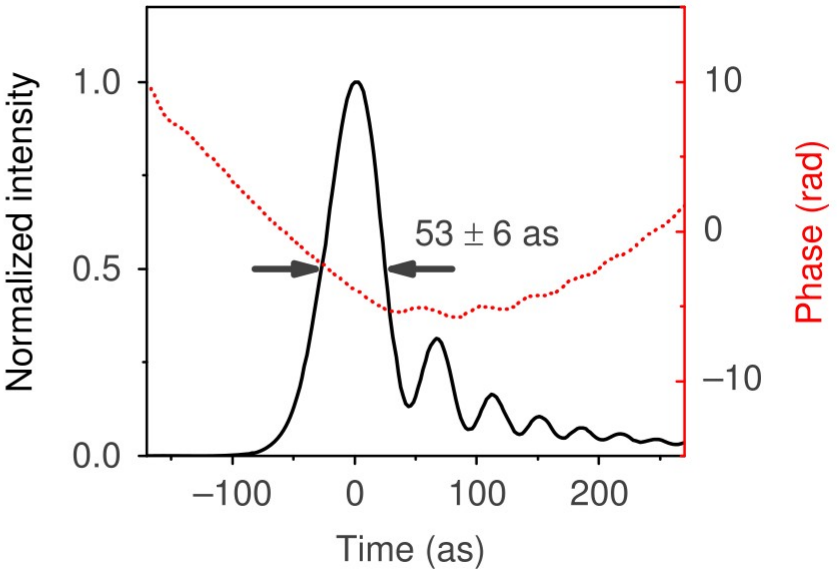
DOI: 10.1038/s41467-017-00321-0 OPEN

53-attosecond X-ray pulses reach the carbon K-edge

Jie Li[1], Xiaoming Ren[1], Yanchun Yin[1], Kun Zhao[1,2], Andrew Chew[1], Yan Cheng[1], Eric Cunningham[1], Yang Wang[1], Shuyuan Hu[1], Yi Wu[1], Michael Chini[3] & Zenghu Chang[1,3]

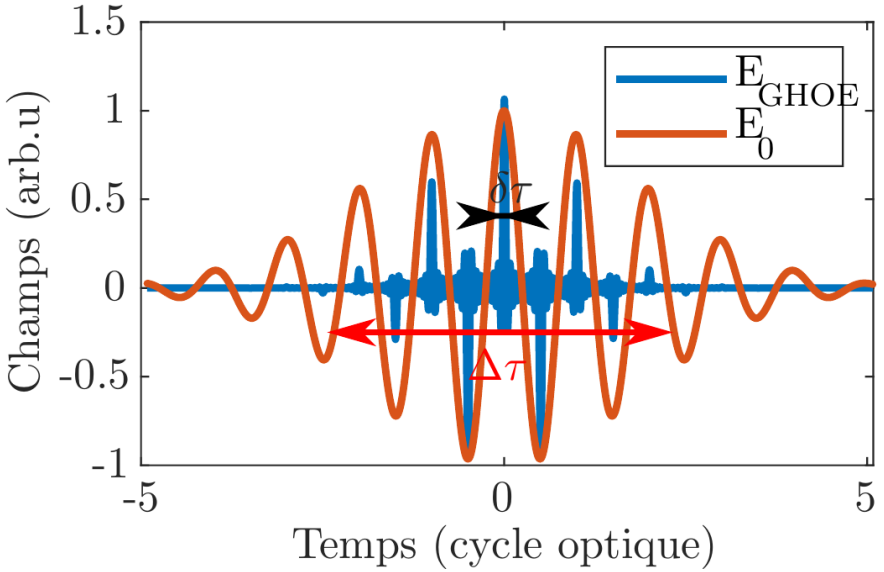
NATURE COMMUNICATIONS | 8: 186 | DOI: 10.1038/s41467-017-00321-0 | www.nature.com/naturecommunications

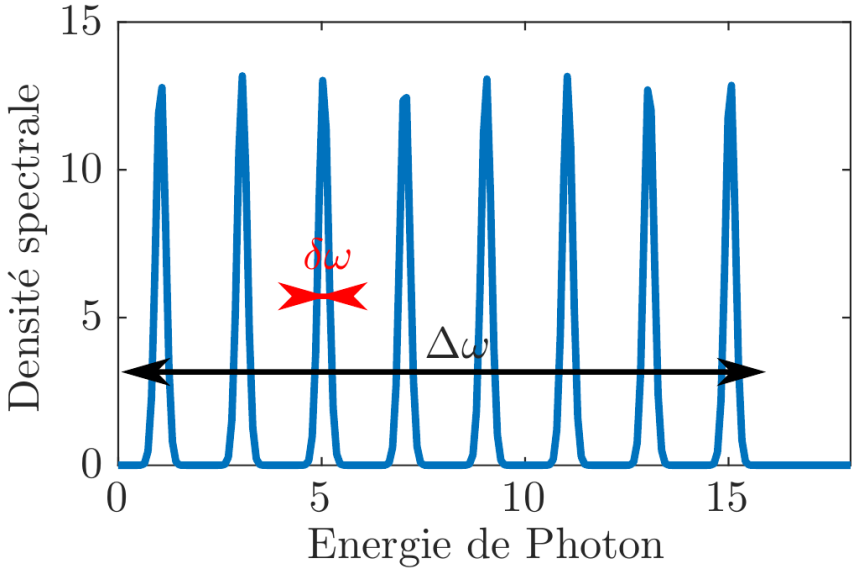




Photon energy reaching > 300 eV
Pulse duration around 50-60 as

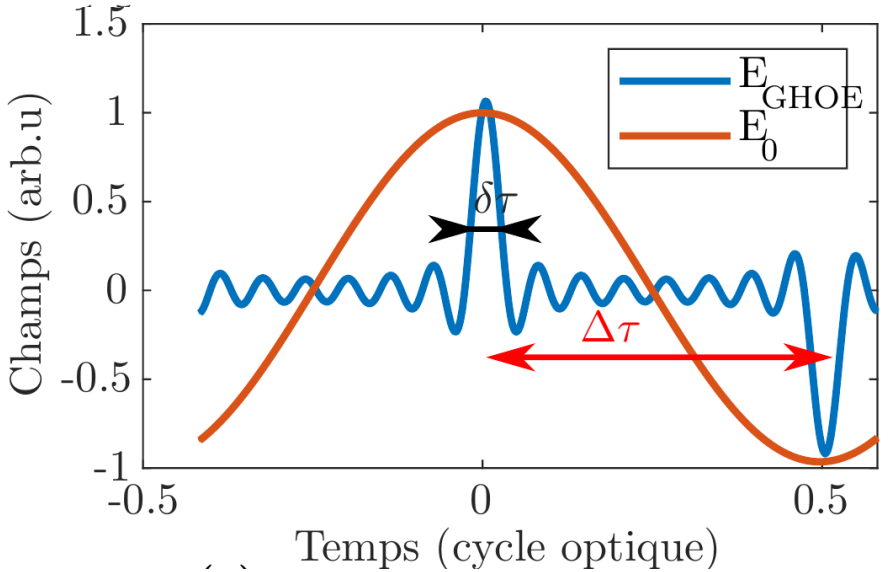
From an attosecond pulse train to a single pulse

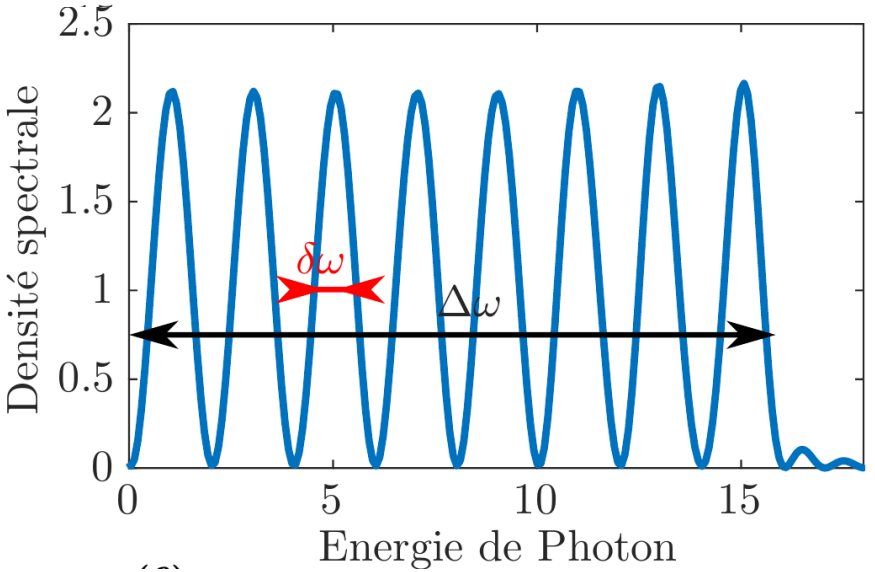




Attosecond pulse train
Spectrum = frequency comb,
because of spectral interference between attosecond pulses in the train

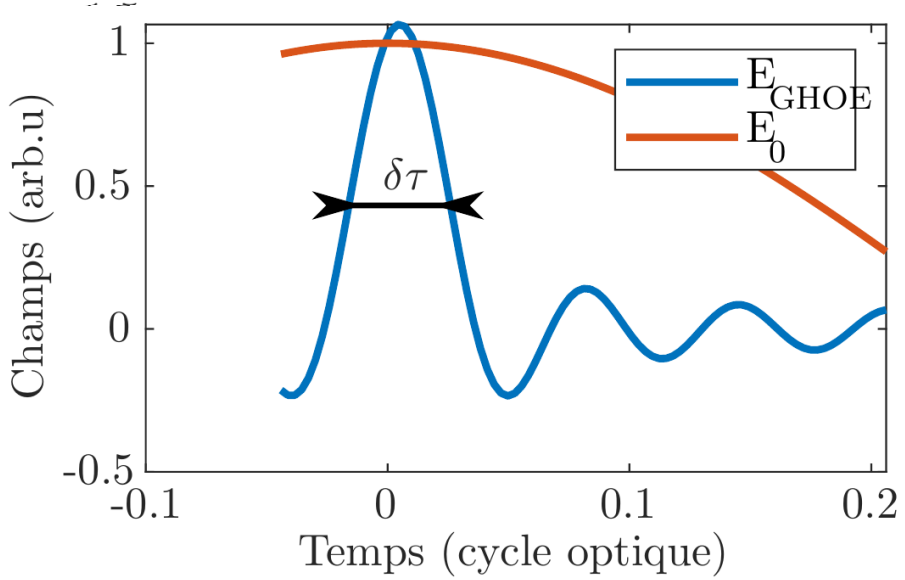
From an attosecond pulse train to a single pulse

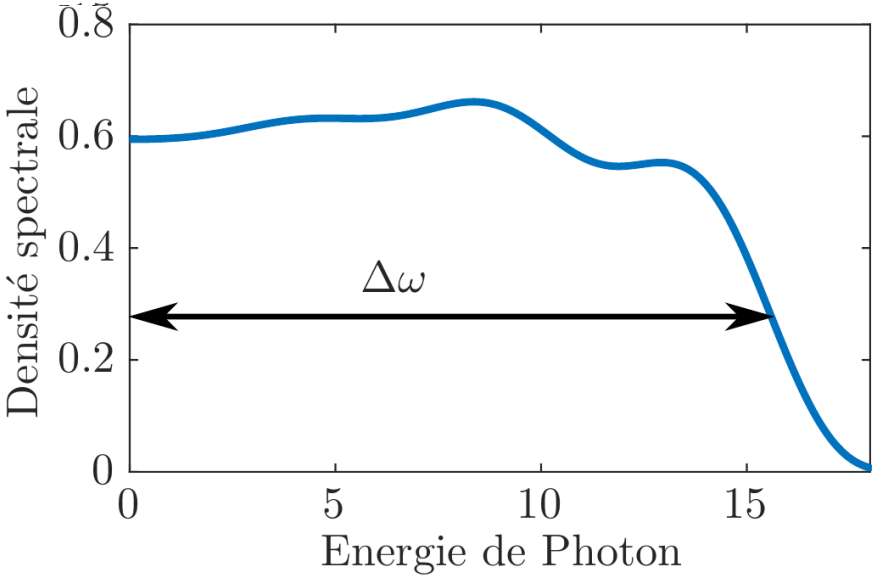




Two attosecond pulses produced
Spectrum = sinusoidal modulation
because of spectral interference between the two attosecond pulses

From an attosecond pulse train to a single pulse





Single attosecond pulses
Spectrum = continuous

Pump-probe attosecond experiment ?

Pump ? Probe ? Observable ?

Conceptually easiest scheme : attosecond XUV pump – attosecond XUV probe

Difficulties :

- Broad bandwidths (intrinsic issue)
- Two-photon transitions in the XUV : low efficiency
- Attosecond sources are not very bright

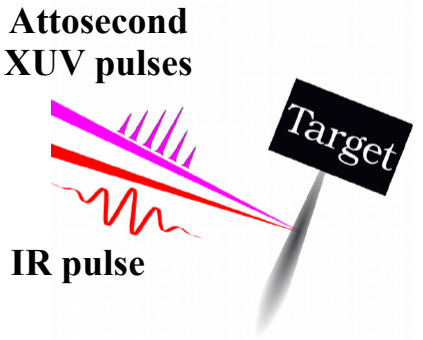
→ **Doable but difficult (Free Electron Lasers are more appropriate)**

Pump-probe attosecond experiment ?

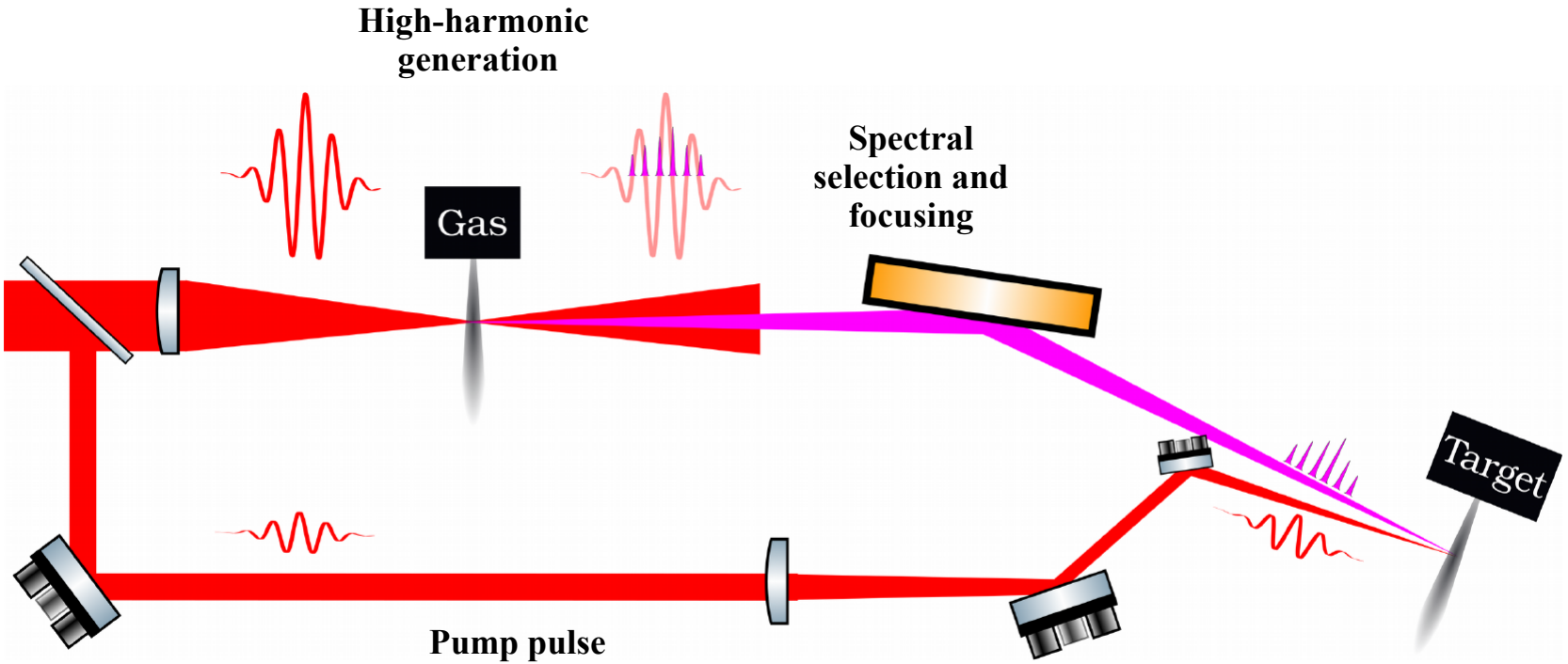
Pump ? Probe ? Observable ?

Conceptually easiest scheme : attosecond XUV pump – attosecond XUV probe

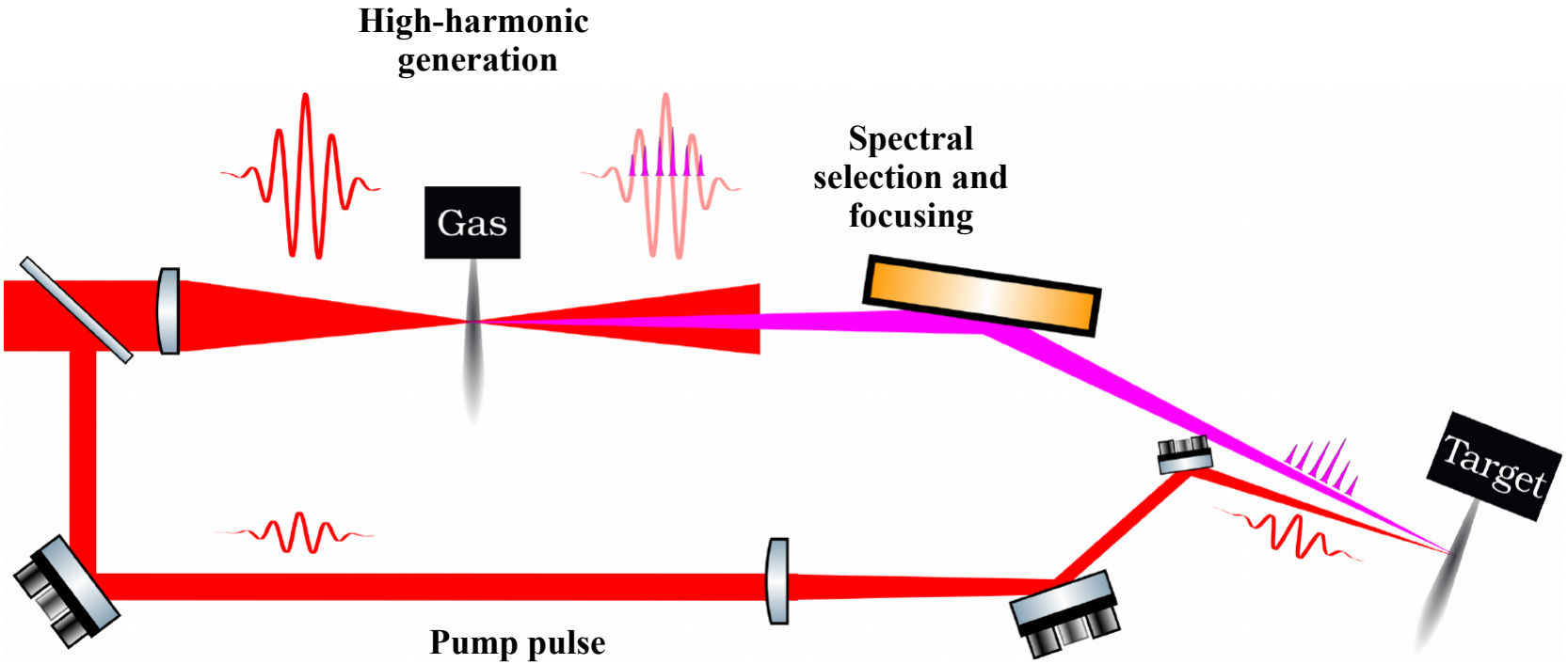
Technically easiest scheme : attosecond XUV pulse + infrared field



Pump-probe attosecond experiment



Pump-probe attosecond experiment



Observables ?
Photoions
Photoelectrons
Photons

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics

Autoionization dynamics

Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

An XUV pump – XUV probe experiment

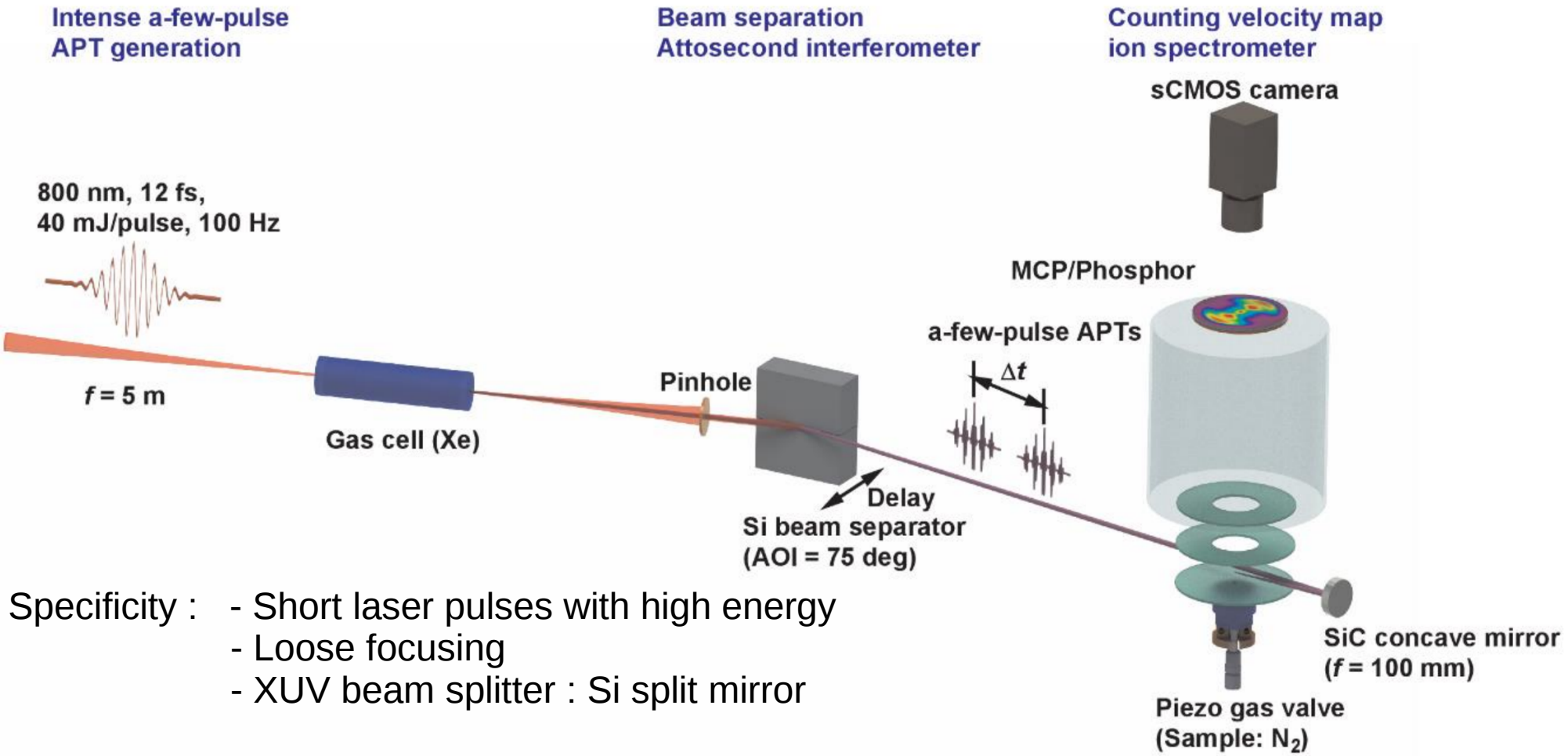
RESEARCH ARTICLE Okino *et al.* Sci. Adv. 2015;1:e1500356 25 September 2015

ULTRAFAST MOLECULAR PHYSICS

Direct observation of an attosecond electron wave packet in a nitrogen molecule

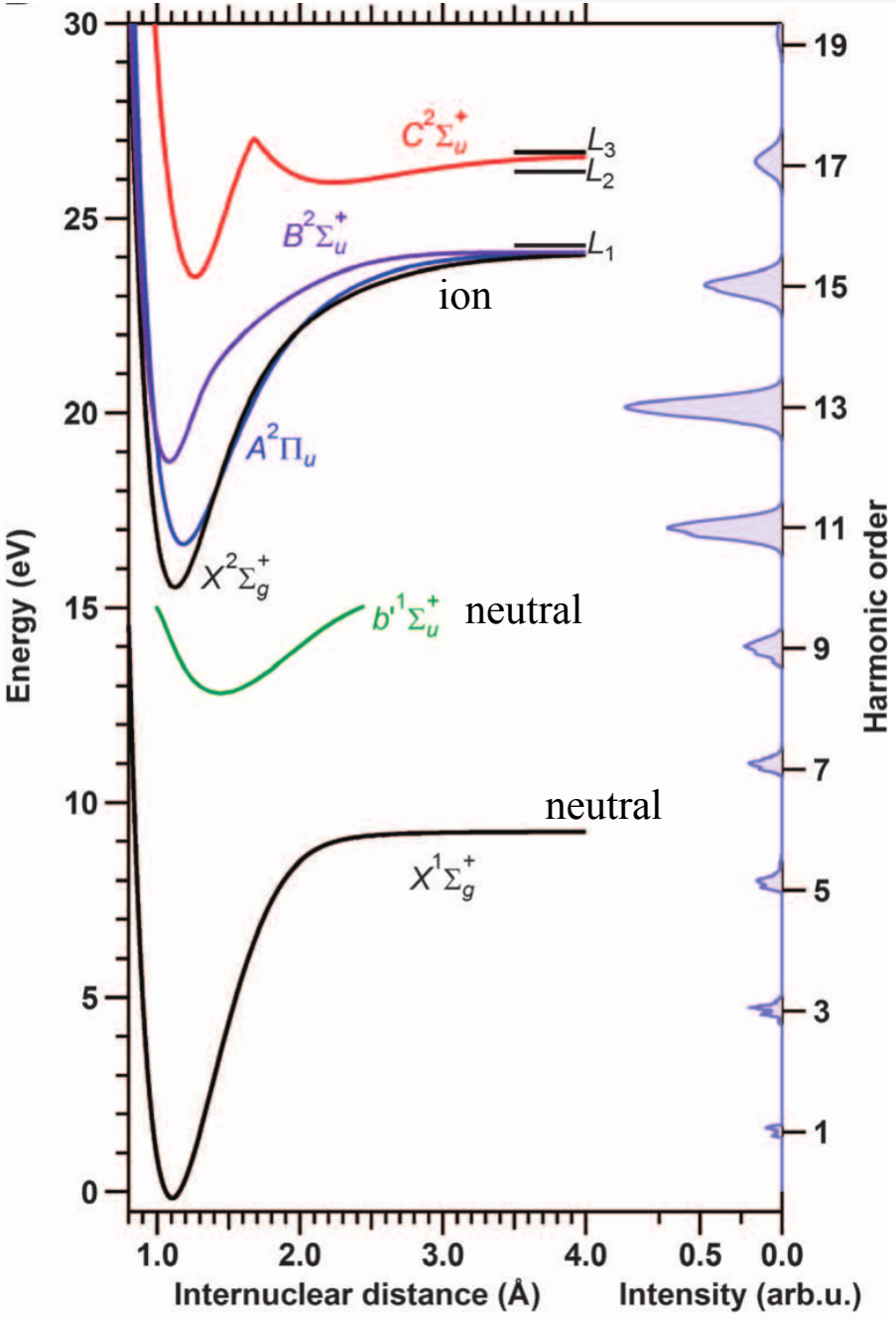
10.1126/sciadv.1500356

Tomoya Okino,[1]* Yusuke Furukawa,[1†] Yasuo Nabekawa,[1] Shungo Miyabe,[1] A. Amani Eilanlou,[1] Eiji J. Takahashi,[1] Kaoru Yamanouchi,[2] Katsumi Midorikawa[1]*



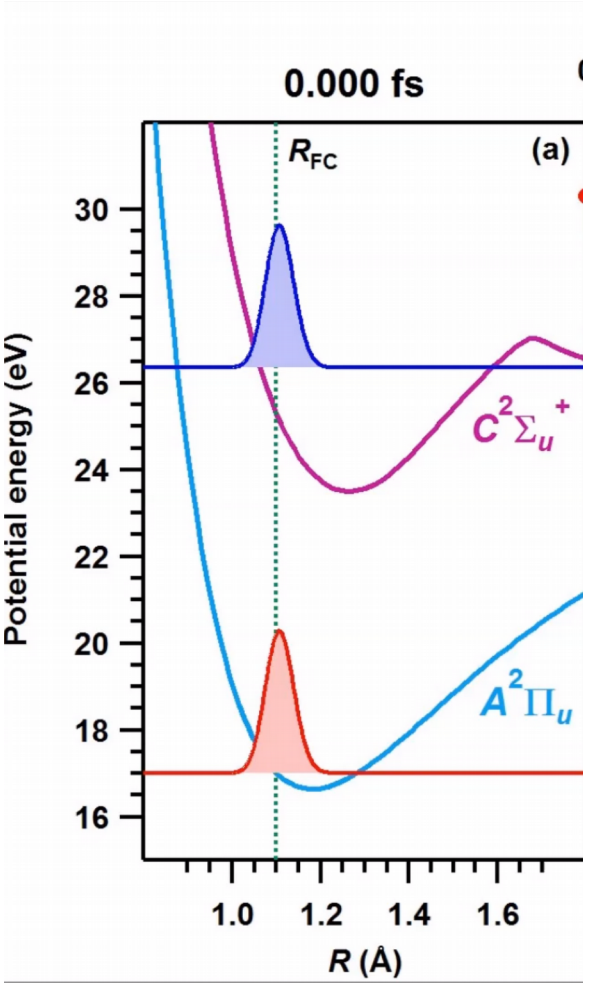
Specificity : - Short laser pulses with high energy
- Loose focusing
- XUV beam splitter : Si split mirror

Potential energy curves in N2



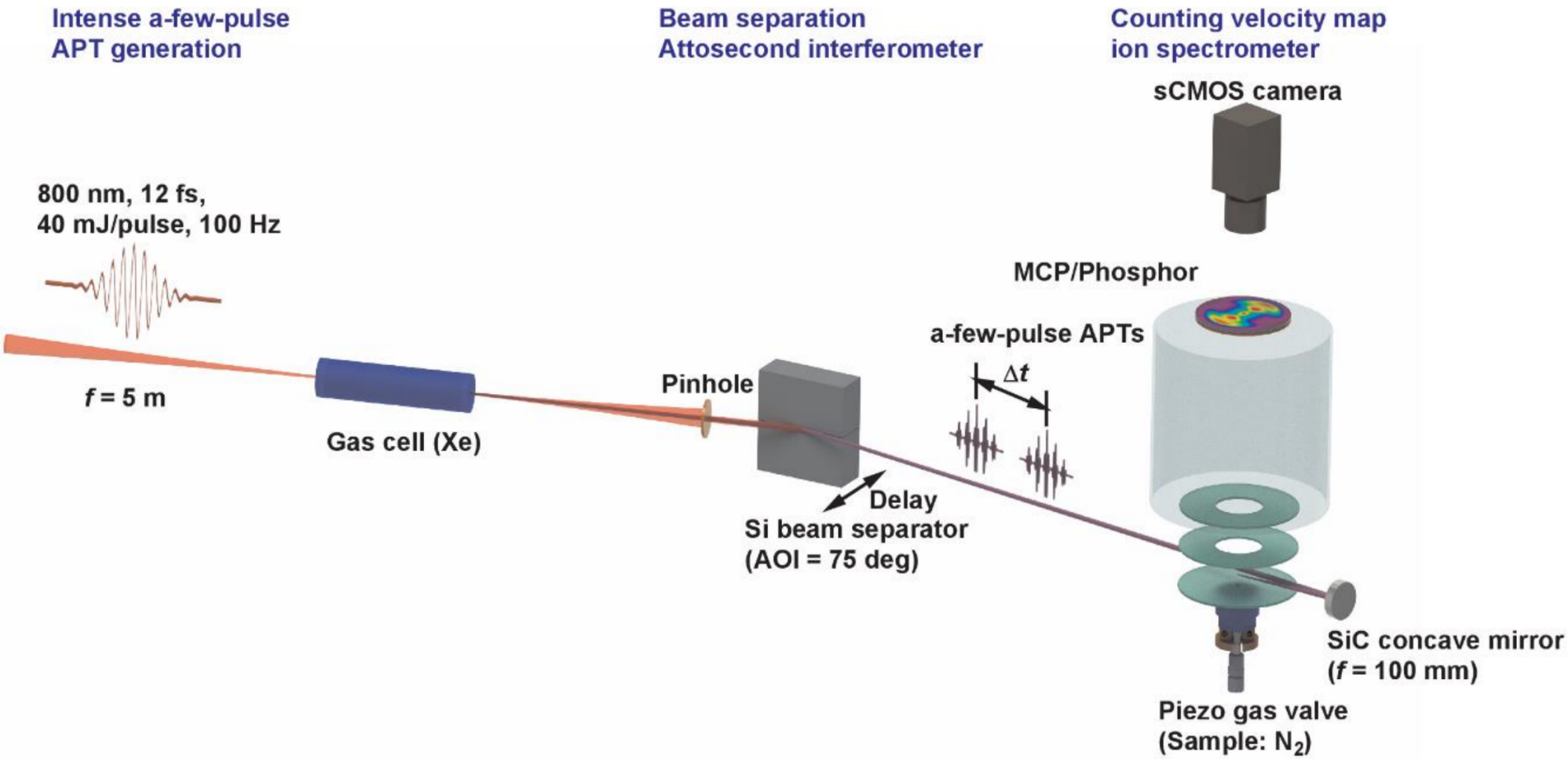
Pump pulse :
excites a coherent superposition
of bound electronic states

→ **triggers electronic and vibrational dynamics**

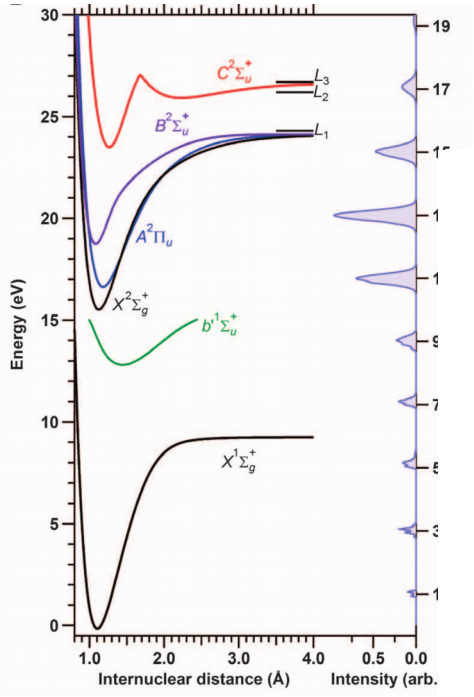


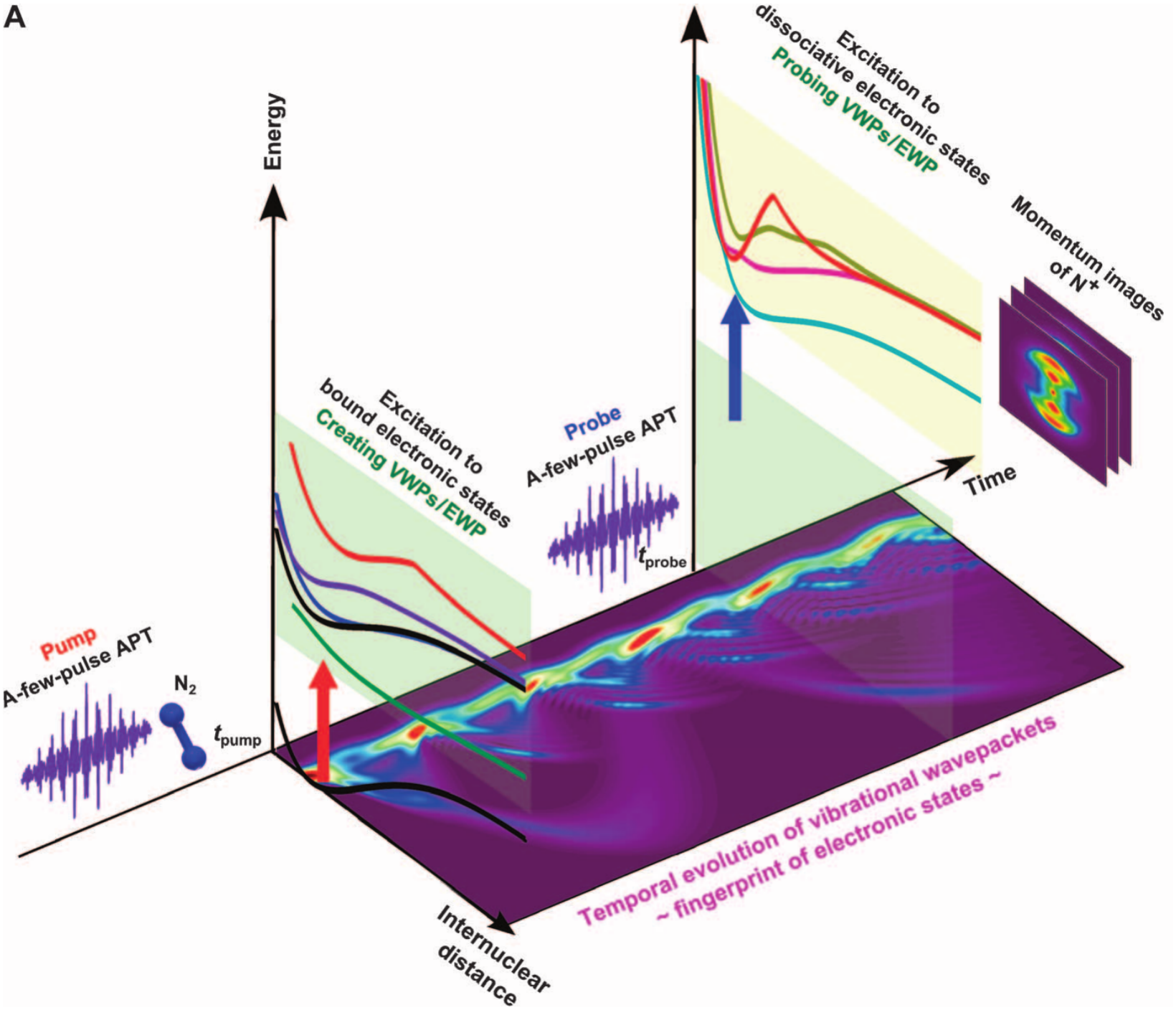
Probe pulse ? Observable ?

Observable ?

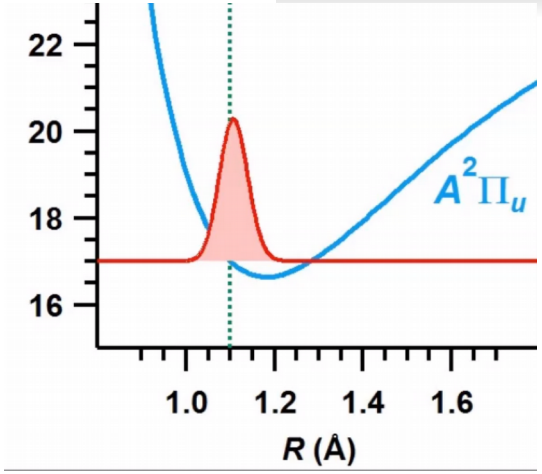

Intense a-few-pulse
APT generation
Beam separation
Attosecond interferometer
Counting velocity map
ion spectrometer
sCMOS camera
800 nm, 12 fs,
40 mJ/pulse, 100 Hz
MCP/Phosphor
a-few-pulse APTs
Δt
f = 5 m
Gas cell (Xe)
Pinhole
Delay
Si beam separator
(AOI = 75 deg)
SiC concave mirror
(f = 100 mm)
Piezo gas valve
(Sample: N2)

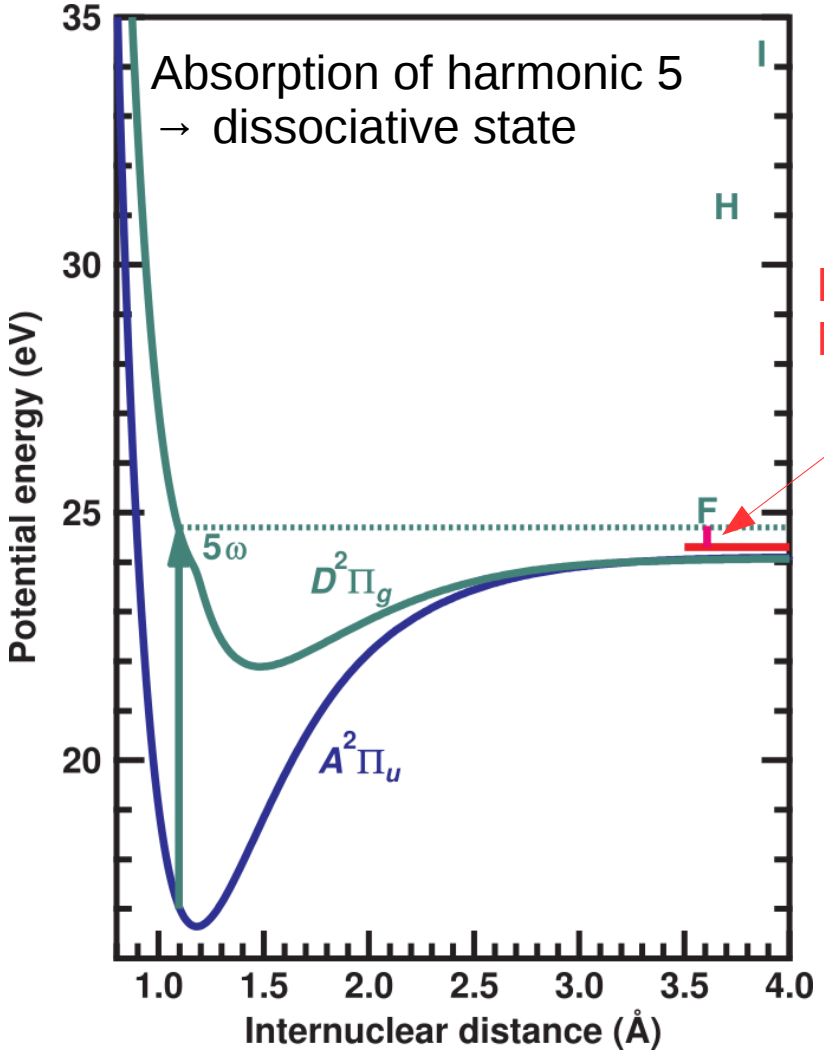
Pump-probe scheme





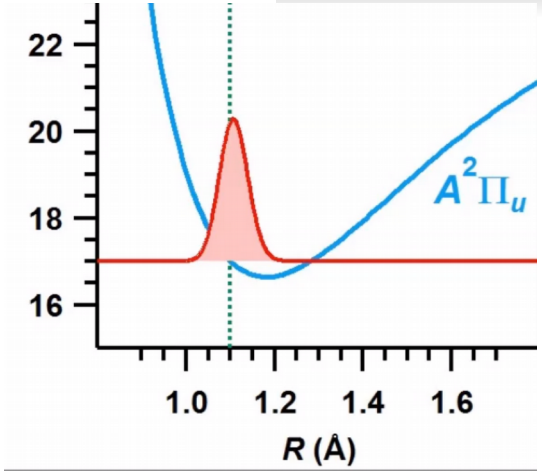
Example : Probing the vibrational dynamics in the A state

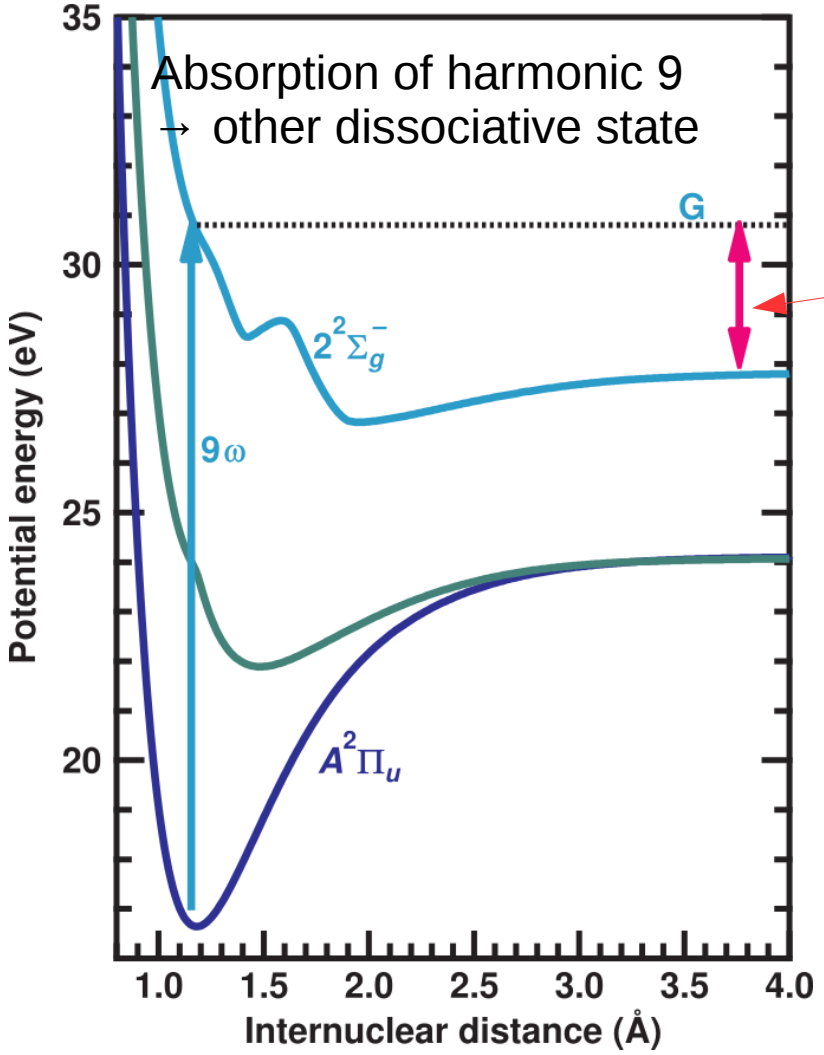




Final kinetic energy of the N+ ion

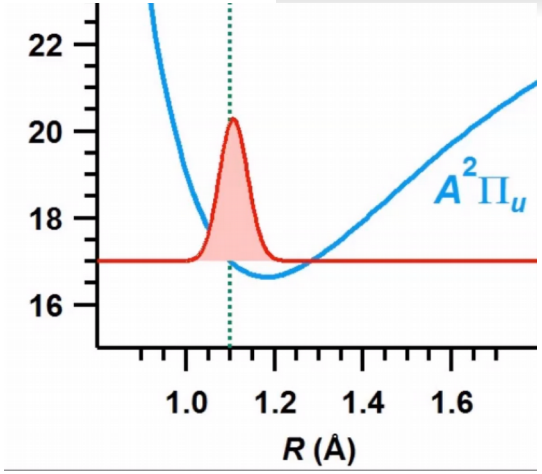
Example : Probing the vibrational dynamics in the A state

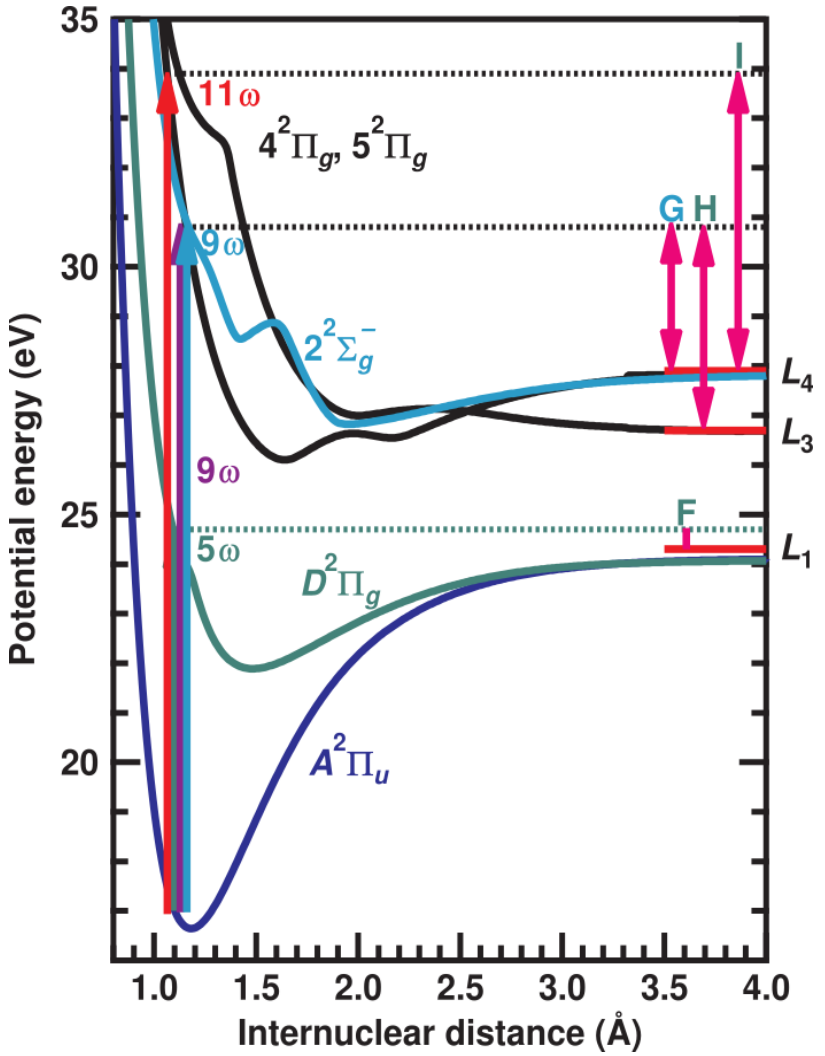




Final kinetic energy of the N+ ion

Example : Probing the vibrational dynamics in the A state



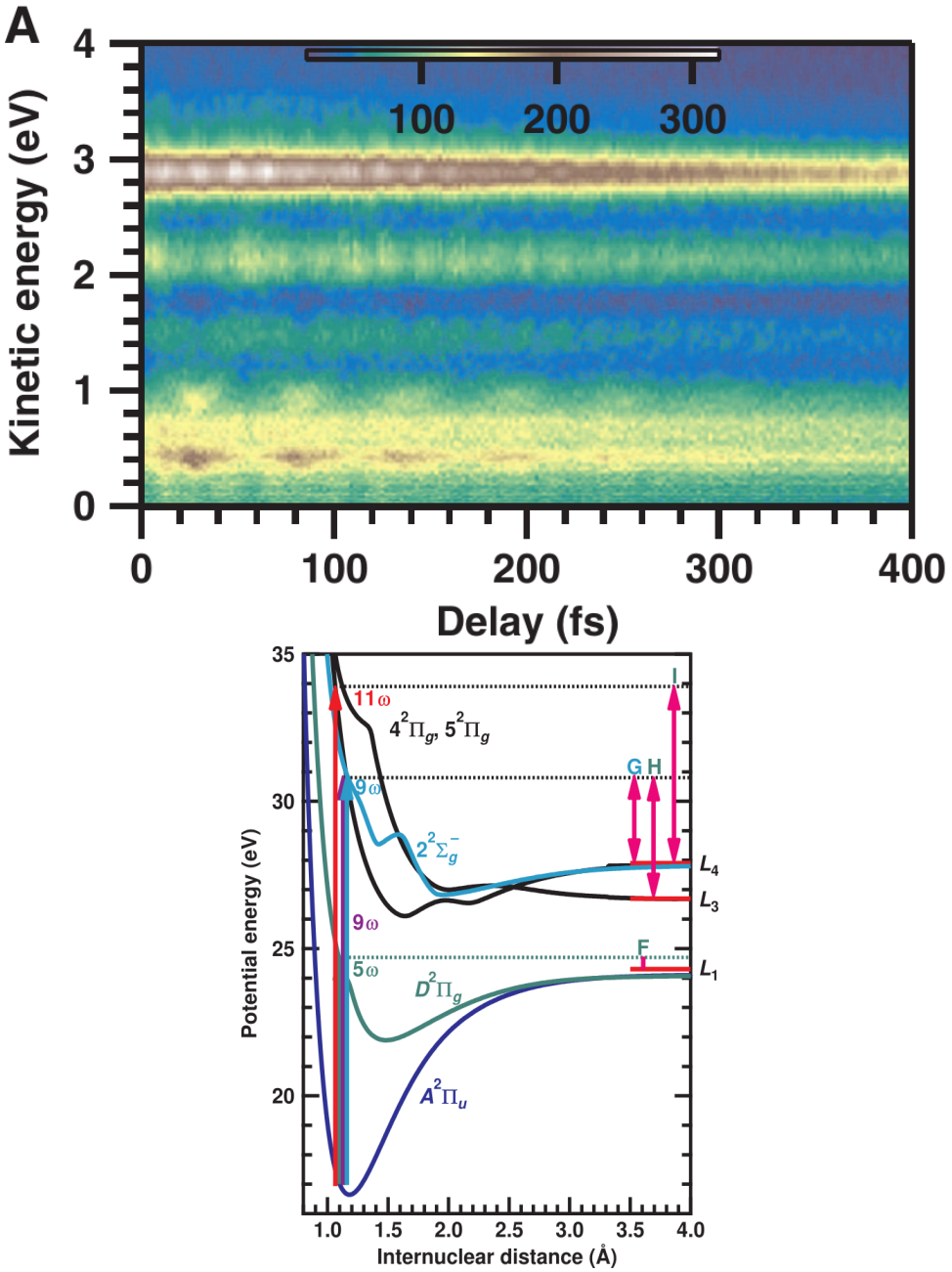


Final kinetic energy of the N+ ion

Multiple spectral components in the probe pulse → multiple kinetic energies
The N+ ion signal at these energies should reflect the vibrational dynamics of the A state

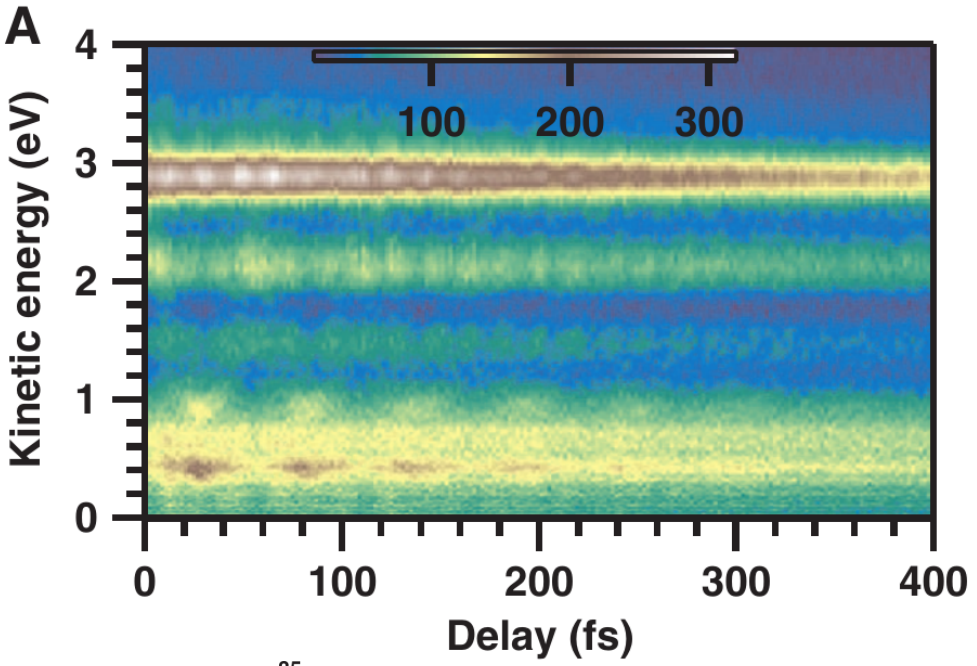
Measurement of vibrational dynamics

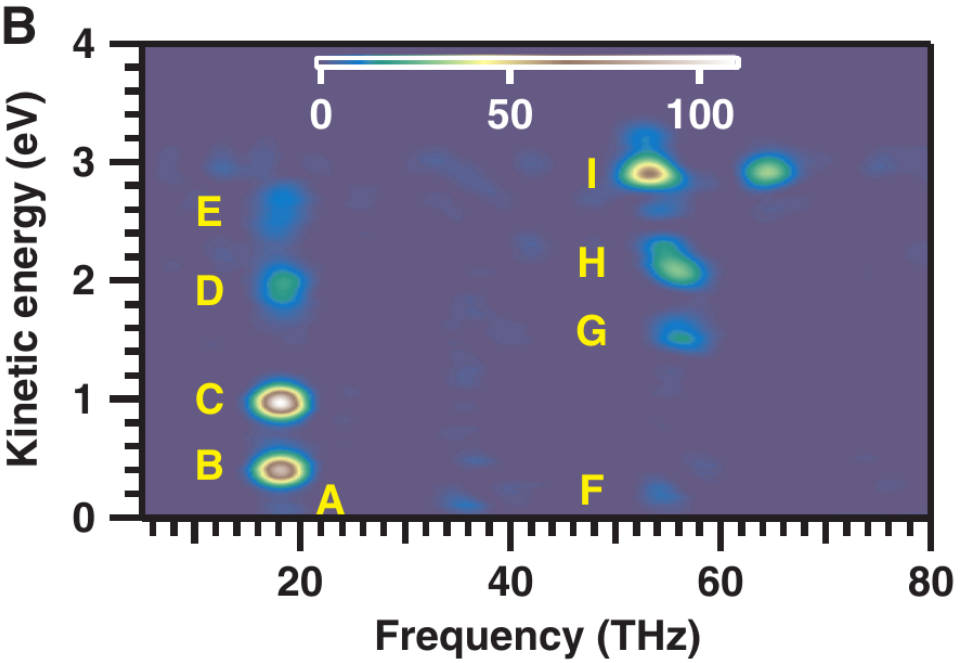
Low resolution measurement at long delays.

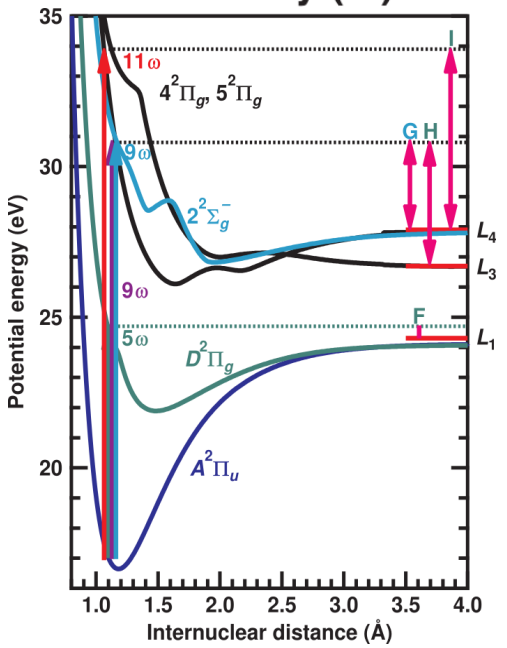


Measurement of vibrational dynamics

Low resolution measurement at long delays.
Fourier transform spectroscopy → vibrational modes for each Ion kinetic energy



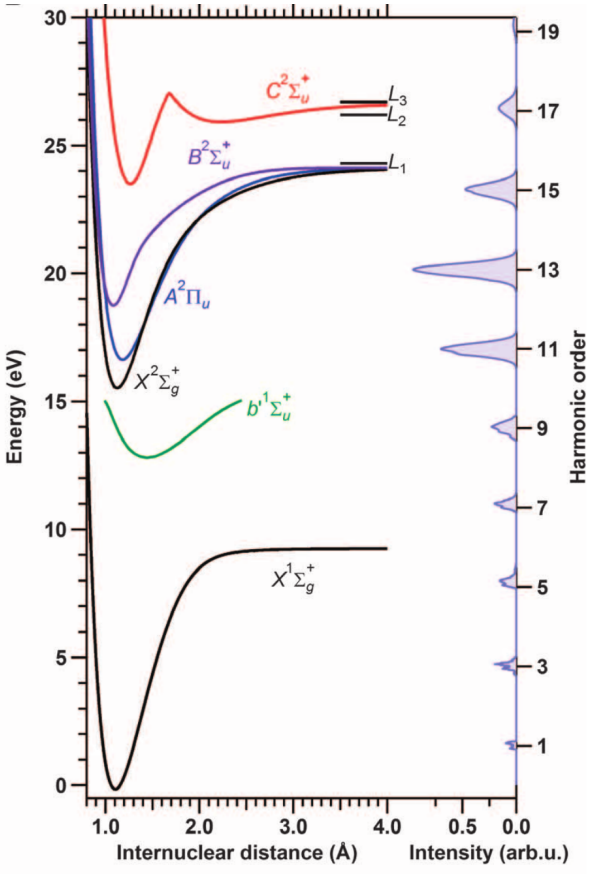




F,G,H,I peaks show similar frequency
→ they all probe the vibration in the A state

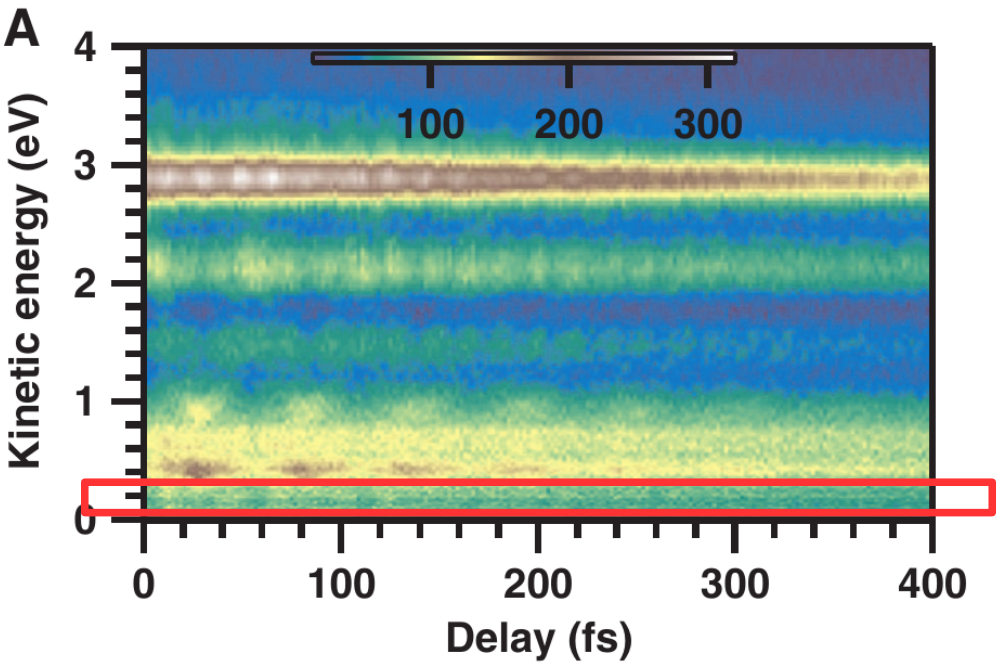
B,C,D,E peaks probe the vibration in another state

Electronic wavepacket



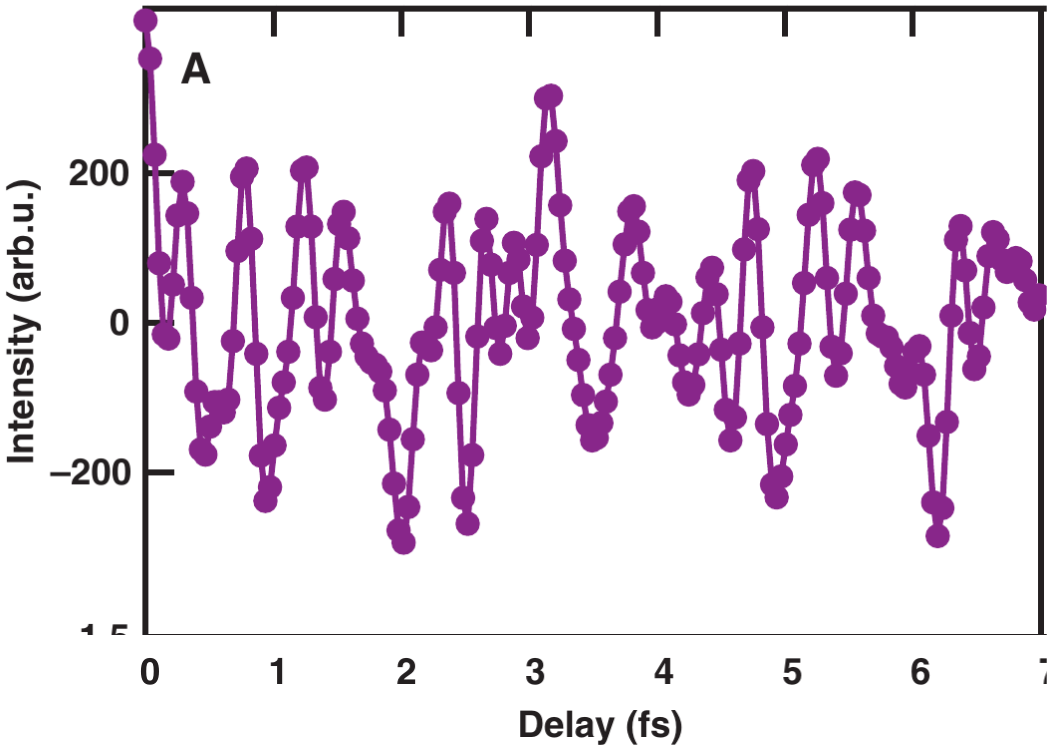
Analysis show that 5 electronic states
lead to N+ fragments with 0.2 eV energy

→ **Electronic wavepacket dynamics ?**

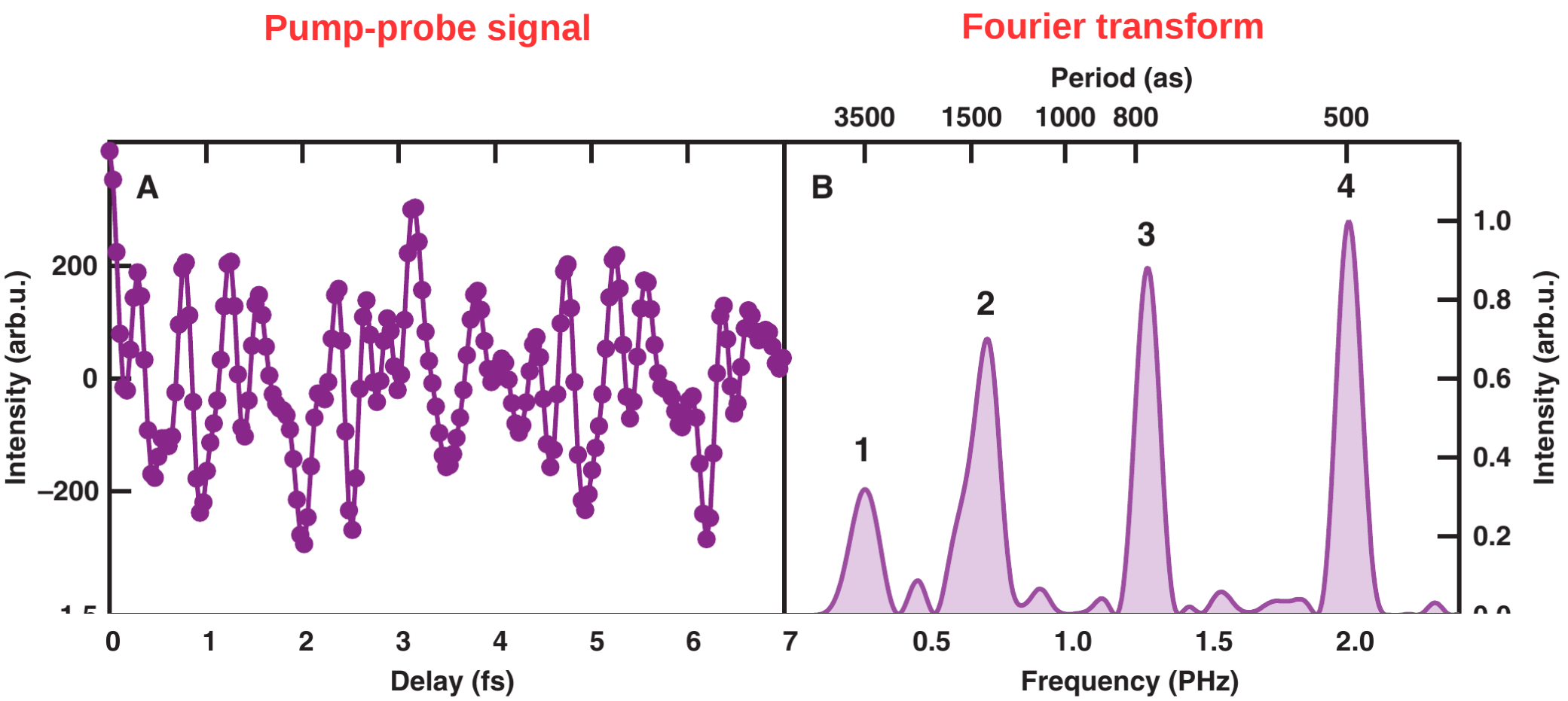


High resolution ion signal at 0.2 eV

Pump-probe signal

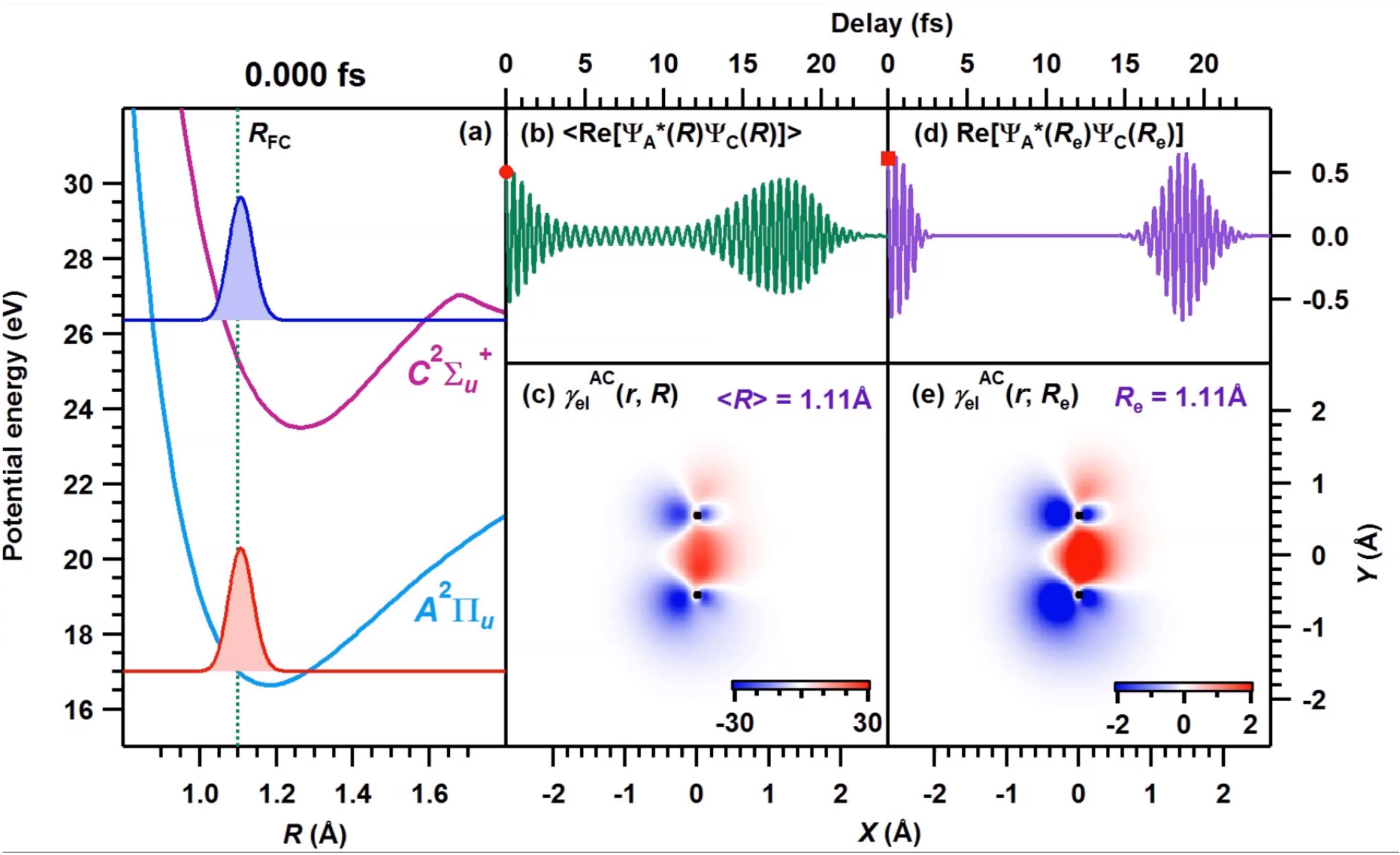


High resolution ion signal at 0.2 eV

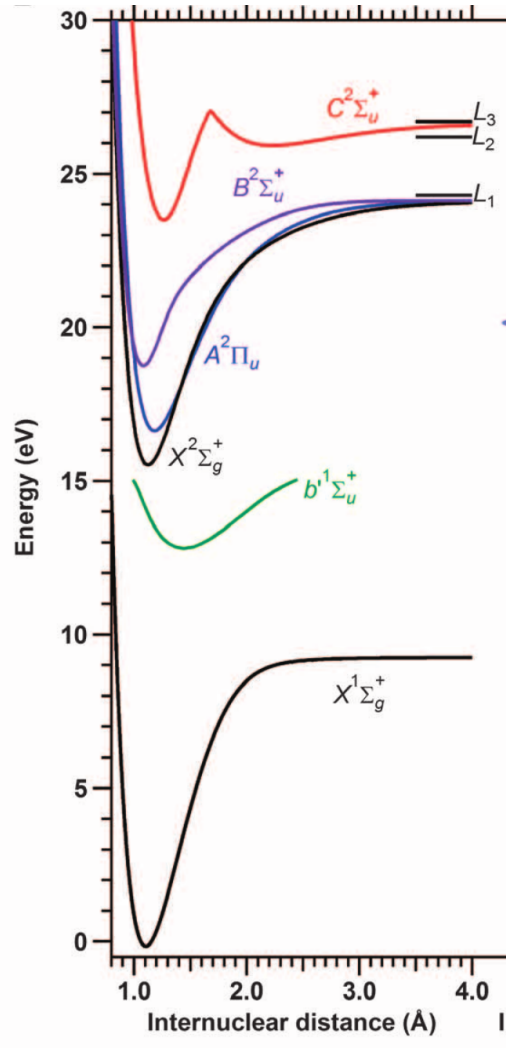


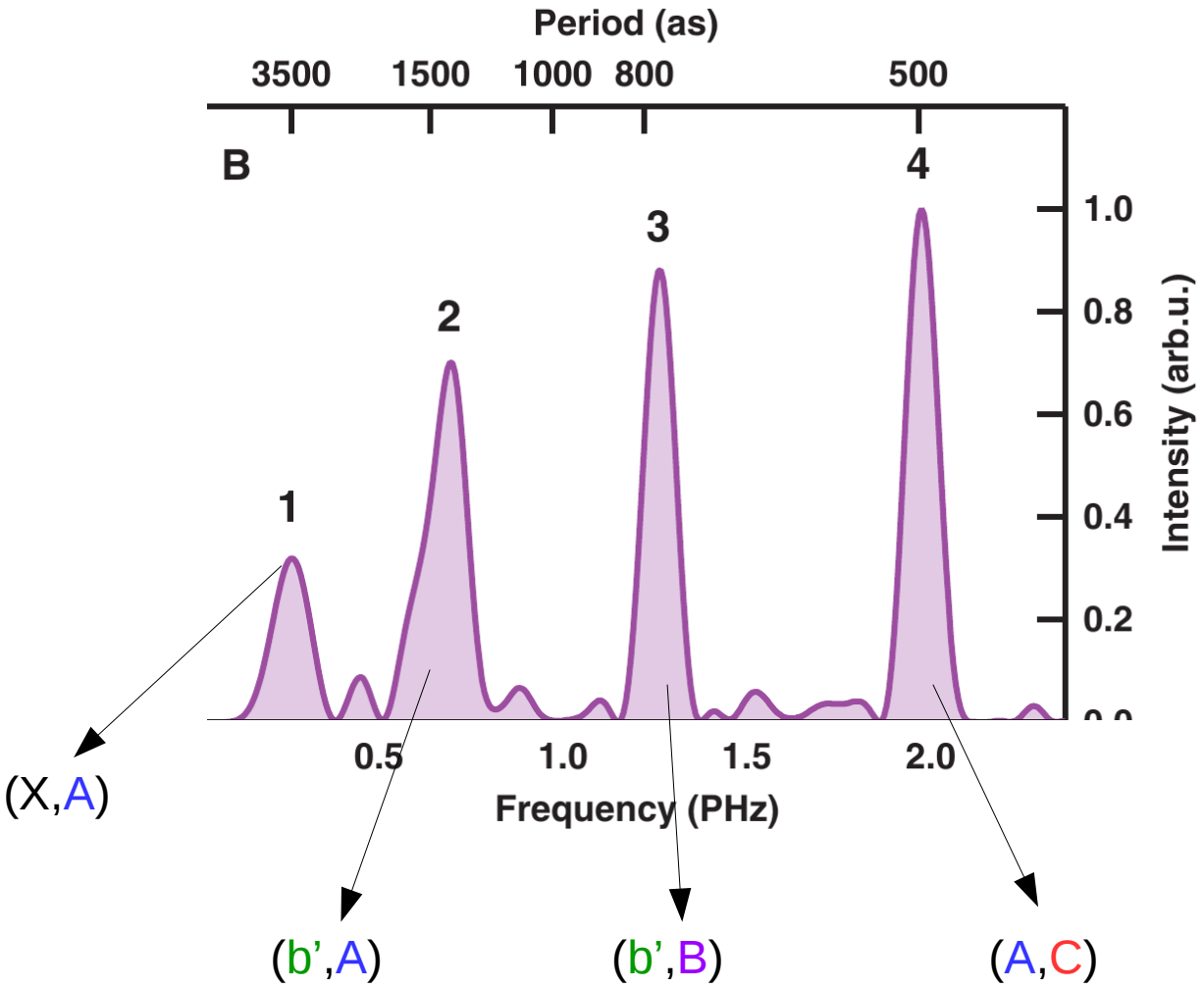
Fast oscillations originating from electronic dynamics

Electronic and vibrational wavepackets

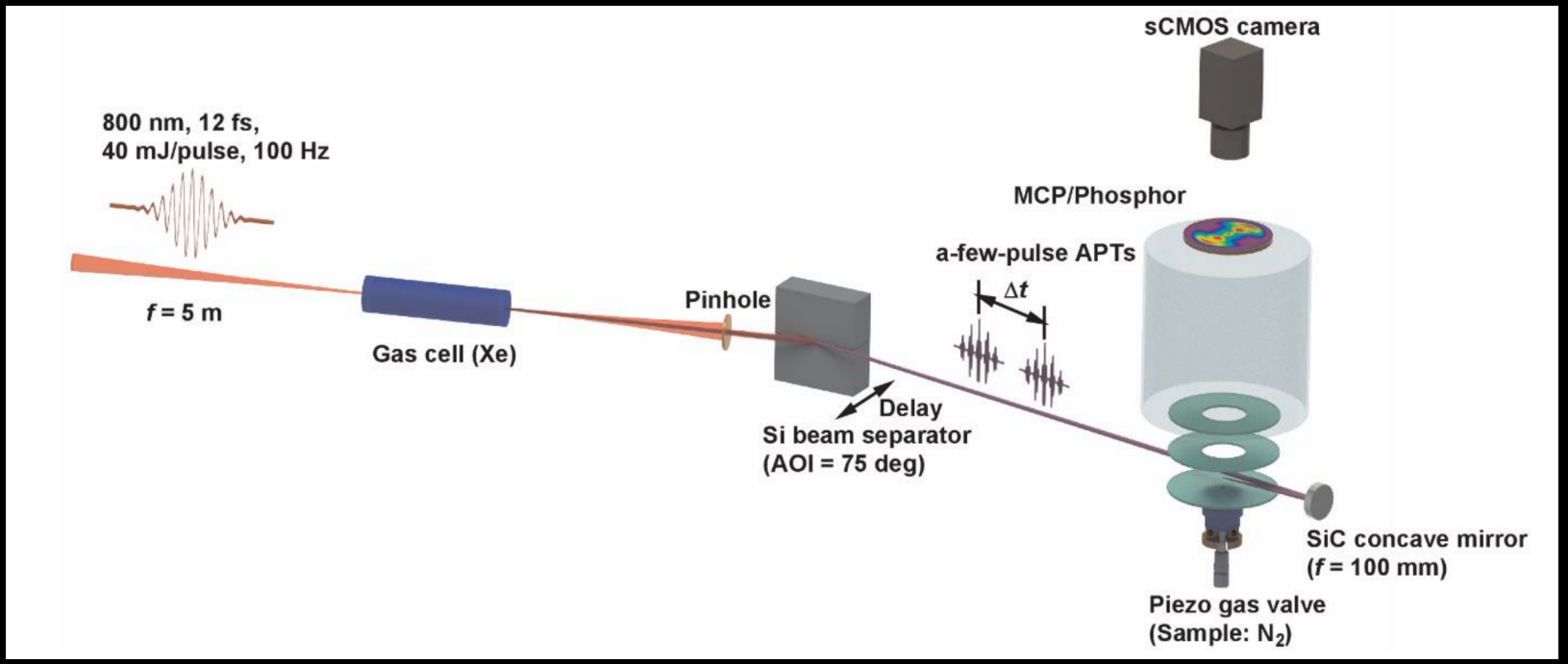


Assignment of electron wavepackets





Conclusions on XUV-XUV Fourier transform spectroscopy



Very difficult experiment – need intense attosecond pulses

Broad bandwidth of attosecond pulses : open many channels in both pump and probe steps
→ Not straightforward interpretations

General issue in attosecond photoionization experiments

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics

Autoionization dynamics

Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Attosecond pump-probe without XUV-XUV ?

Ultrafast electron dynamics in phenylalanine initiated by attosecond pulses

F. Calegari,[1] D. Ayuso,[2] A. Trabattoni,[3] L. Belshaw,[4] S. De Camillis,[4] S. Anumula,[3]
F. Frassetto,[5] L. Poletto,[5] A. Palacios,[2] P. Decleva,[6] J. B. Greenwood,[4]
F. Martín,[2,7]* M. Nisoli[1,3]*

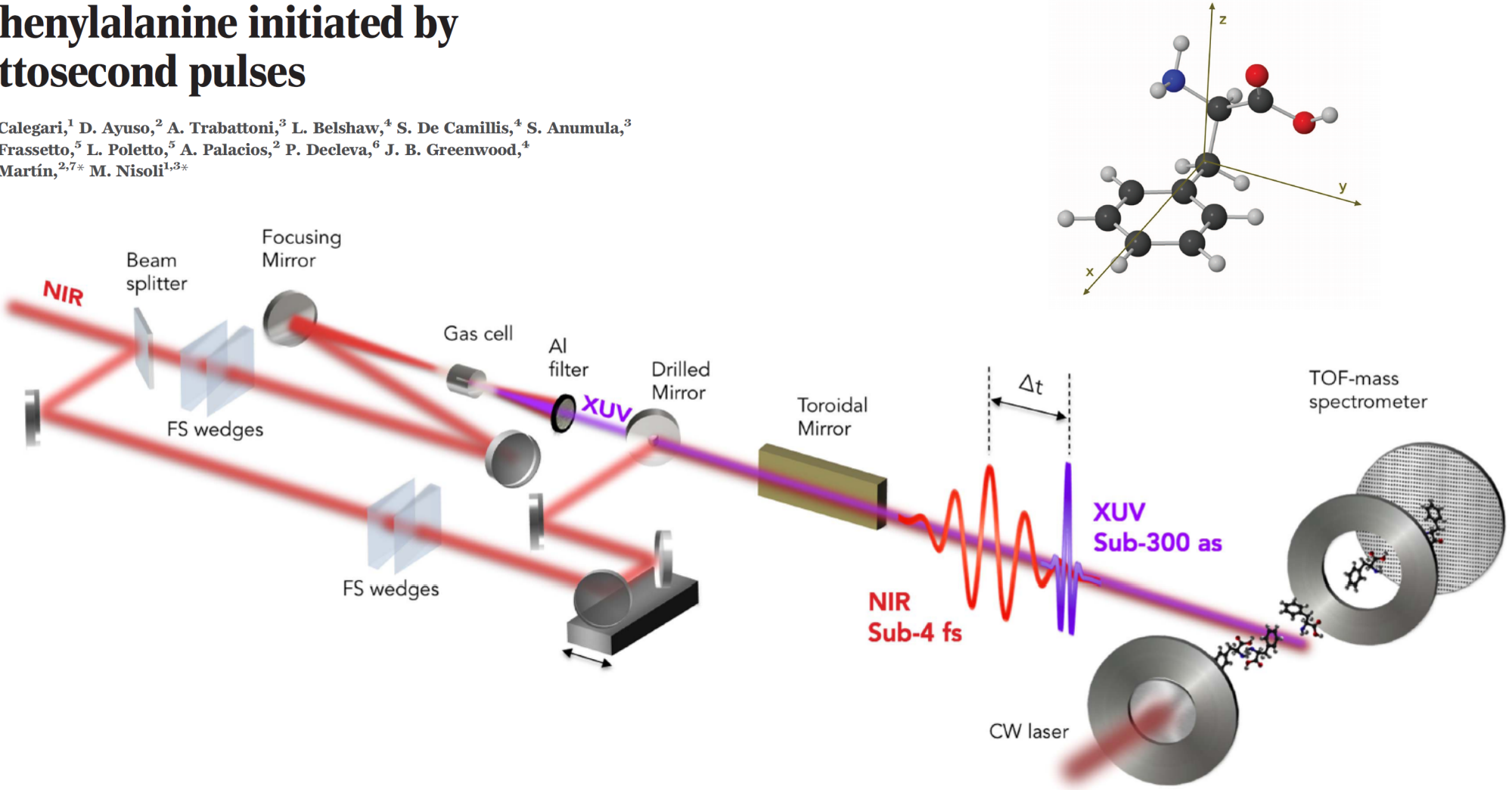


Figure 7. Scheme of the attosecond setup used to initiate and track electron dynamics in phenylalanine.

Pump : 300 as XUV pulse

Probe: 4 fs IR pulse

Observable : dication signal

Photoionization of phenylalanine – theory

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Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **49** (2016) 142001 (25pp)
doi:10.1088/0953-4075/49/14/142001

Topical Review

Charge migration induced by attosecond pulses in bio-relevant molecules

Francesca Calegari[1], Andrea Trabattoni[2], Alicia Palacios[3], David Ayuso[3], Mattea C Castrovilli[1], Jason B Greenwood[4], Piero Decleva[5], Fernando Martín[3,6,7] and Mauro Nisoli[1,2]

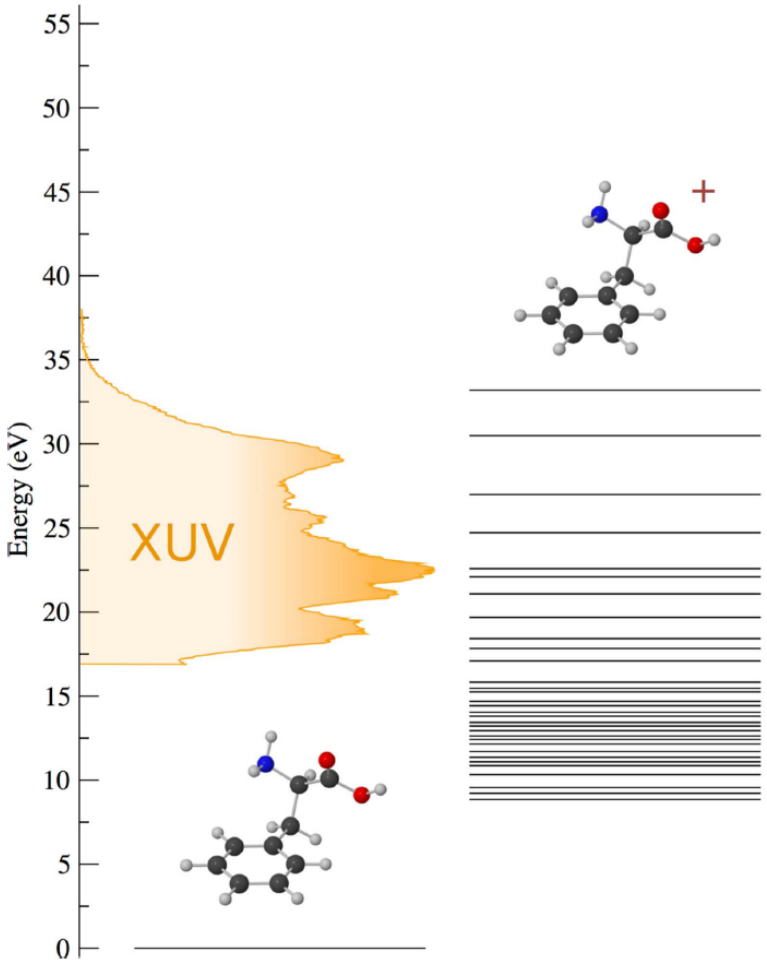


Figure 14. Energy level diagram containing all the states of singly charged phenylalanine populated by the XUV pulse, whose energy distribution is included as a shadowed area in the axis bar, all the states of doubly charged phenylalanine and those for the system doubly charged immonium + neutral carboxyl.

Many ionization channel open by attosecond photoionization

Photoionization of phenylalanine – theory

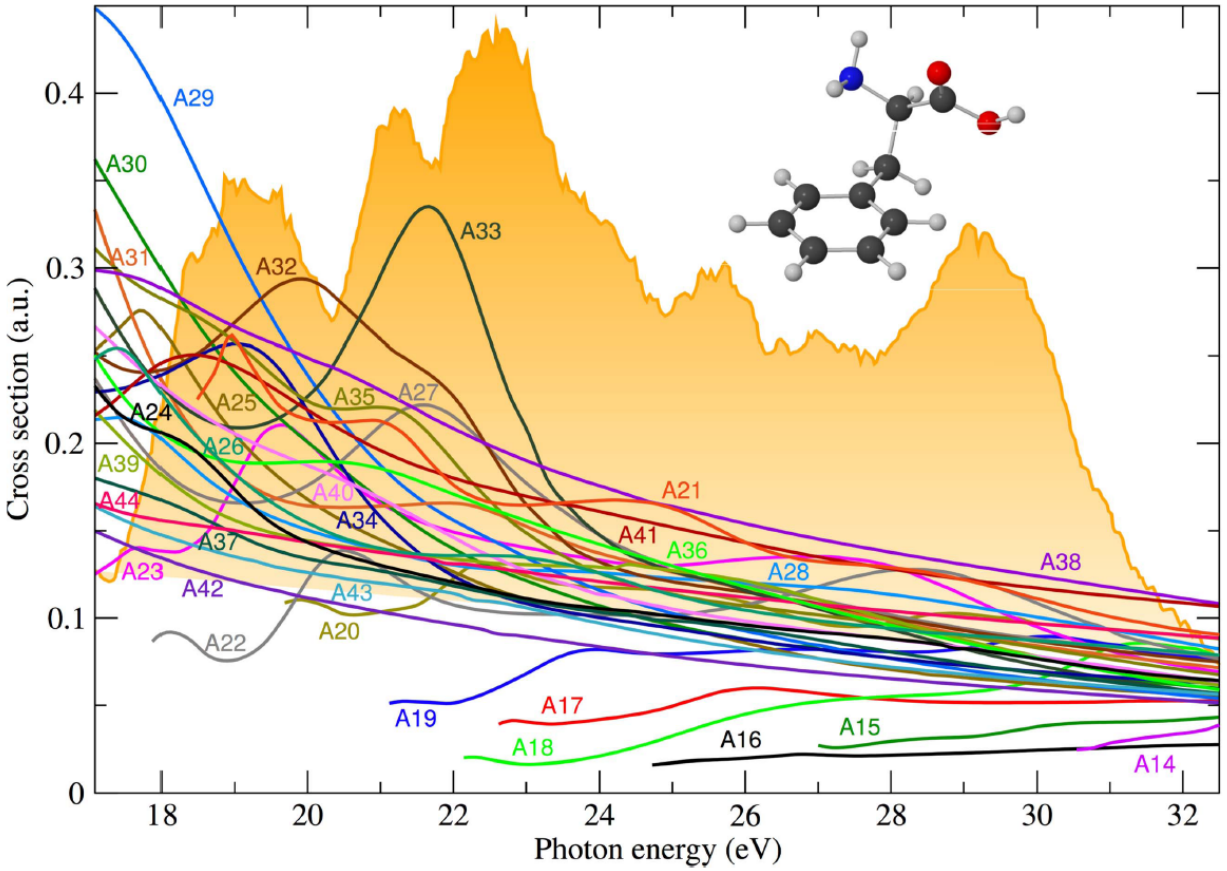


Figure 13. Photoionization cross sections of phenylalanine from different molecular orbitals calculated using the static-exchange DFT method. Numbers and colors denote the molecular orbitals from where the electron is emitted in each case. The filled orange line in the background corresponds to the energy spectrum of the attosecond pump pulse used in the experimental set-up shown in section 3.2 and plotted in figure 8.

Many ionization channel open by attosecond photoionization

Photoionization of phenylalanine

Pump : Coherent superposition of multiple ionic states
→ Wavepacket in the ion

Dynamics ?

Simple beating between ionic states ?
Role of electronic correlation ?
At longer timescales, influence of nuclear motion ?

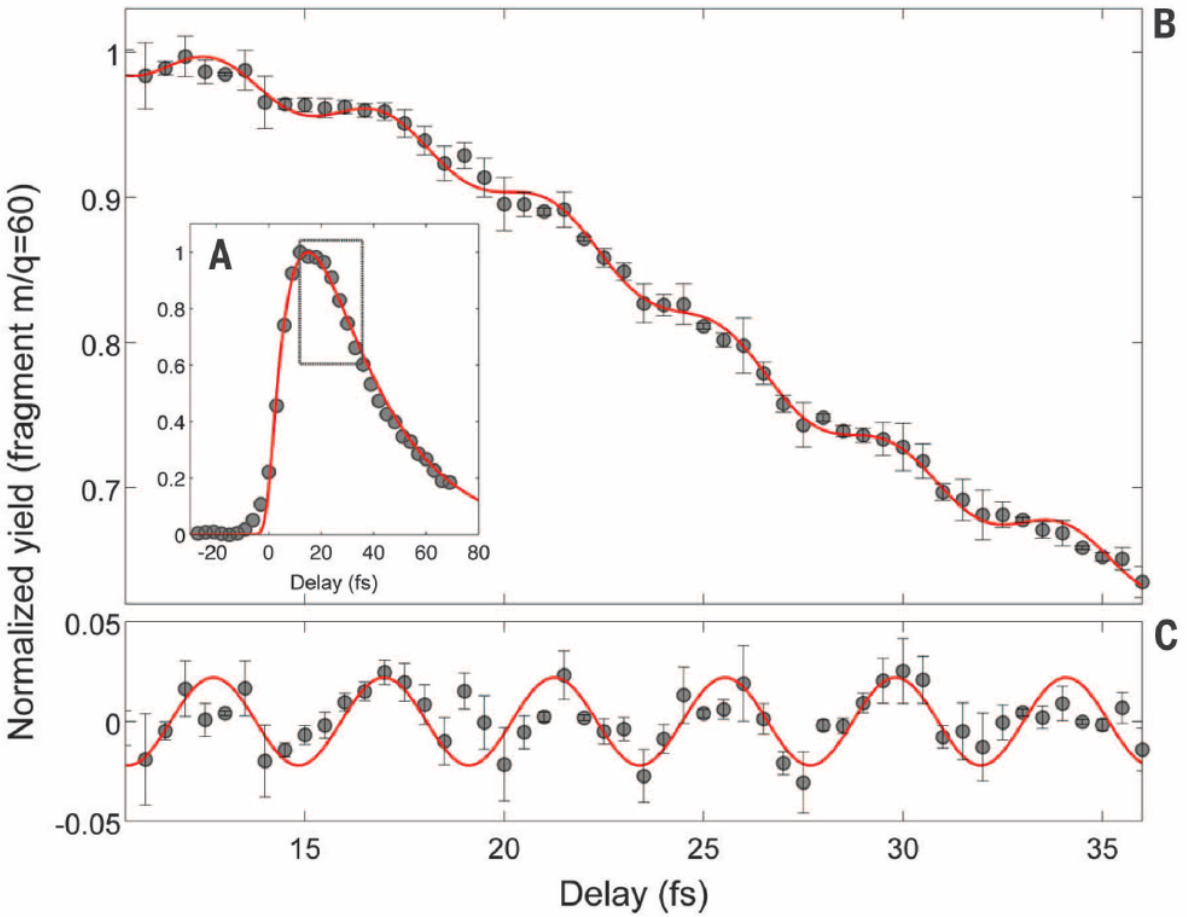
What probe ?

Ionize the ion with strong infrared field

What observable ?

Number of doubly charged ions

Experimental signal



Ion yield

Oscillating part of the signal

Fig. 2. Pump-probe measurements. (**A**) Yield of doubly charged immonium ion (mass/charge = 60) as a function of pump-probe delay, measured with 3-fs temporal steps. The red line is a fitting curve with an exponential rise time of 10 fs and an exponential relaxation time of 25 fs. (**B**) Yield of doubly charged immonium ion versus pump-probe delay measured with 0.5-fs temporal steps, within the temporal window shown as dotted box in (A). Error bars show the standard error of the results of four measurements. The red line is the fitting curve given by the sum of the fitting curve shown in (A) and a sinusoidal function of frequency 0.234 PHz (4.3-fs period). (**C**) Difference between the experimental data and the exponential fitting curve displayed in (A). Red curve is a sinusoidal function of frequency 0.234 PHz.

Oscillations at 0,234 PHz frequency – 4.3fs period

Theoretical study : ionized orbitals

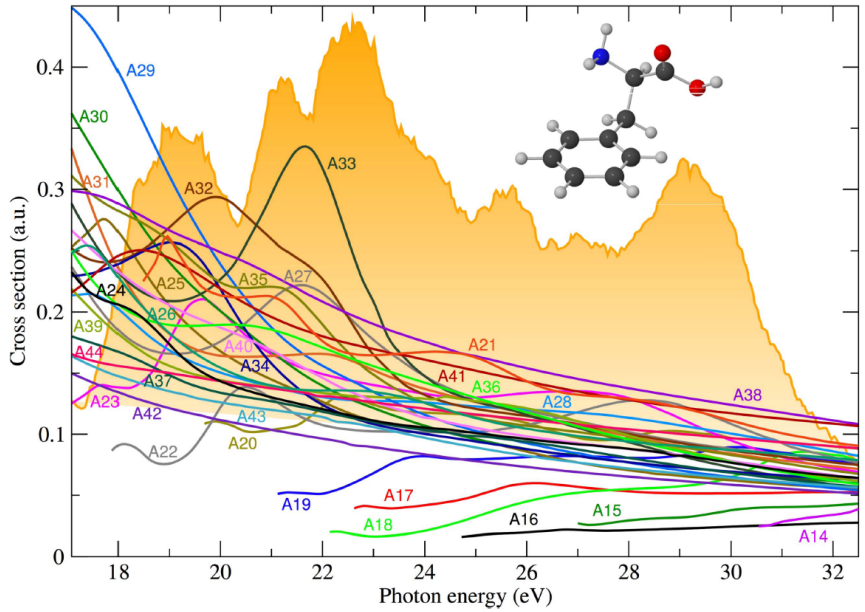


Figure 13. Photoionization cross sections of phenylalanine from different molecular orbitals calculated using the static-exchange DFT method. Numbers and colors denote the molecular orbitals from where the electron is emitted in each case. The filled orange line in the background corresponds to the energy spectrum of the attosecond pump pulse used in the experimental set-up shown in section 3.2 and plotted in figure 8.

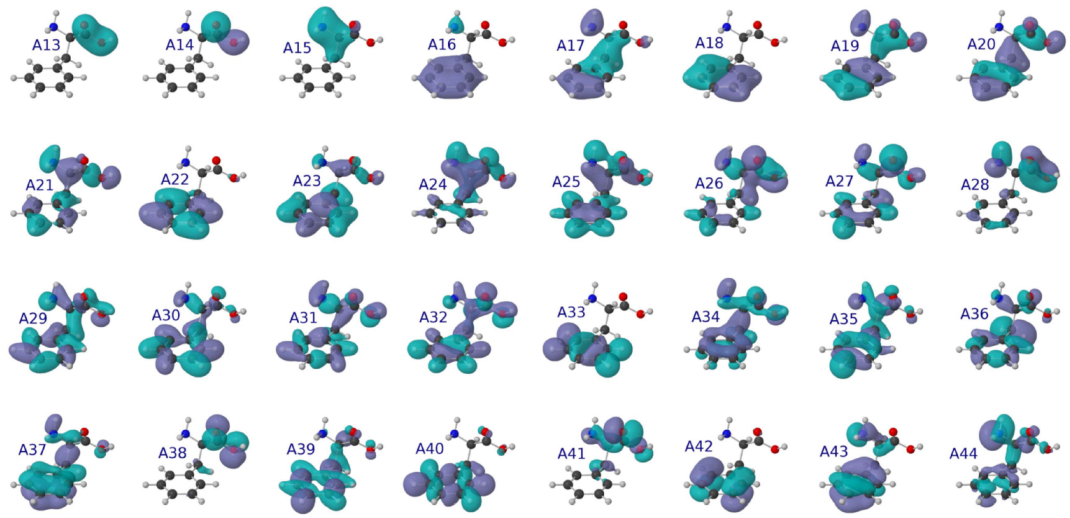
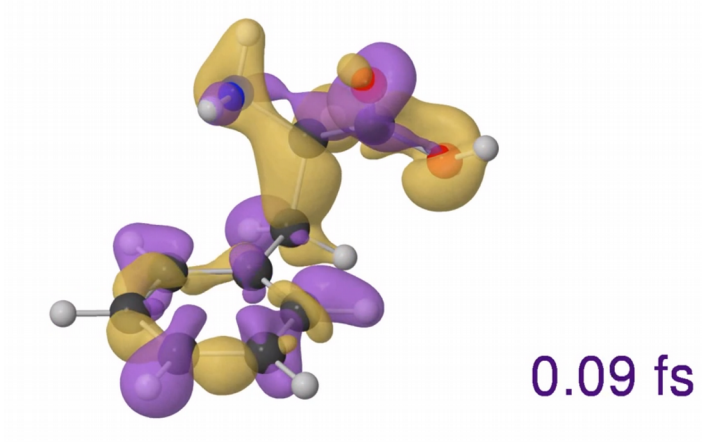


Figure 12. Occupied Kohn–Sham orbitals of the phenylalanine molecules obtained using the LB94 functional in a basis set of B-spline functions as explained in the text.

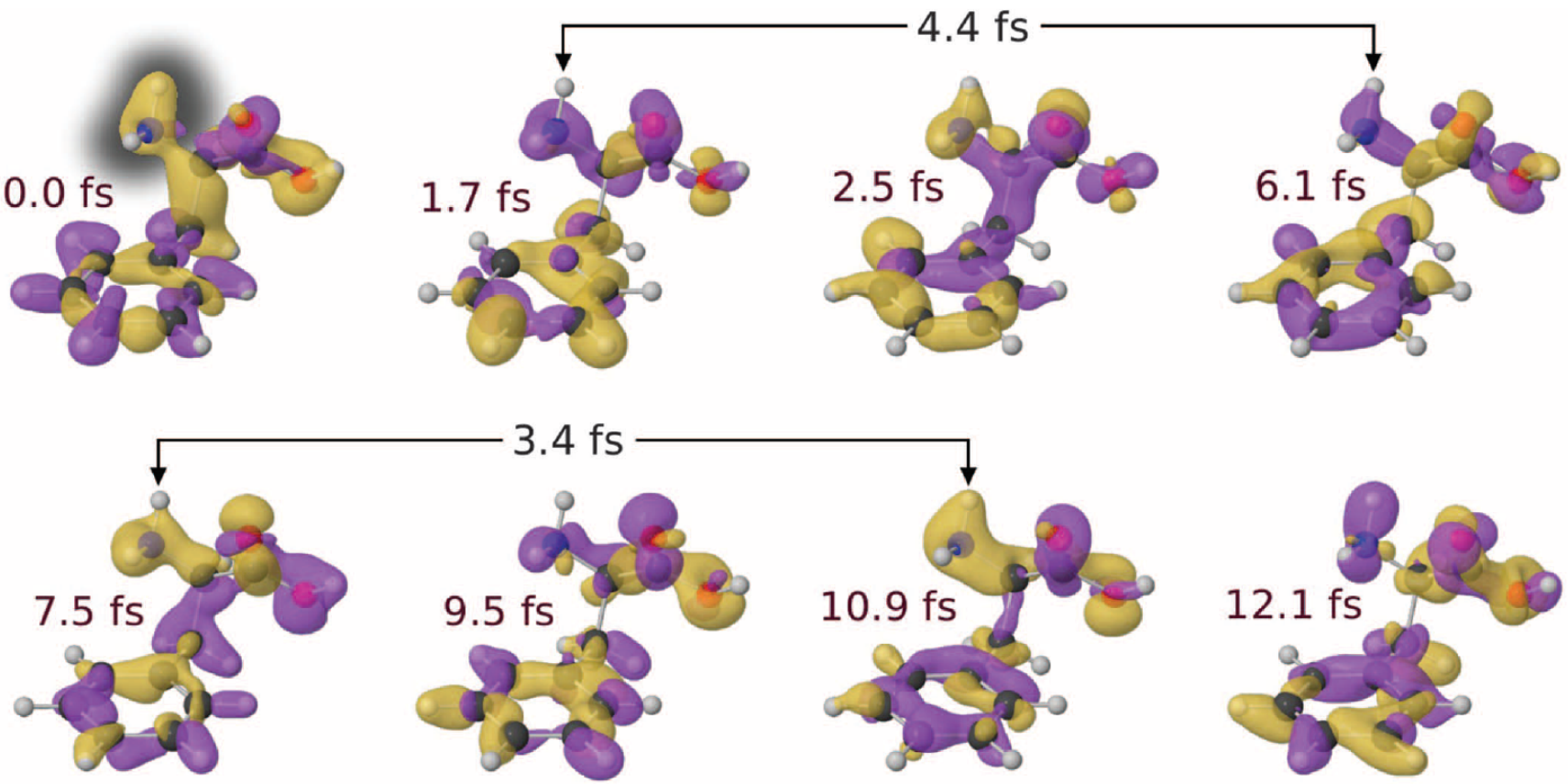
Many accessible ionic states

→ **Extremely complex dynamics**



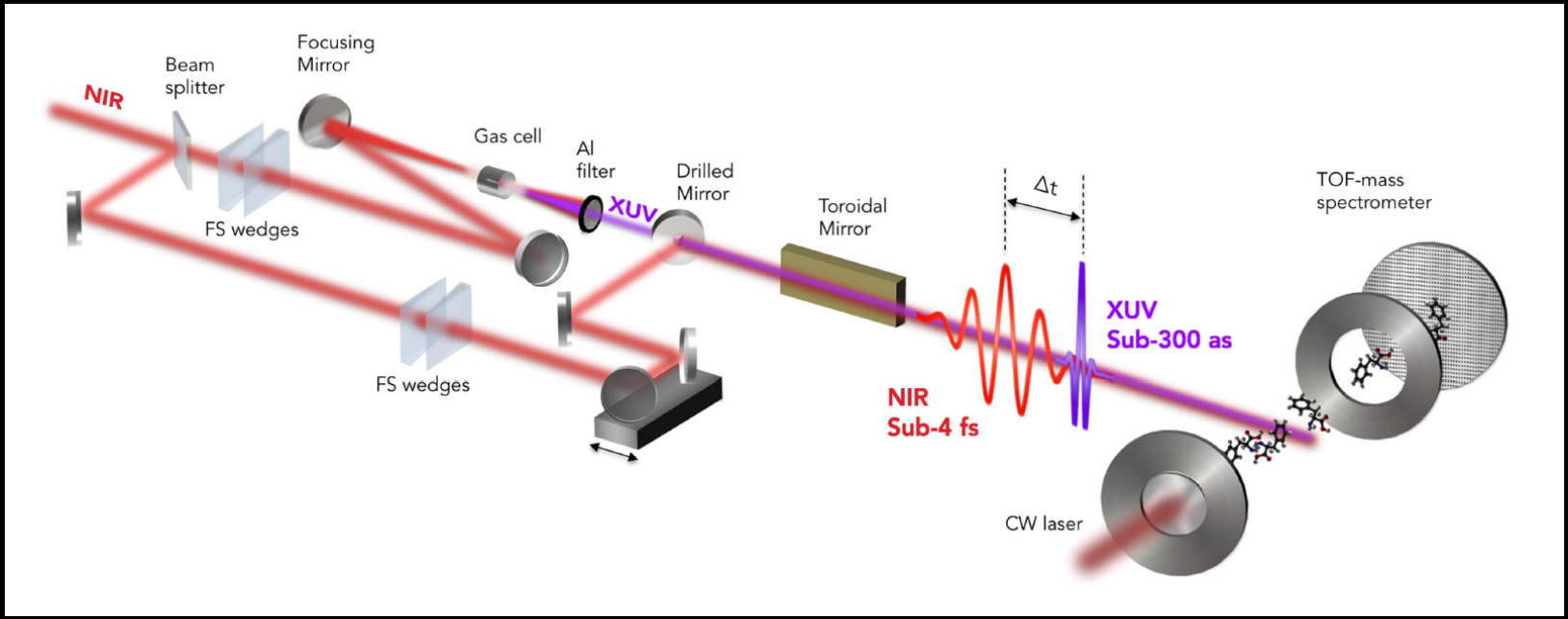
Theoretical evolution of the hole

How come the experiment sees a simple oscillating pattern ?



The double ionization yield oscillates with the same frequency as the density in the amino group

Conclusions on charge migration measurements



Attosecond charge migration can be probed by an XUV-IR scheme

No one would have predicted that the experiment would probe the hole density on the amino group.

The results demonstrate the role electronic correlation in the hole dynamics of phenylalanine, and a much weaker role in tryptophan

The experimental observable has low dimensionality : it is simply a number of ions vs delay

Increasing the dimensionality (eg measuring electrons in coincidence with the ions) would provide richer information, but the interpretation may not be easier

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics

Autoionization dynamics

Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Generation of attosecond pulses

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Electron escape dynamics – principle of the measurement

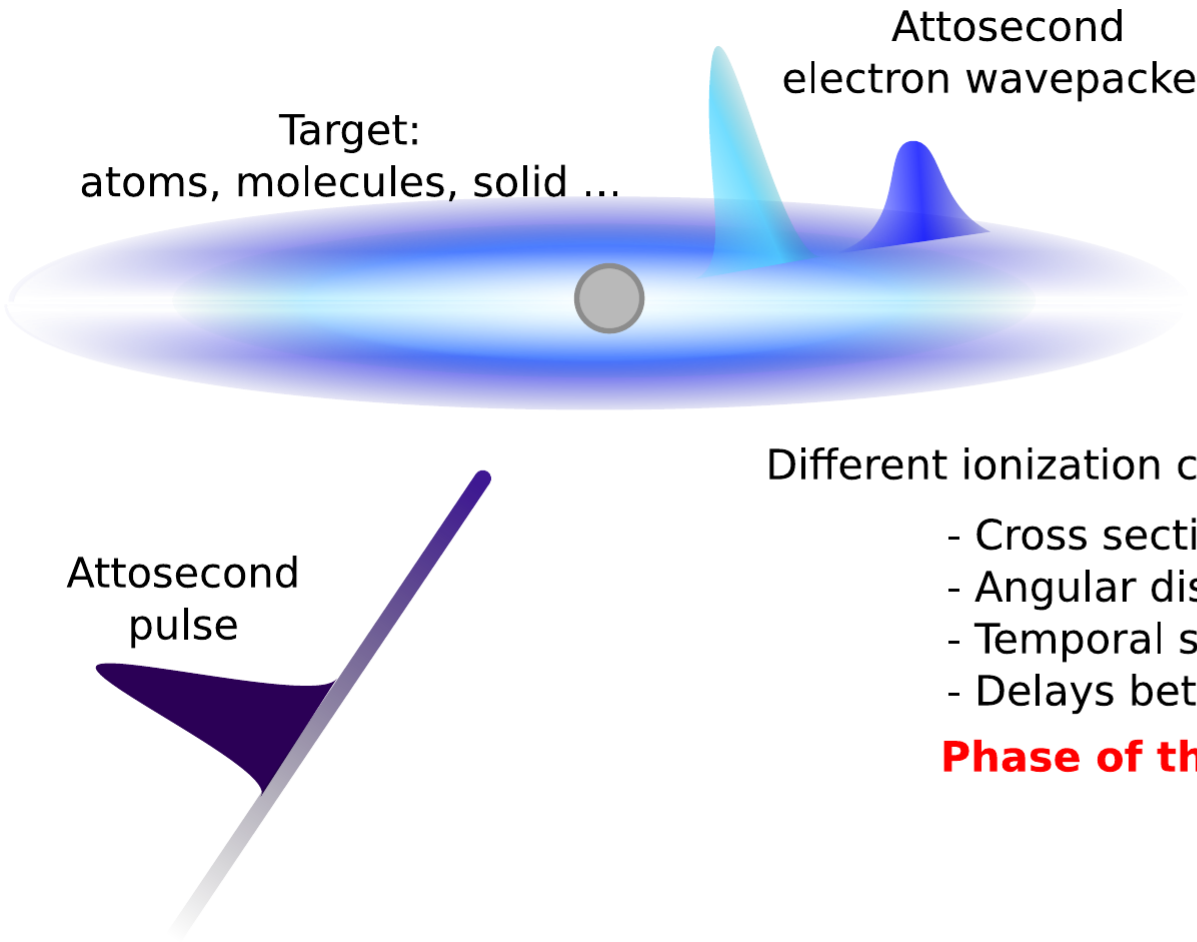
Autoionization dynamics

Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Photoionization dynamics



Different ionization channels:

- Cross sections
- Angular distributions
- Temporal shape of the electron wavepackets?
- Delays between electron wavepackets?

Phase of the photoionization matrix element

Attosecond metrology enables investigating photoionization in the time-domain

Wigner delays

PHYSICAL REVIEW VOLUME 98, NUMBER 1 APRIL 1, 1955

Lower Limit for the Energy Derivative of the Scattering Phase Shift

EUGENE P. WIGNER
Palmer Physical Laboratory, Princeton University, Princeton, New Jersey
(Received December 10, 1954)

It is shown that the derivative of the scattering phase shift with respect to energy, $d\eta/dE$, must exceed a certain limit if the interaction of scattered particle and scatterer vanishes beyond a certain distance. This limitation of $d\eta/dE$ is, fundamentally, a consequence of the principle of causality; it is derived, however, from a property of the derivative matrix R.

The ionized electron escapes by scattering off the ionic potential

The scattering determines the angular structure of the electron wavepacket

The electron acquires a phase η during the scattering process
This scattering phase depends on the kinetic energy of the electron

→ an energy-dependent phase induces a modification of the temporal profile

Wigner delay : scattering of the electron in the ionic potential

$$\tau_W = d\eta/dE$$

IOP Publishing Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **45** (2012) 183001 (32pp) doi:10.1088/0953-4075/45/18/183001

Scattering phase

TUTORIAL

Introduction to attosecond delays in photoionization

J M Dahlström[1], A L'Huillier[2] and A Maquet[3,4]

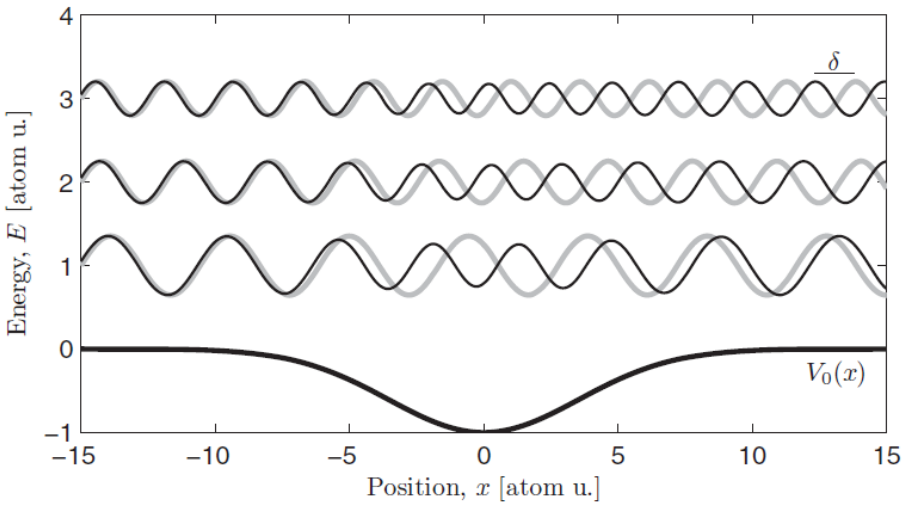


Figure 8. Electrons passing through an attractive potential $V_0(x)$. The real WKB solutions (thin black curves), equation (51), are compared to the real free-electron states (thick grey curve) at three different energies: $\epsilon = 1, 2, 3$ au of energy (27.2 eV). The phase of the electron wavefunction varies more rapidly in the potential, which leads to an accumulated phase difference δ compared to the free case. (Note that the modulations of the wavefunctions should be interpreted in the third dimension of the graph, and not as an energy modulation.)

Ex : Two classical particles start from x=-15 with the same velocity at the same time.
One travels on a flat surface
The other one on the surface V0(x) depicted above.
Which one arrives first at x=+15 ?

IOP Publishing Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **45** (2012) 183001 (32pp) doi:10.1088/0953-4075/45/18/183001

Scattering phase

TUTORIAL

Introduction to attosecond delays in photoionization

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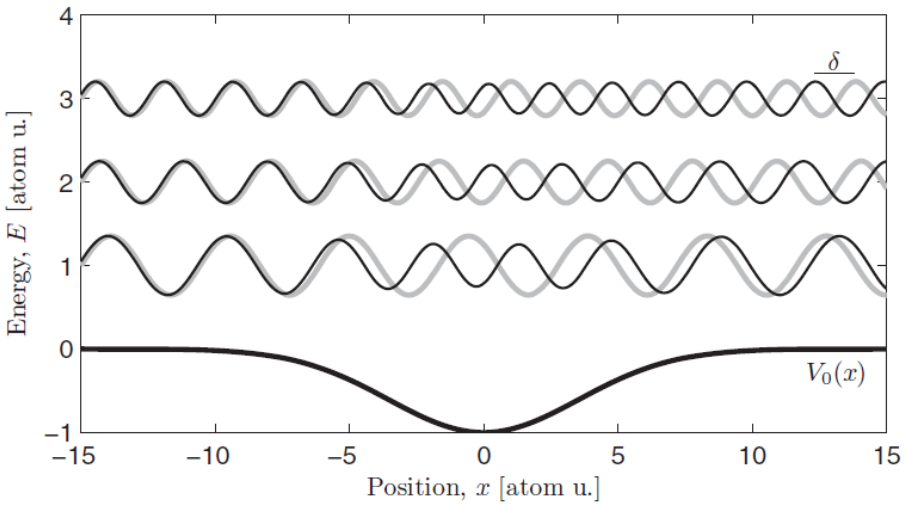
J. Phys. B: At. Mol. Opt. Phys. **45** (2012) 183001



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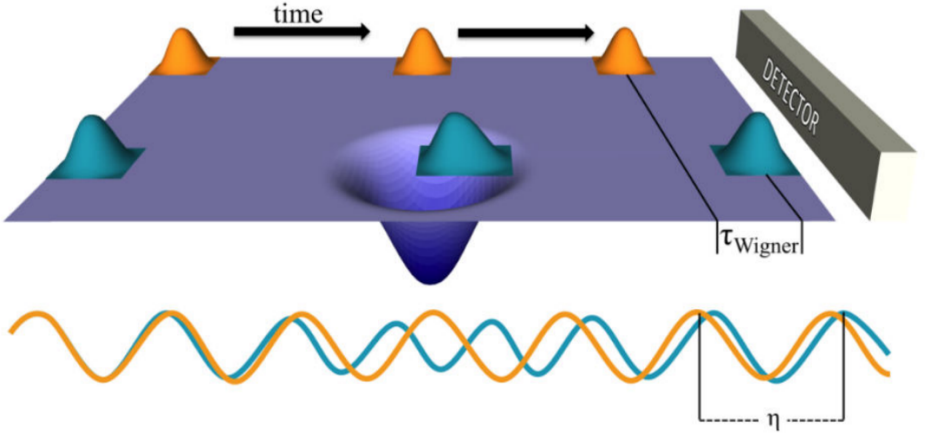

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One travels on a flat surface
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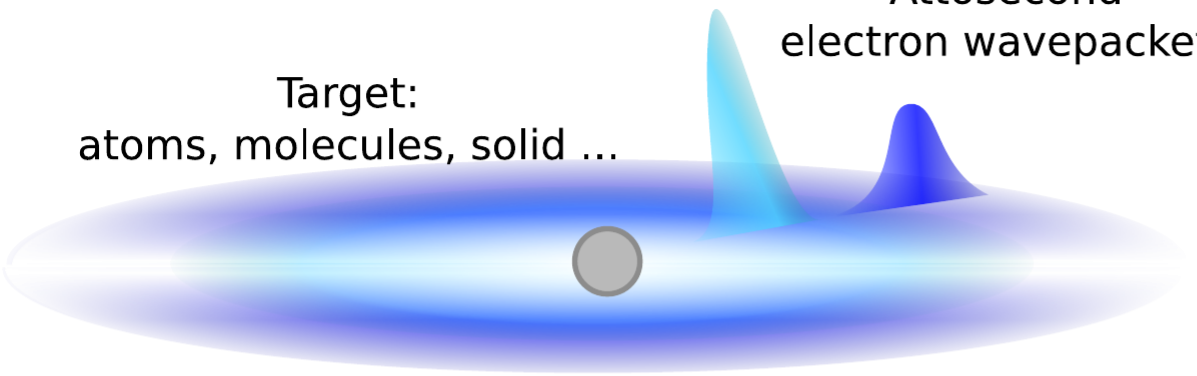
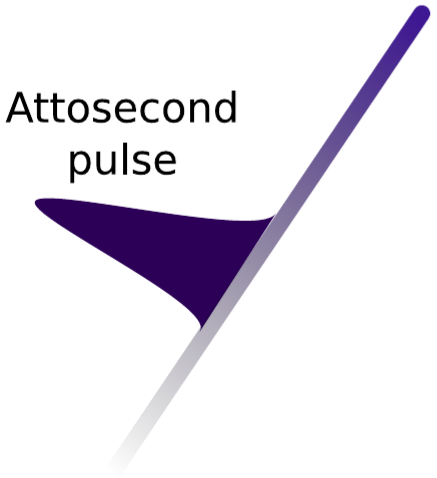
Which one arrives first at x=+15 ?

Measuring scattering phases ?



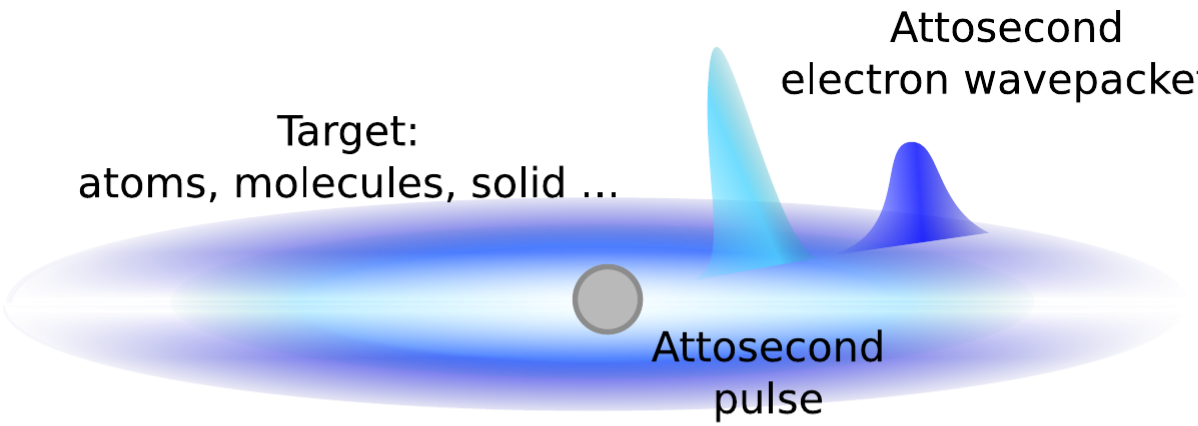


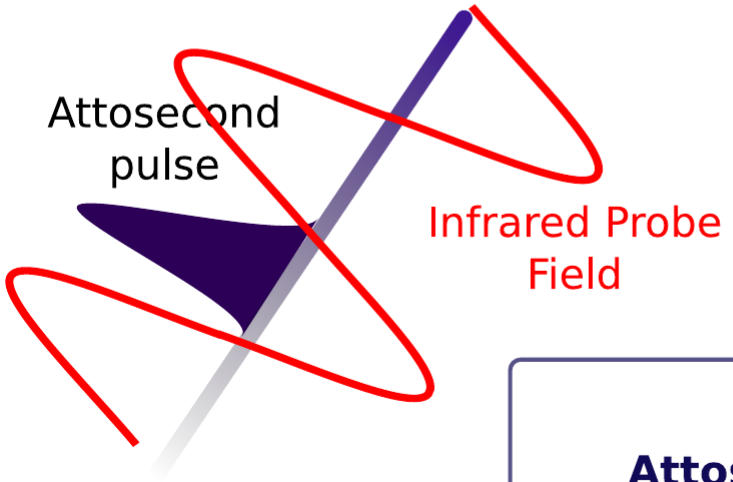
Different ionization channels:

- Cross sections
- Angular distributions
- Temporal shape of the electron wavepackets?
- Delays between electron wavepackets?

Phase of the photoionization matrix element

Measuring scattering phases ?





Different ionization channels:

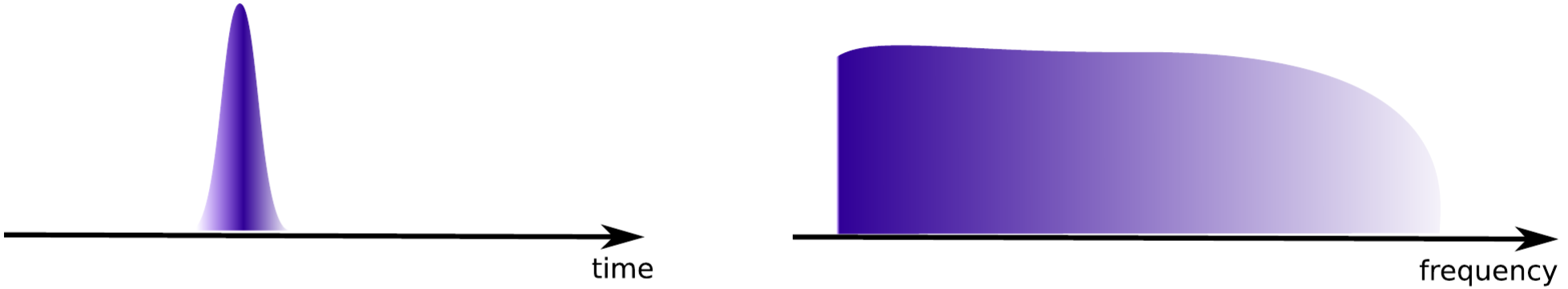
- Cross sections
- Angular distributions
- Temporal shape of the electron wavepackets?
- Delays between electron wavepackets?

Phase of the photoionization matrix element

Measured with an additional IR field:
Attosecond streak camera, RABBITT, FROG-CRAB...

Attosecond molecular photoionization

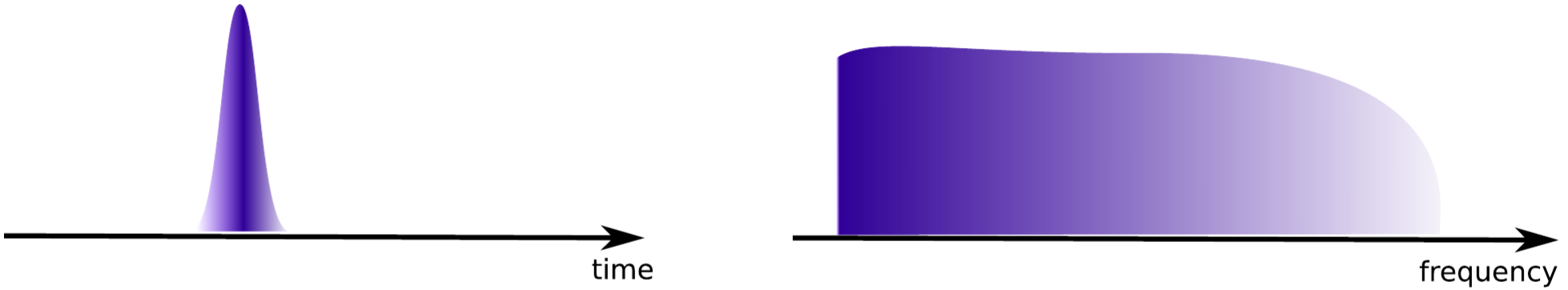
Should we use a single attosecond pulse ?



Temporal resolution but NO spectral resolution !

Attosecond molecular photoionization

Should we use a single attosecond pulse ?

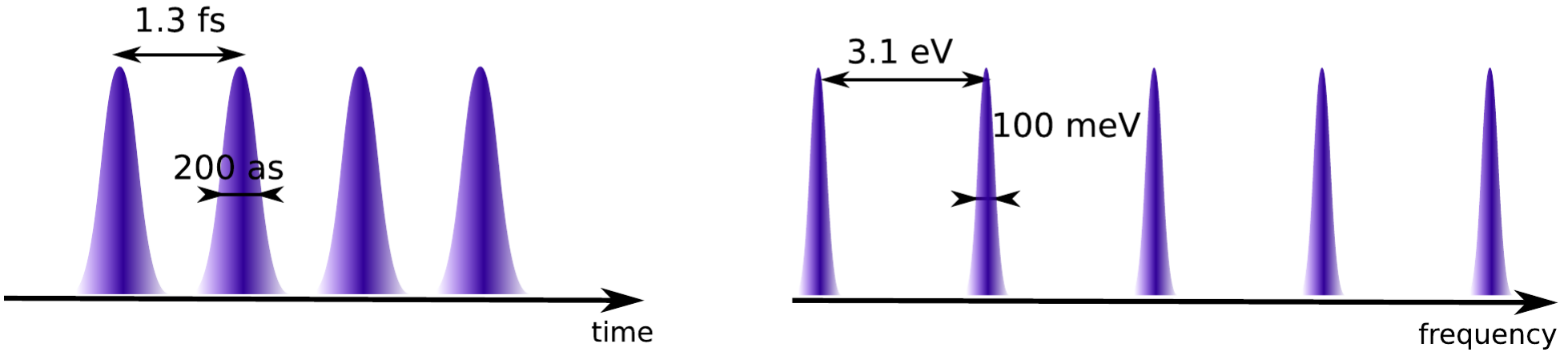


Temporal resolution but NO spectral resolution !

Molecules: ionization channels can be close in energy

Need attosecond temporal resolution and sub-eV spectral resolution !

Solution: use an attosecond pulse train



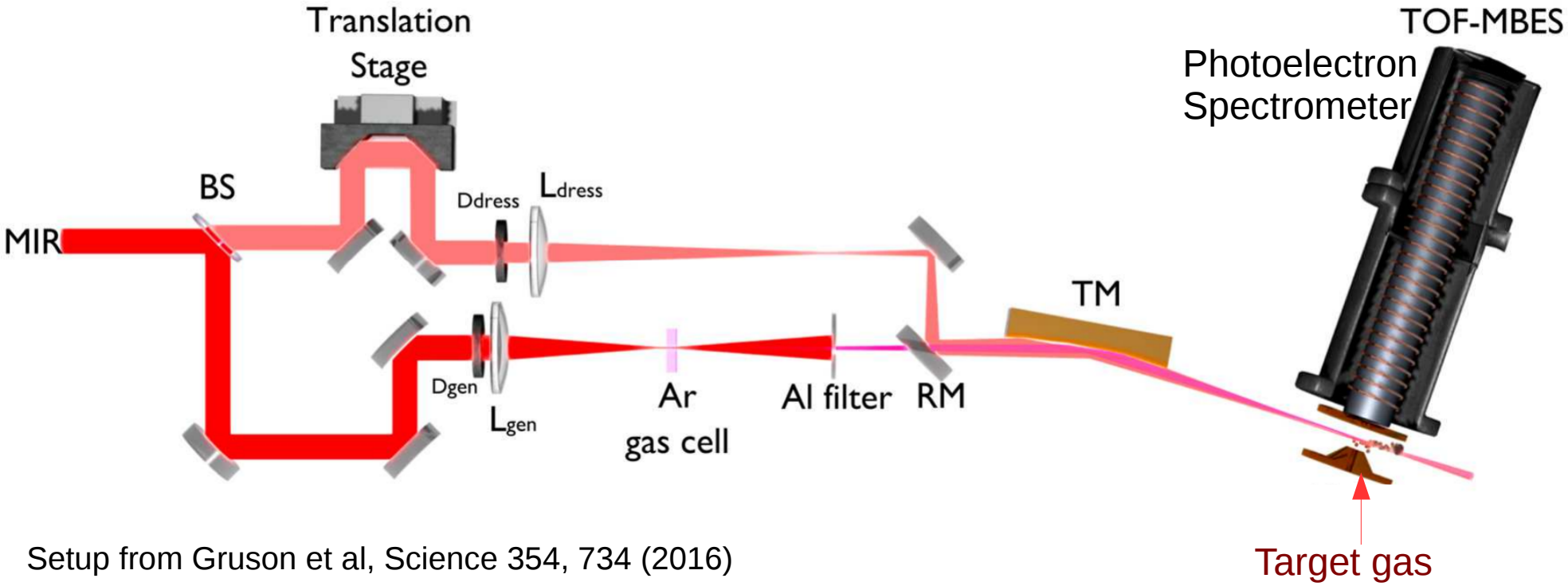
Attosecond interferometry : RABBIT

Reconstruction of Attosecond Beating by Interference of Two-photon Transitions

Principle :

V. Véniard et al., PRA 54, 721 (1996)

Ionization of the target gas by an attosecond pulse train + IR



Setup from Gruson et al, Science 354, 734 (2016)

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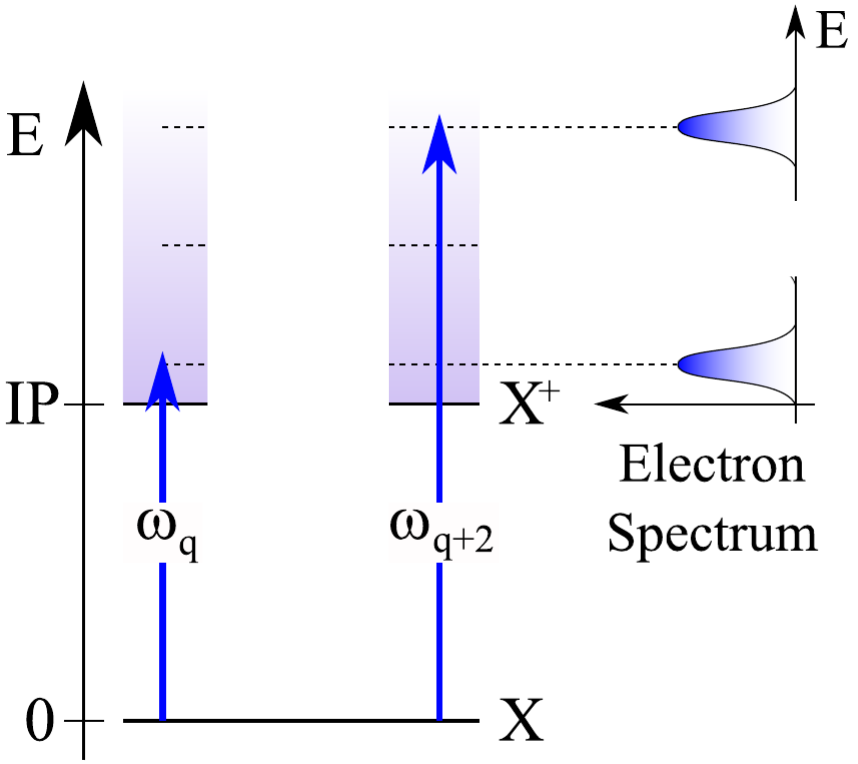

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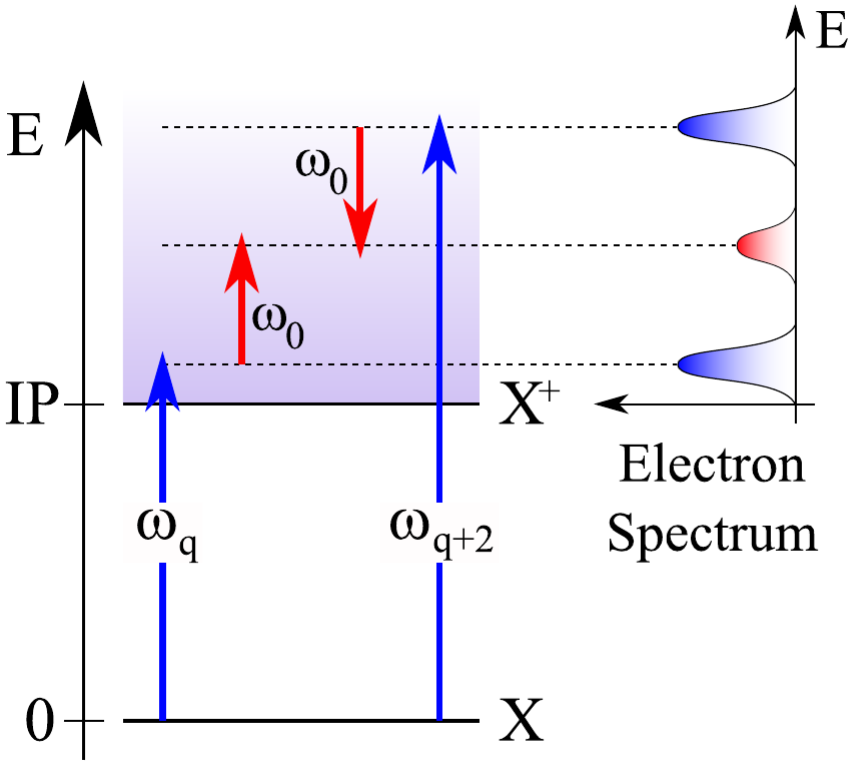

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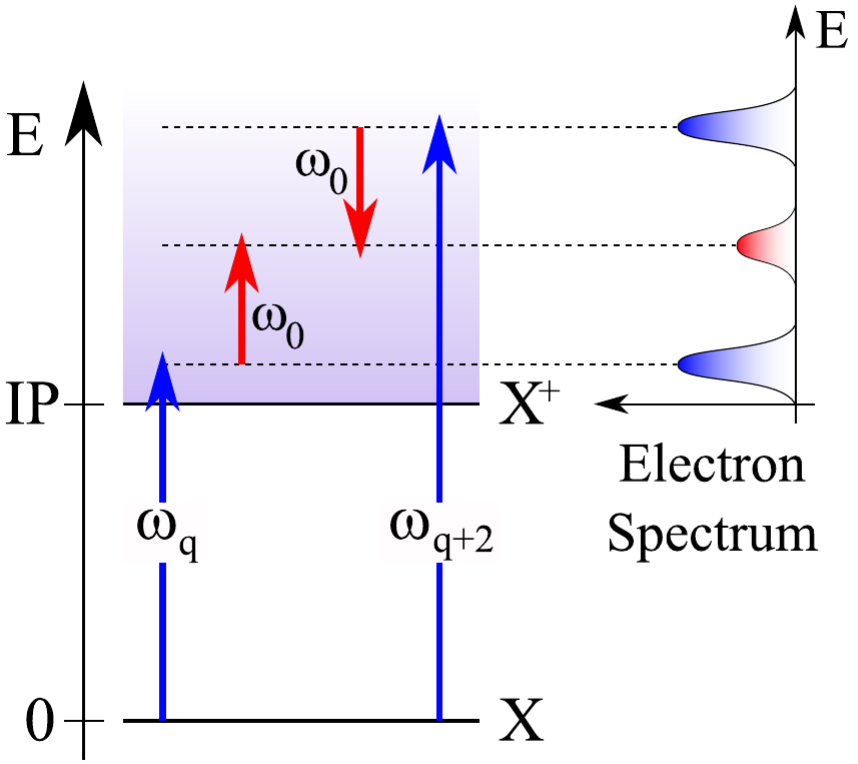
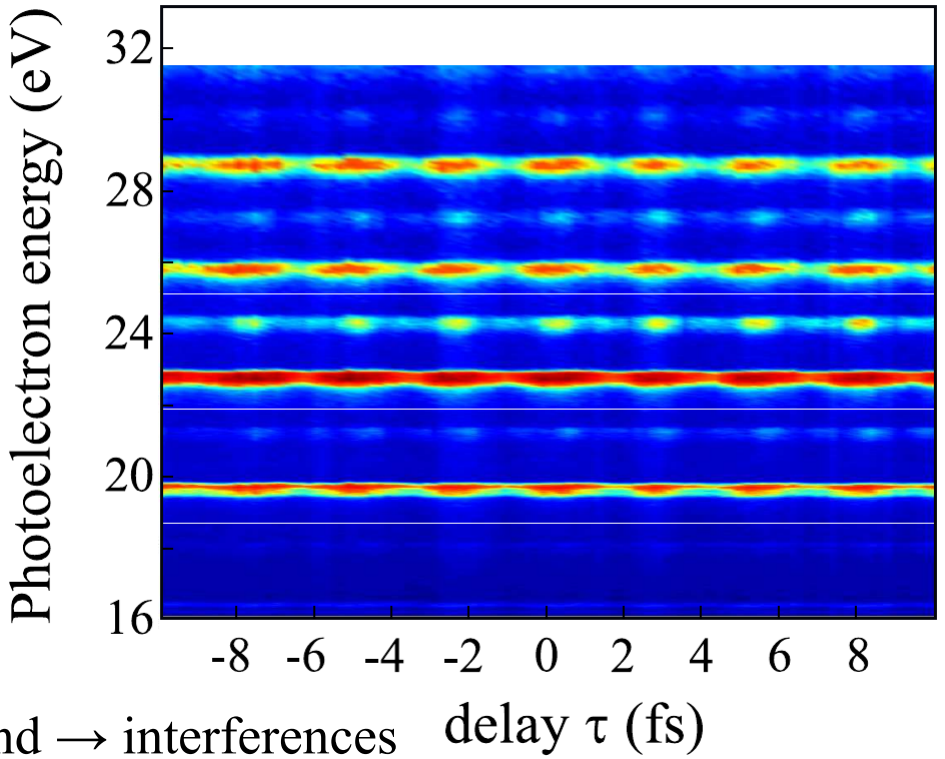




Two quantum paths lead to the same sideband → interferences

$$S_{2q} = S^0_{2q} \cos\left(2\omega_0\tau + 2\varphi_0 + \varphi_{2q+1} - \varphi_{2q-1} + \theta_{2q+1} - \theta_{2q-1}\right)$$

IR phase

Phase difference between 2 consecutive harmonics

Atomic (or molecular) phase difference

Phase of the sideband oscillations

$$S_{2q} = S^{0}_{2q} \cos\left(2\omega_0\tau + 2\varphi_0 + \varphi_{2q+1} - \varphi_{2q-1} + \theta_{2q+1} - \theta_{2q-1}\right)$$

IR phase

Phase difference between 2 consecutive harmonics

Atomic (or molecular) phase difference

IR phase : determined by the delay between the IR field and attosecond pulse train

Harmonic phase difference : characteristic of the attosecond pulse train (target independent)

Phase θ :

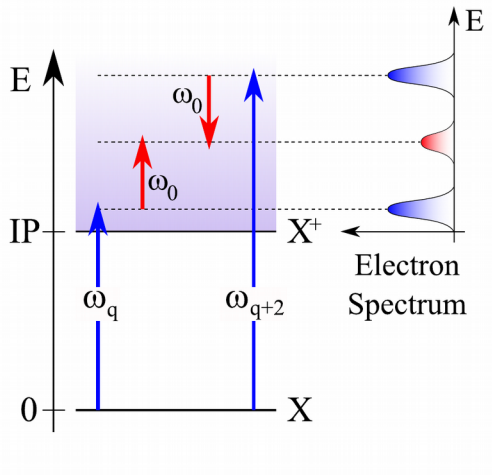
Phase of the two photon matrix element leading to sideband 2q

by absorbing harmonic 2q-1 and one IR photon → θ_{2q-1}

by absorbing harmonic 2q+1 and emitting one IR photon → θ_{2q+1}

Intrinsic to the ionized target

Related to the scattering phase, but different because of the IR field.



Simple example : photoionization of argon

PRL 106, 143002 (2011) PHYSICAL REVIEW LETTERS week ending 8 APRIL 2011

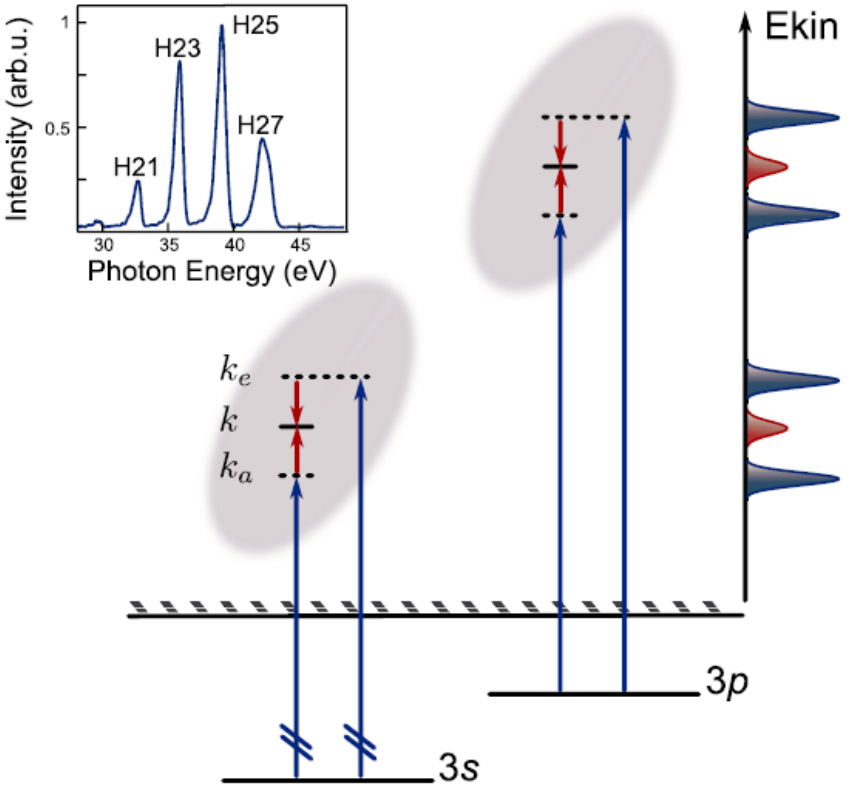
Probing Single-Photon Ionization on the Attosecond Time Scale

K. Klünder,[1] J. M. Dahlström,[1] M. Gisselbrecht,[1] T. Fordell,[1] M. Swoboda,[1] D. Guénot,[1] P. Johnsson,[1] J. Caillat,[2] J. Mauritsson,[1] A. Maquet,[2] R. Taïeb,[2] and A. L'Huillier[1,*]

[1]*Department of Physics, Lund University, P.O. Box 118, 22100 Lund, Sweden*

[2]*Laboratoire de Chimie Physique-Matière et Rayonnement, Université Pierre et Marie Curie, 11, Rue Pierre et Marie Curie, 75231 Paris Cedex, 05, France*

(Received 15 December 2010; published 5 April 2011; publisher error corrected 14 April 2011)



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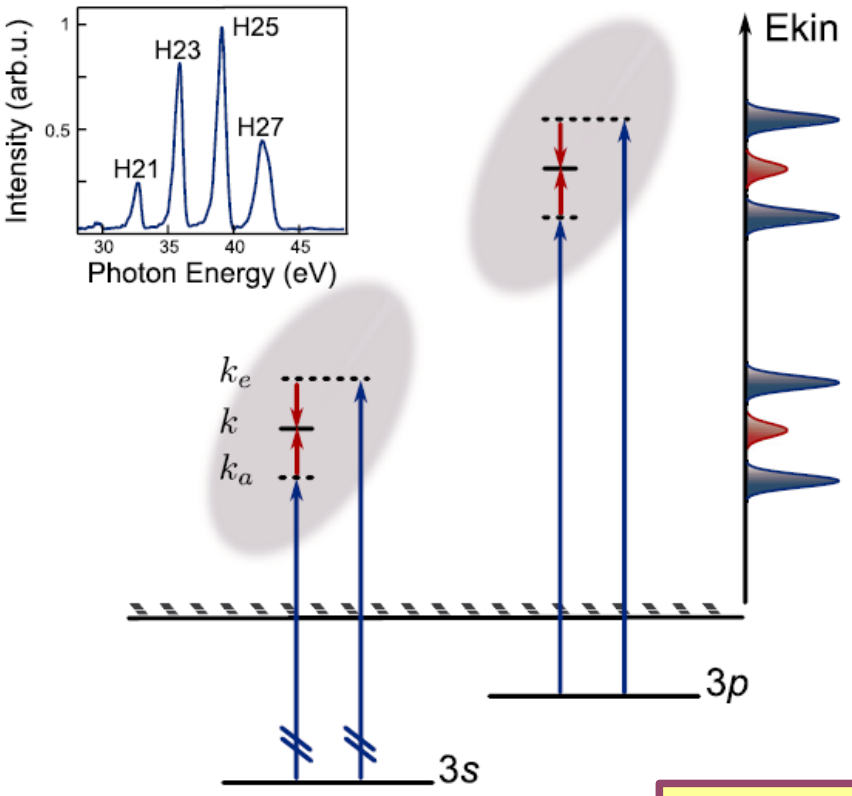
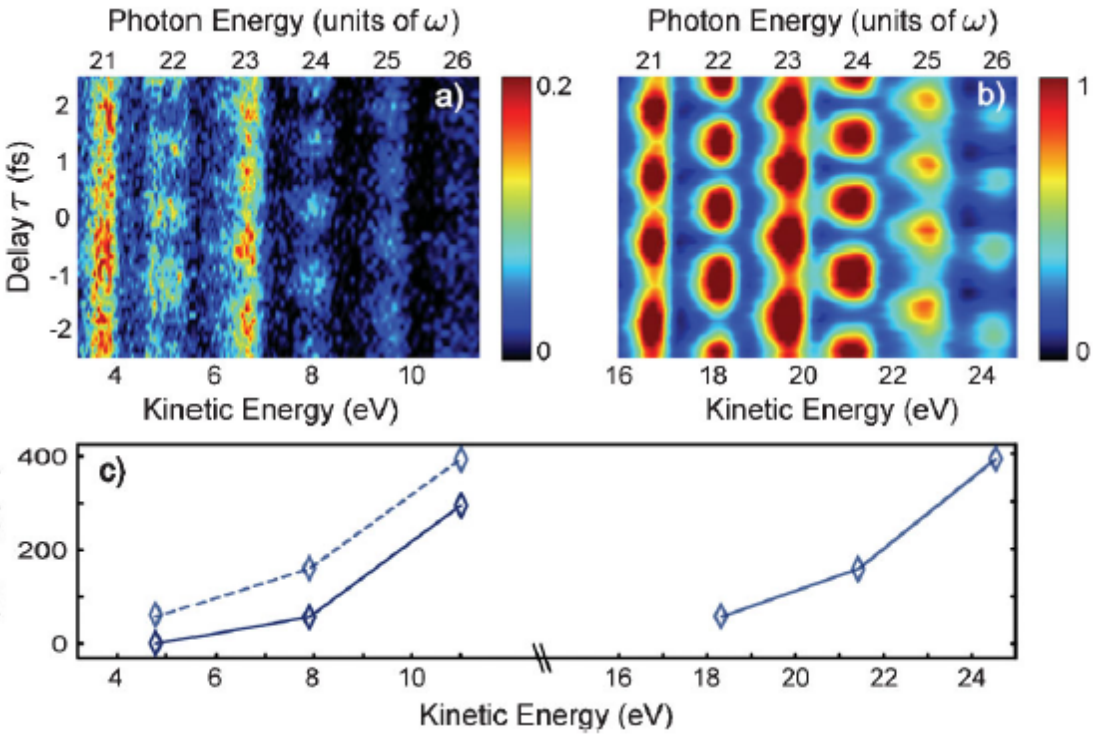




Electrons from 3s are ejected before electrons from 3p

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics – N2

Autoionization dynamics

Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Attosecond photoionization of N2

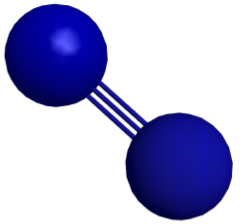
PHYSICAL REVIEW A **80**, 011404(R) (2009)

Phase-resolved attosecond near-threshold photoionization of molecular nitrogen

S. Haessler,[1] B. Fabre,[2] J. Higuet,[2] J. Caillat,[3] T. Ruchon,[1] P. Breger,[1] B. Carré,[1] E. Constant,[2] A. Maquet,[3]
E. Mével,[2] P. Salières,[1] R. Taïeb,[3] and Y. Mairesse[2]
[1]*CEA-Saclay, IRAMIS, Service des Photons, Atomes et Molécules, 91191 Gif-sur-Yvette, France*
[2]*CELIA, Université Bordeaux I, UMR 5107 (CNRS, Bordeaux 1, CEA), 351 Cours de la Libération, 33405 Talence Cedex, France*
[3]*UPMC, Université Paris 06, CNRS, UMR 7614, LCPMR, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 5, France*

- Generate an attosecond pulse train in Argon and characterize it by RABBITT using Argon as detection gas medium (Calculated Atomic phase)

- Use this attosecond pulse train to perform molecular RABBITT on N_2



$$S_{2q} = S_{2q}^{0} \cos\left(2\omega_0\tau + 2\varphi_0 + \varphi_{2q+1} - \varphi_{2q-1} + \theta_{2q+1} - \theta_{2q-1}\right)$$

IR phase — known

Phase difference between 2 consecutive harmonics — known

Molecular phase difference

Attosecond photoionization of N2

PHYSICAL REVIEW A **80**, 011404(R) (2009)

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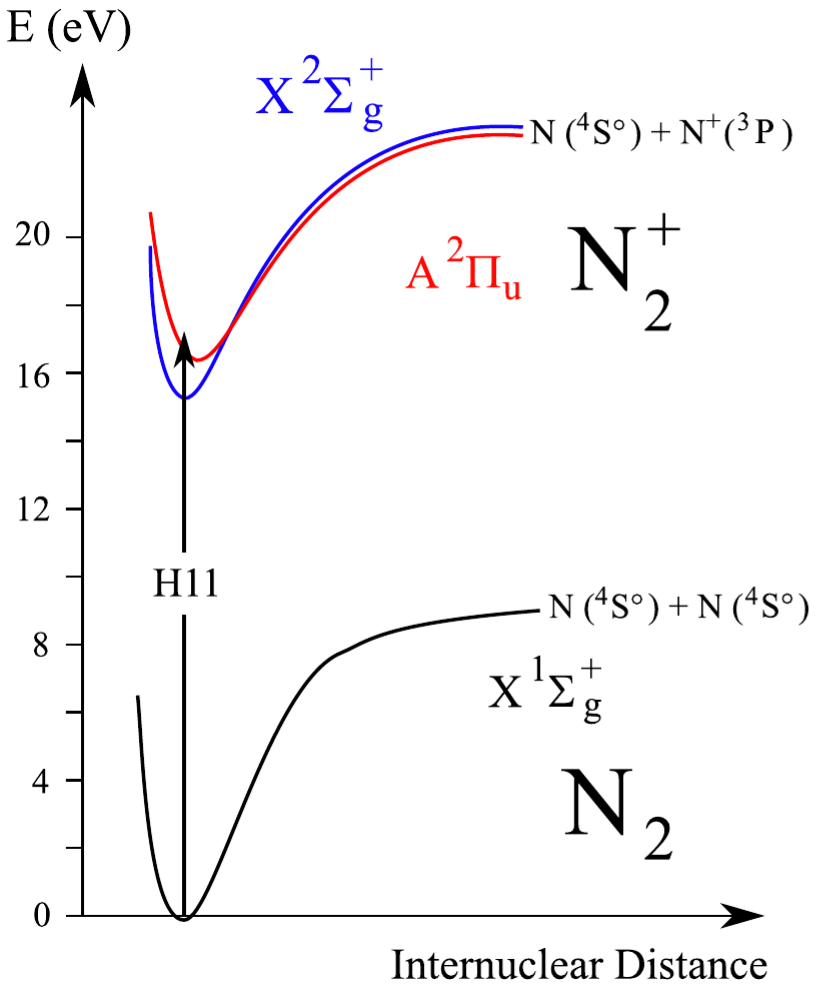
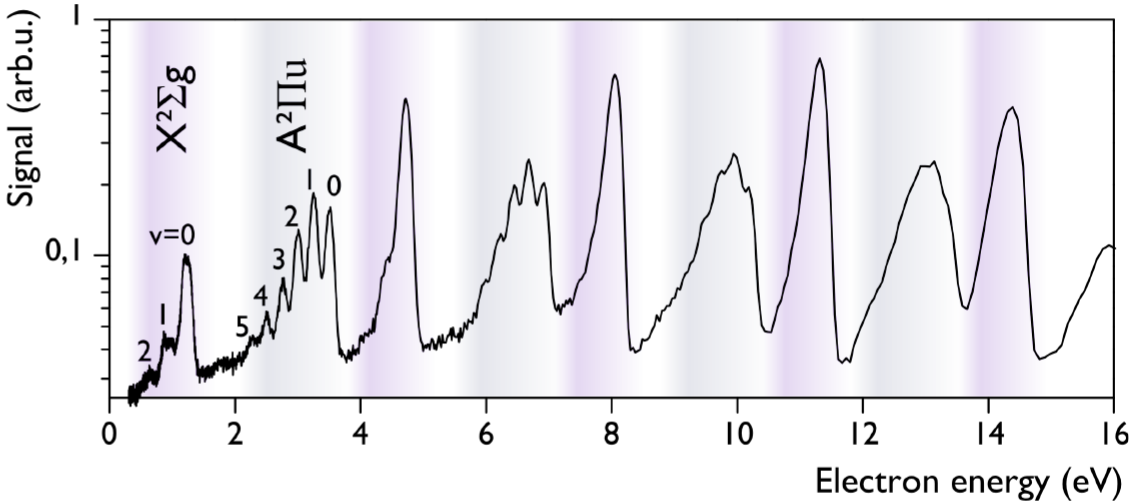


photoelectron spectrum averaged over 2000 laser shots



- Two electronic states are reachable
- Vibrationaly resolved for low energy electrons

Attosecond photoionization of N2

PHYSICAL REVIEW A **80**, 011404(R) (2009)

Phase-resolved attosecond near-threshold photoionization of molecular nitrogen

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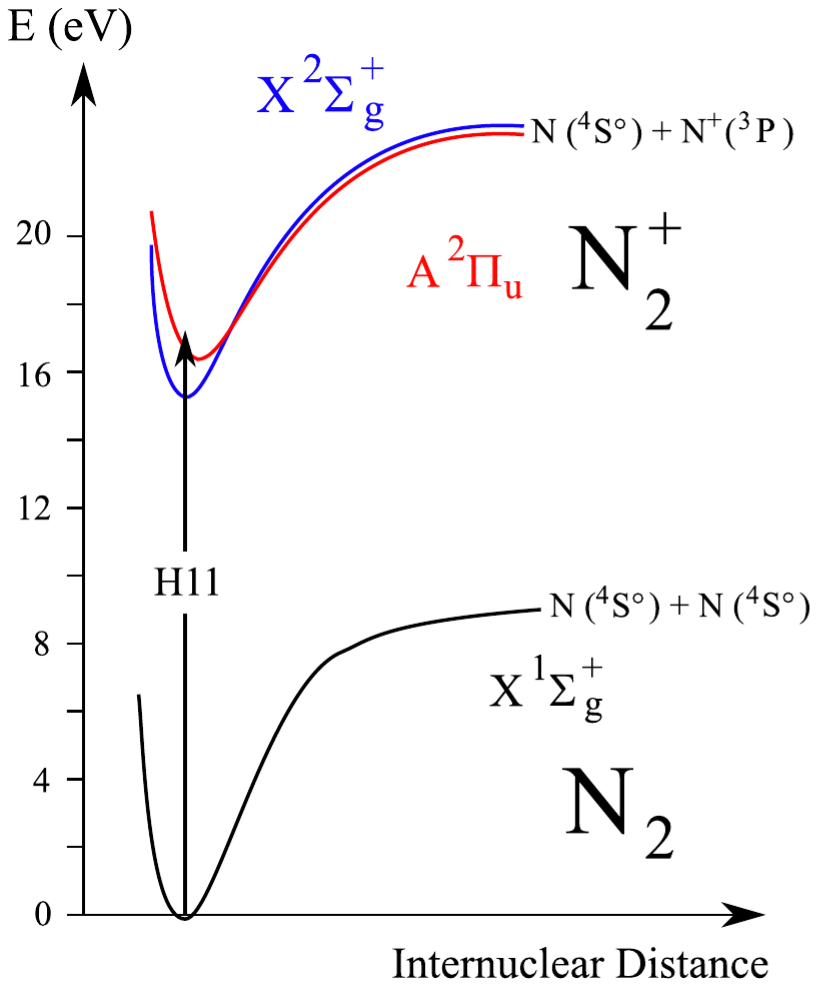
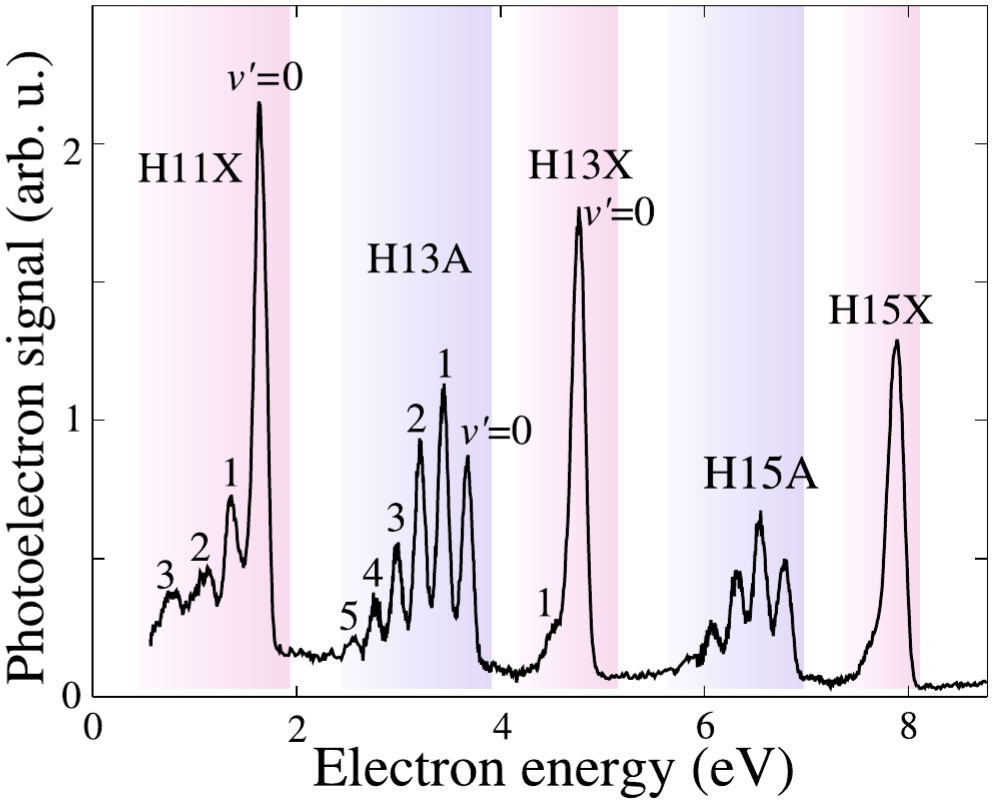
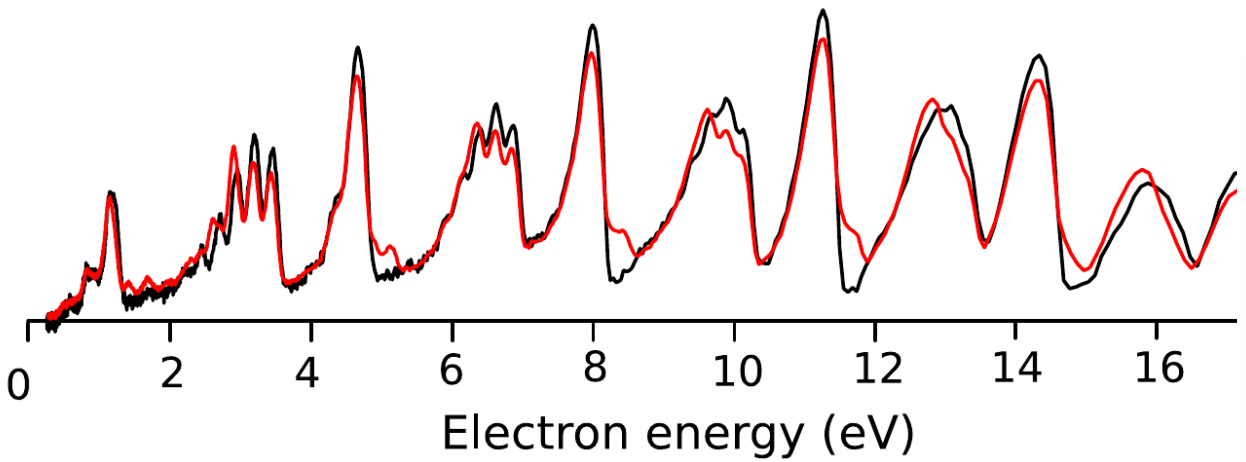


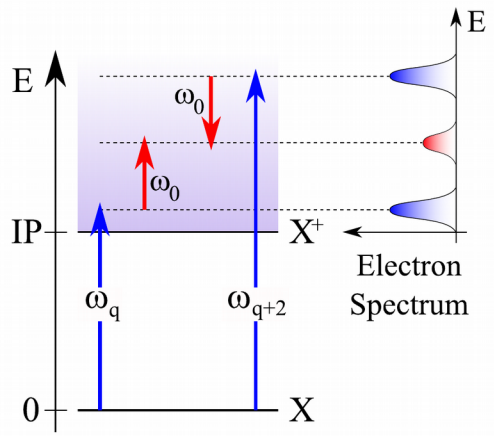
Concatenation of photoelectron spectra averaged over 2000 laser shots



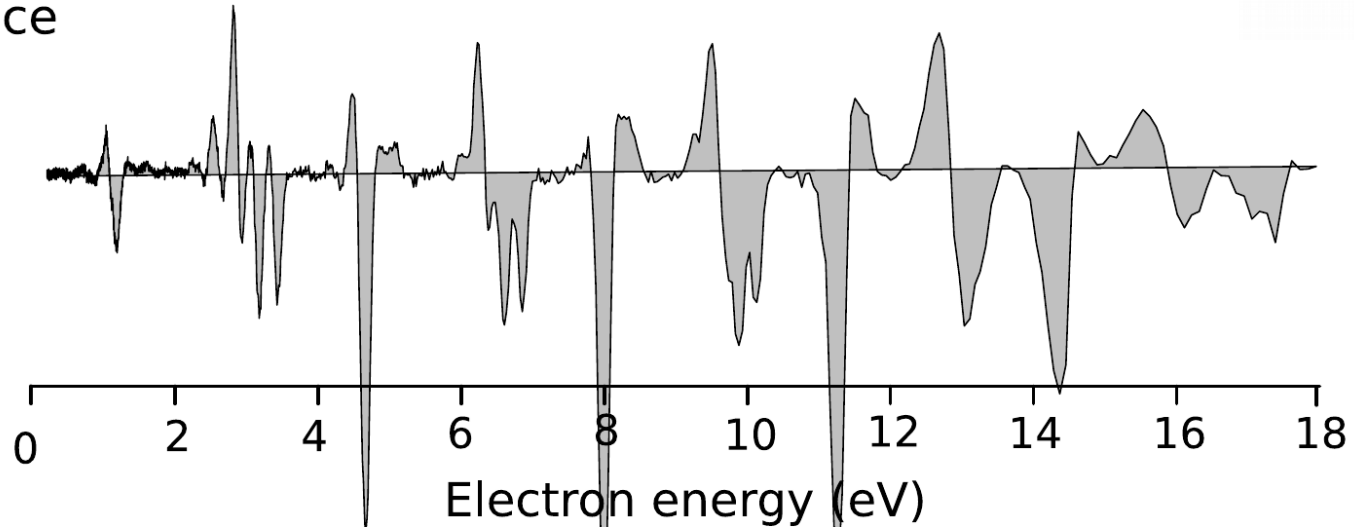
Attosecond photoionization of N2

Photoelectron spectrum



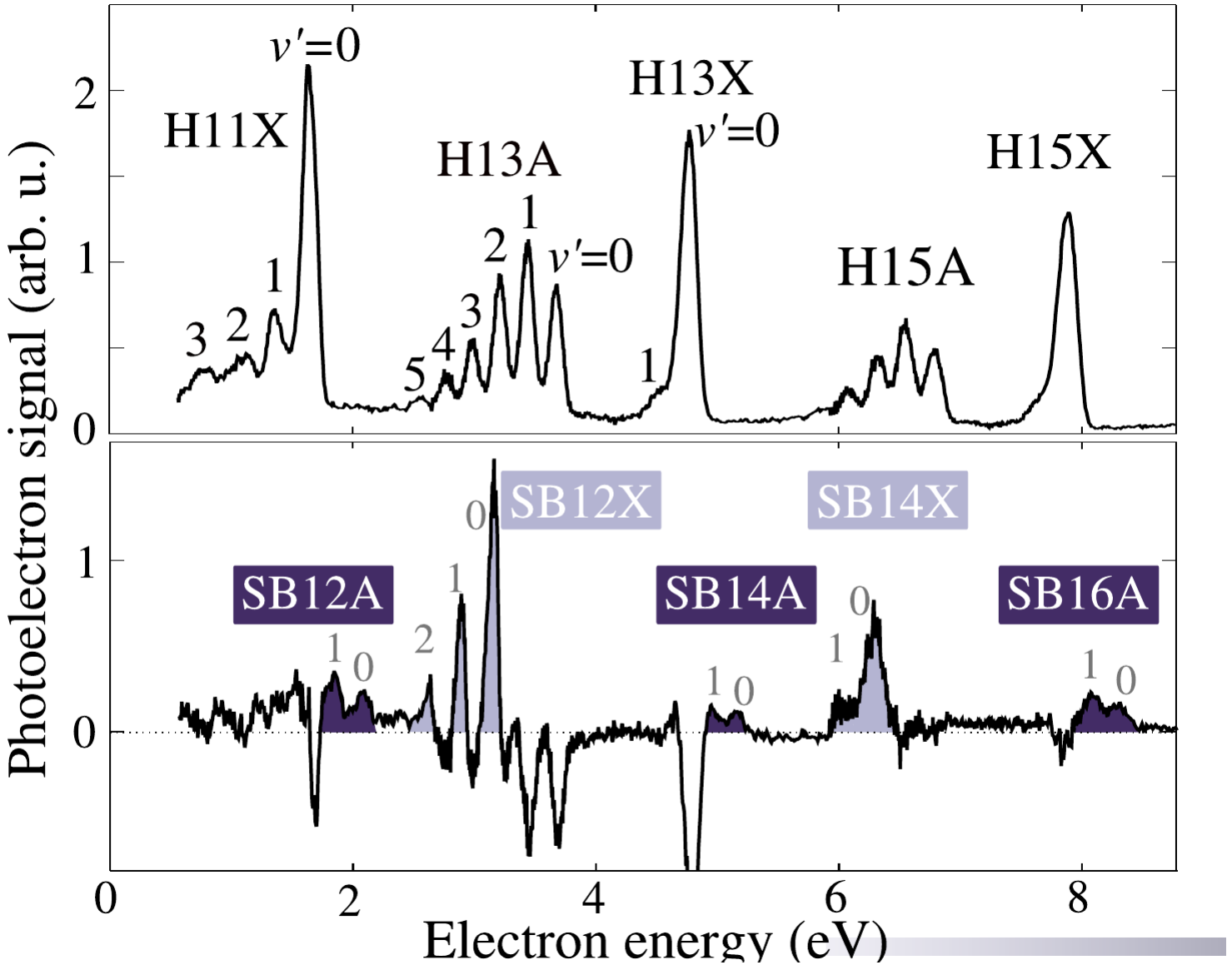


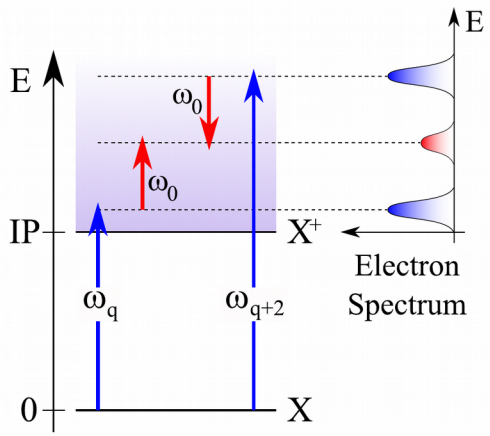
Difference



Decyphering the specrtum

PHYSICAL REVIEW A **80**, 011404(R) (2009)

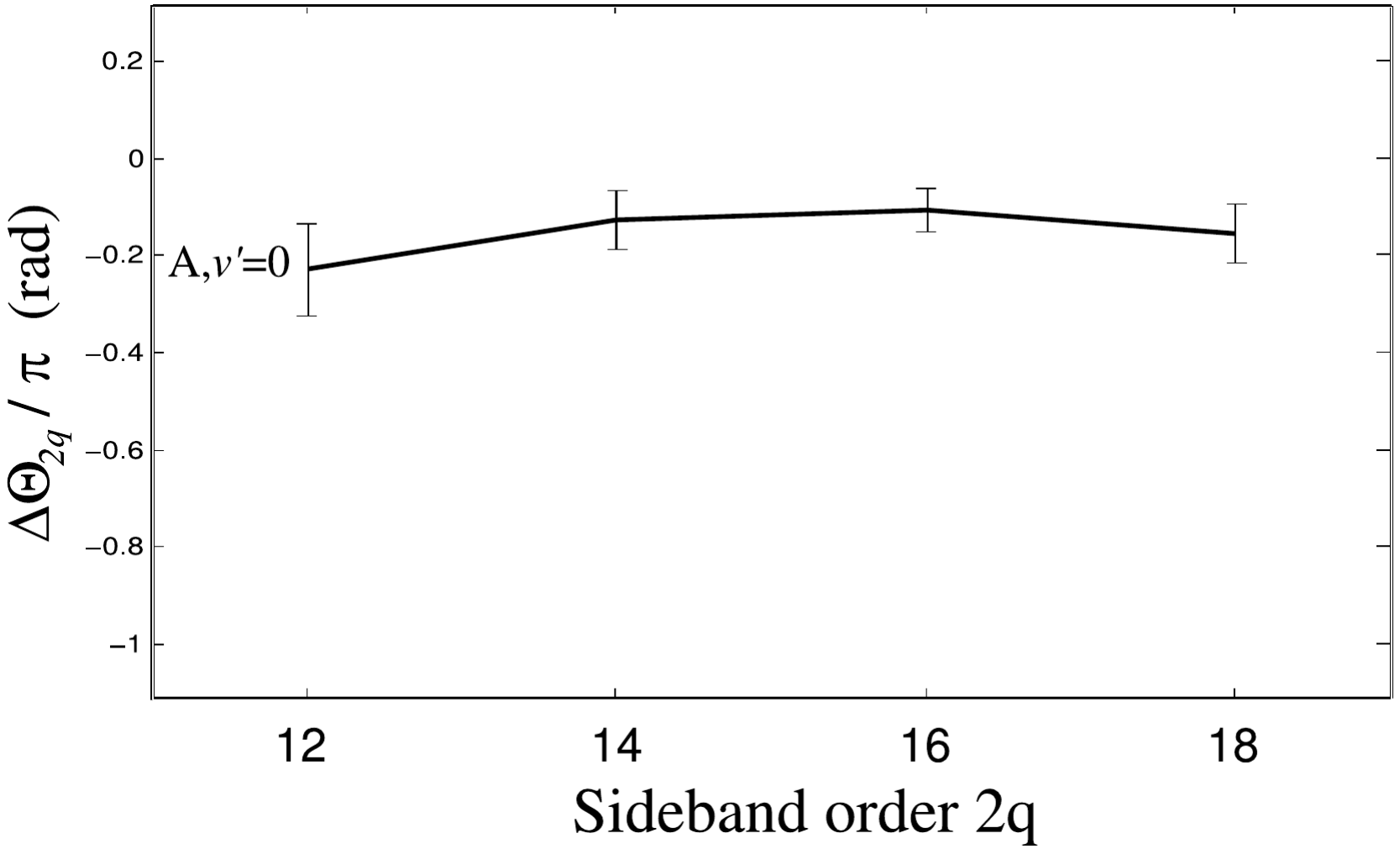




Electronically and vibrationally resolved attosecond measurement

Vibrationally-resolved photoionization phases

PHYSICAL REVIEW A **80**, 011404(R) (2009)



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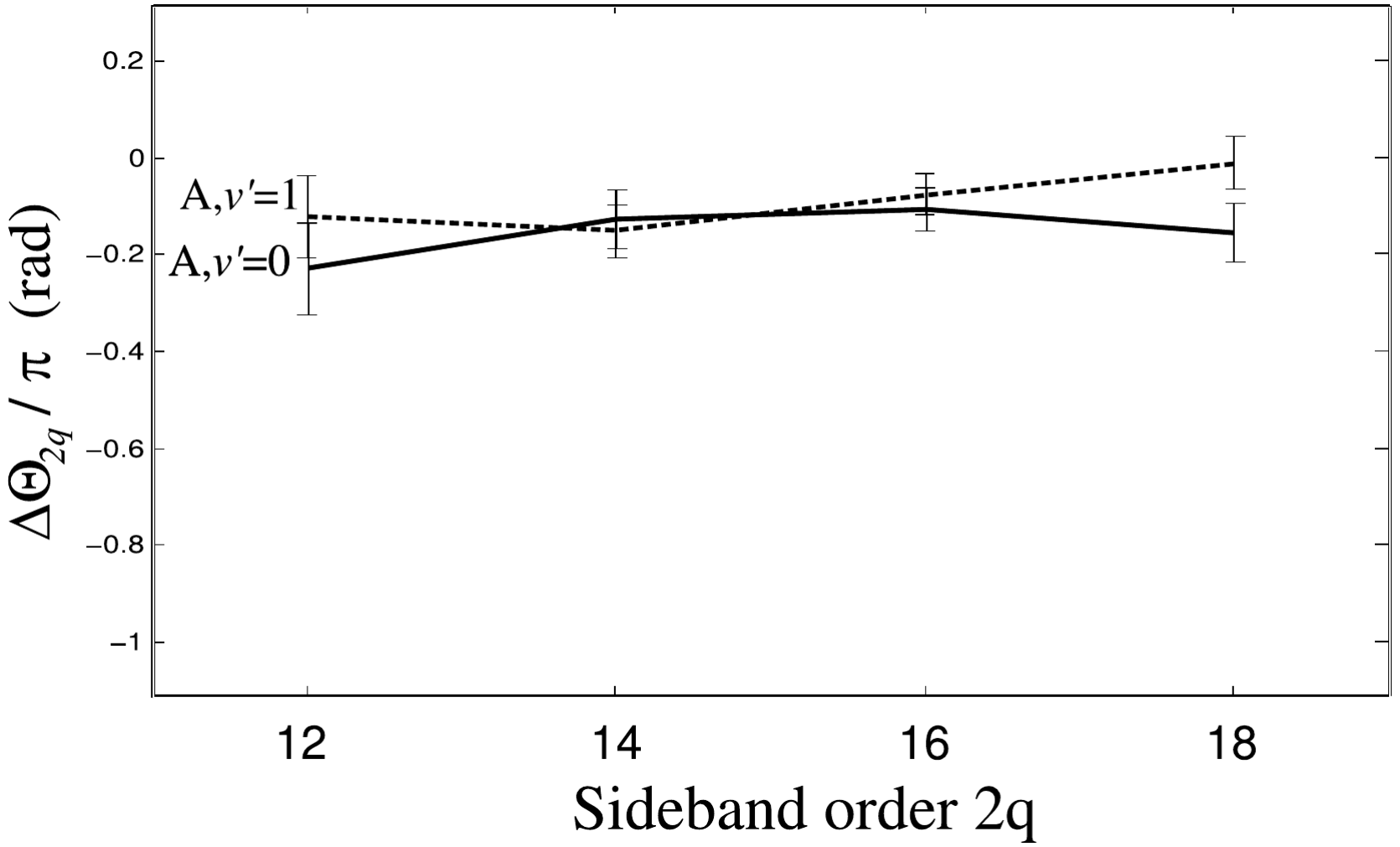

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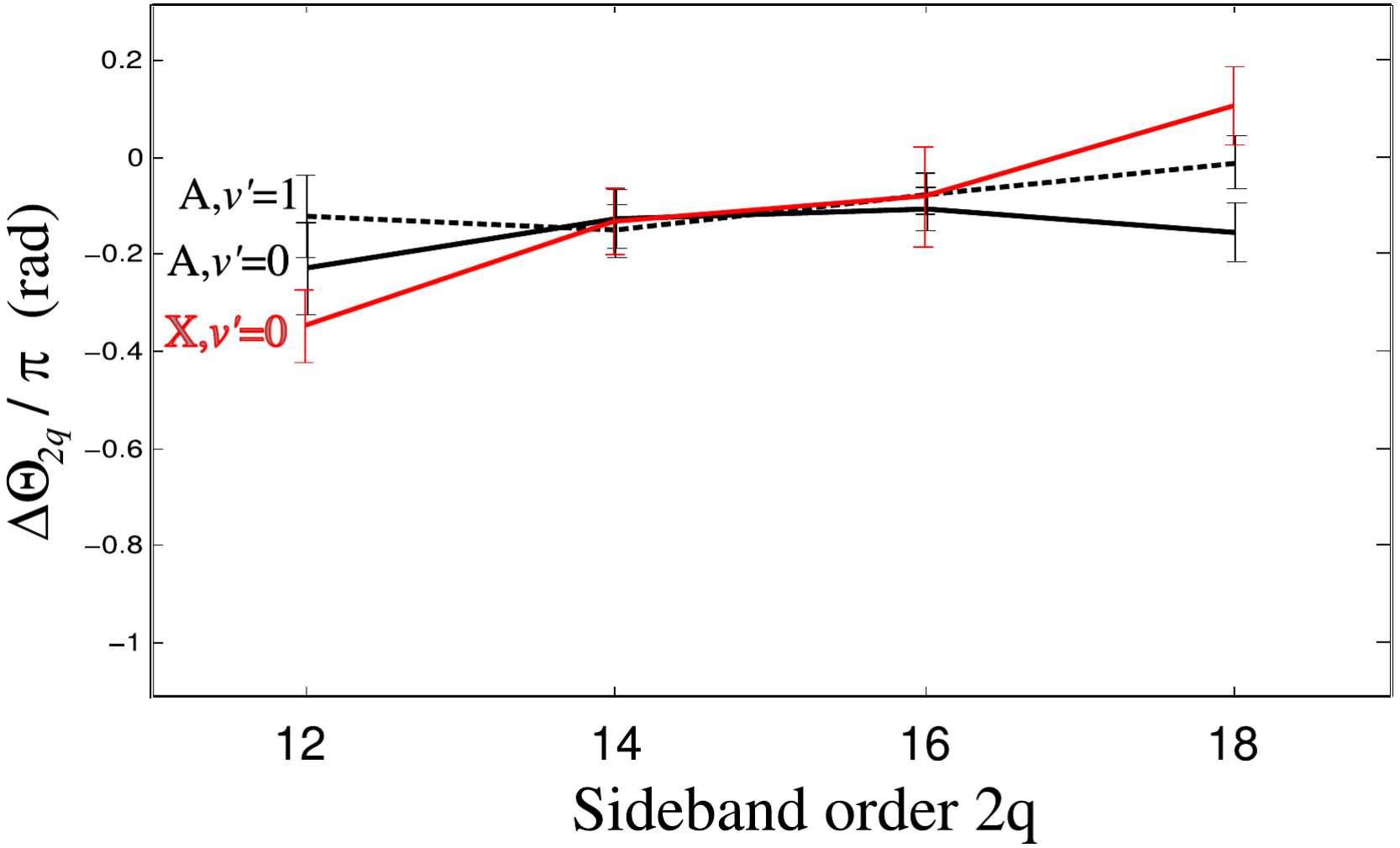
PHYSICAL REVIEW A **80**, 011404(R) (2009)



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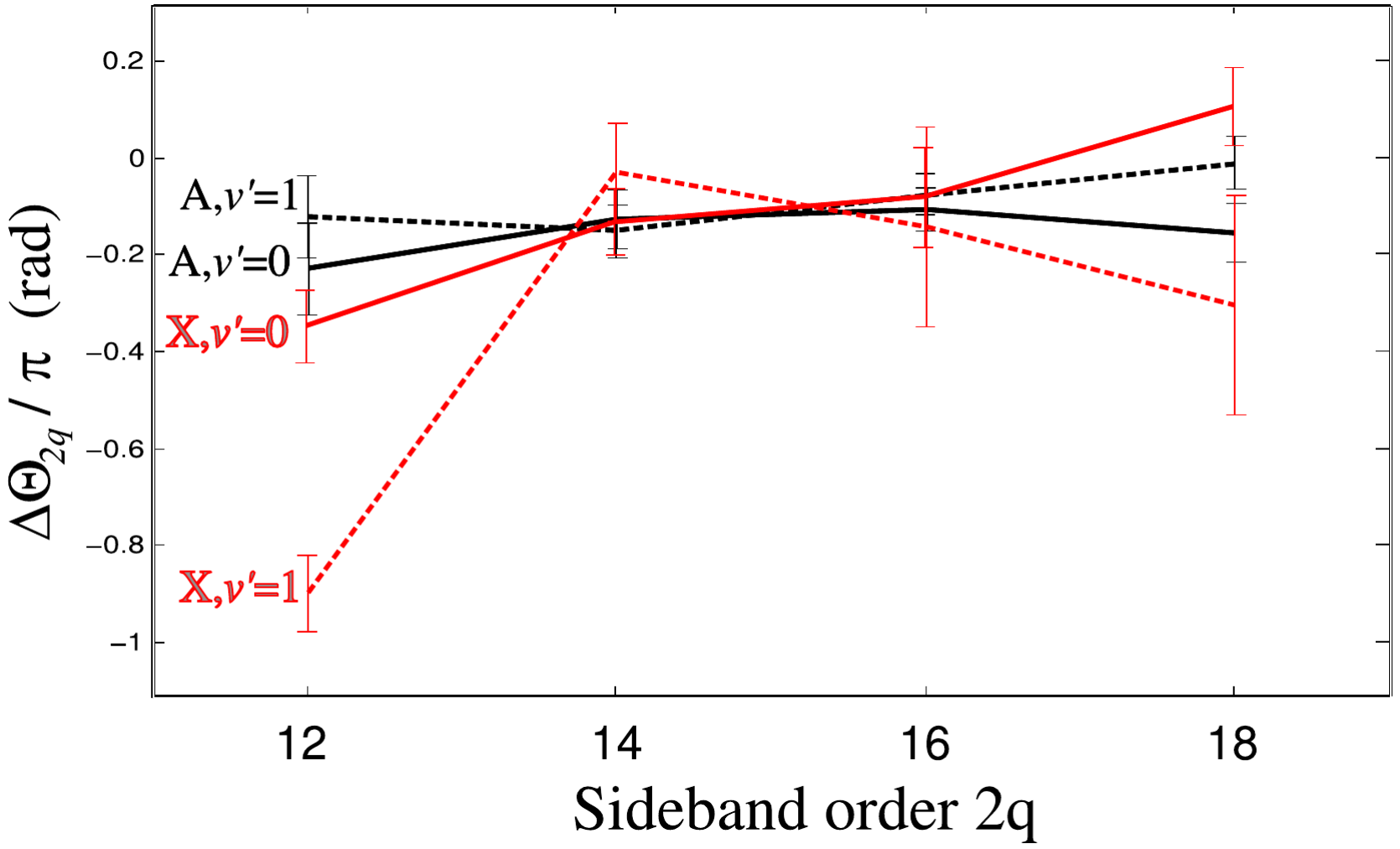
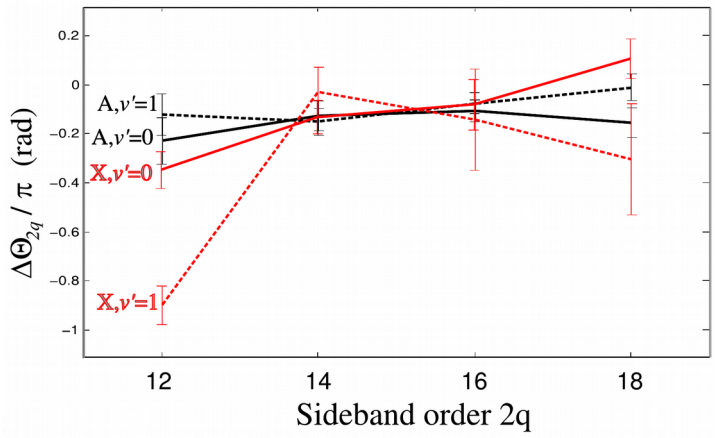
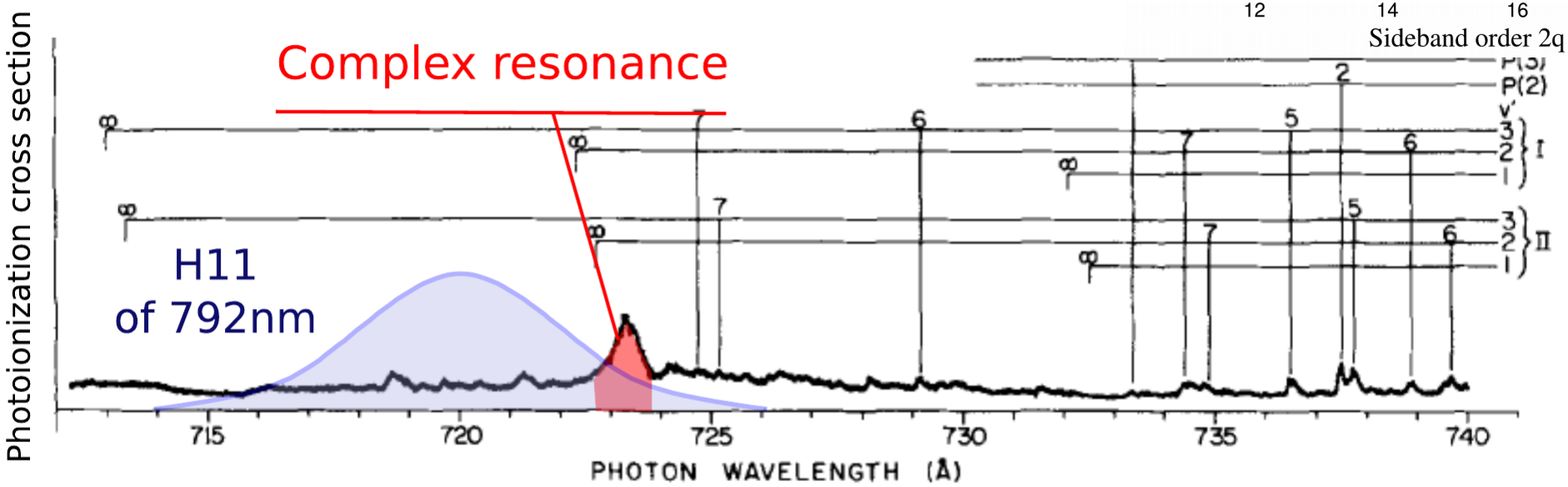
PHYSICAL REVIEW A **80**, 011404(R) (2009)



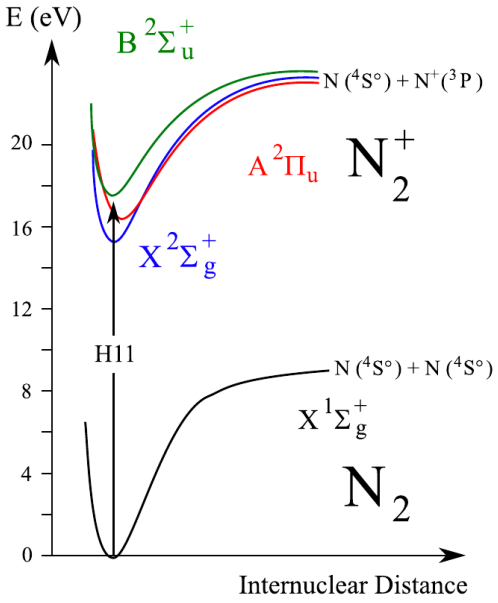
Interpretation



- Influence of a resonance for the X ionization channel



Dehmer et al, JCP 80, 1030 (1984)



Hopfield resonance converging to B state of the ion

→ **Phase shift due to autoionization (see later)**

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics – CO

Autoionization dynamics

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High-harmonic spectroscopy

Laser-induced electron diffraction

Orientation-dependent stereo Wigner time delay and electron localization in a small molecule

J. Vos[1*], L. Cattaneo[1], S. Patchkovskii[2], T. Zimmermann[3,4], C. Cirelli[1,5], M. Lucchini[1†], A. Kheifets[6], A. S. Landsman[3,4], U. Keller[1]

Vos *et al.*, *Science* **360**, 1326–1330 (2018)

Orientation-dependent delay in CO

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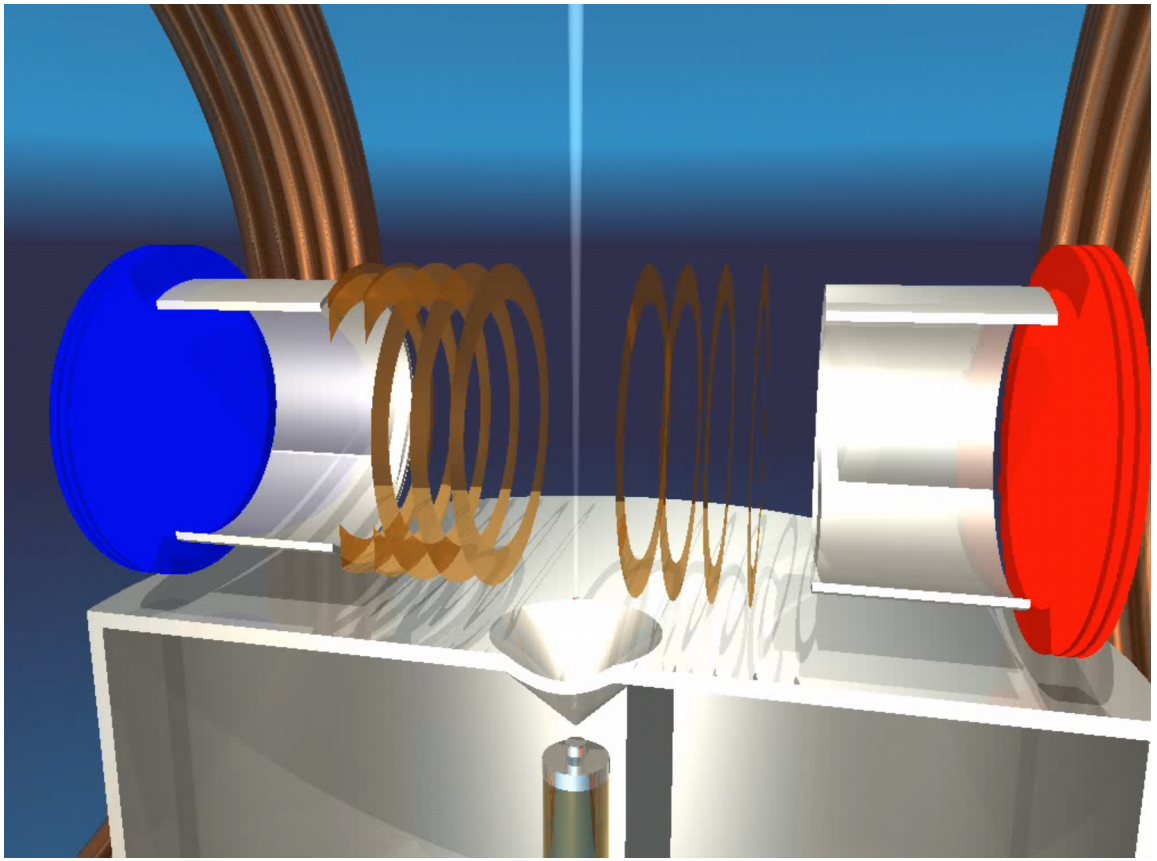
Vos *et al.*, *Science* **360**, 1326–1330 (2018)

Photoionization of CO by an attosecond pulse train + IR field (RABBIT)

Detection of electrons and ions in coincidence – COLTRIMS/Reaction Microscope



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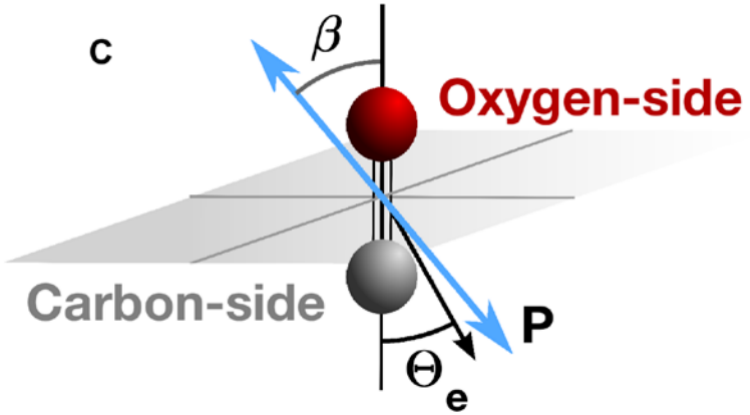
Vos *et al.*, *Science* **360**, 1326–1330 (2018)

Photoionization of CO by an attosecond pulse train

Detection of electrons and ions in coincidence – COLTRIMS/Reaction Microscope
→ 3D momentum distribution of electrons and ions

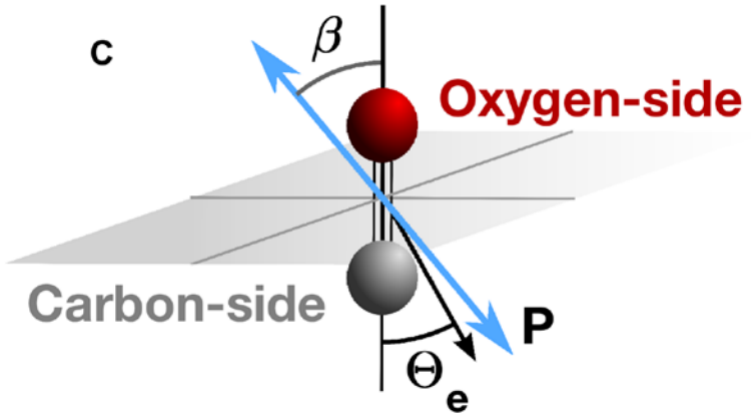
→ A RABBIT trace is measured :
- for each orientation of the ion with respect to the XUV polarization P
- for each angle of ejection of the electron with respect to the intramolecular axis
- for electrons ejected from the O side or the C side



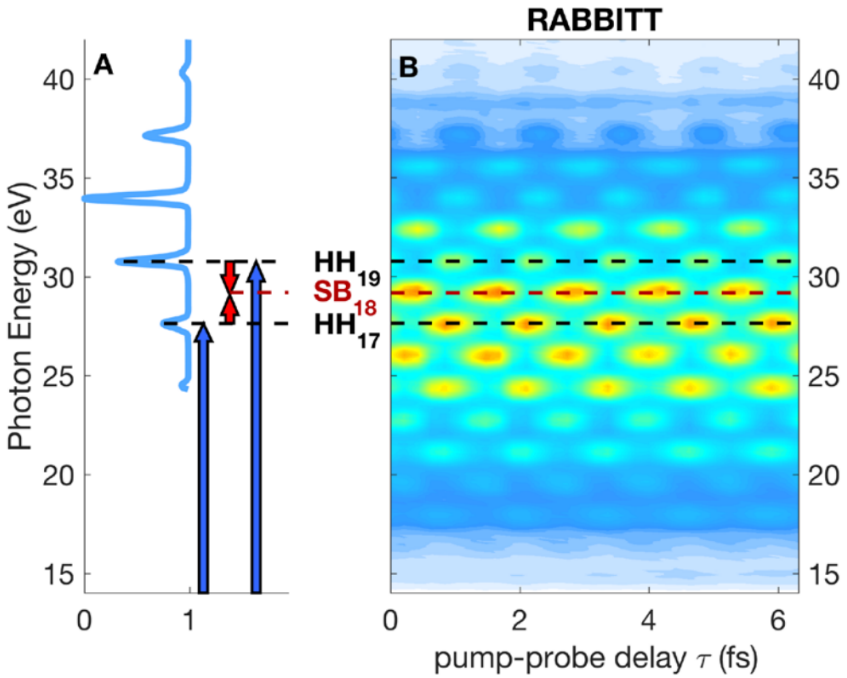
Stereo Wigner delay : $\tau_{SW} = \frac{\Delta\phi_W(\text{carbon side}) - \Delta\phi_W(\text{oxygen side})}{2\omega_{IR}}$

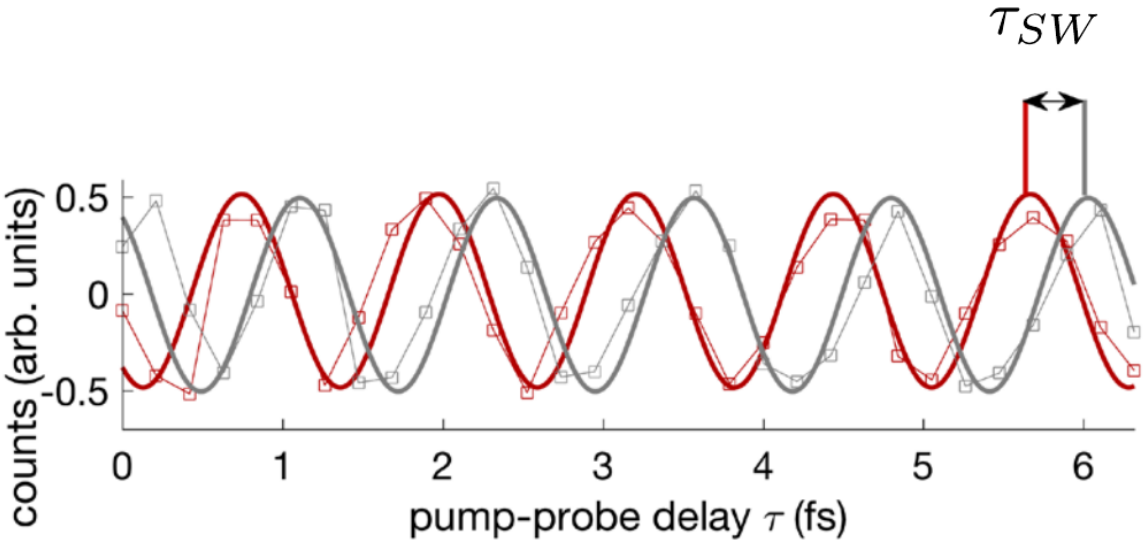
Orientation-dependent delay in CO

Vos *et al.*, *Science* **360**, 1326–1330 (2018)



$$\tau_{SW} = \frac{\Delta\phi_W(\text{carbon side}) - \Delta\phi_W(\text{oxygen side})}{2\omega_{IR}}$$



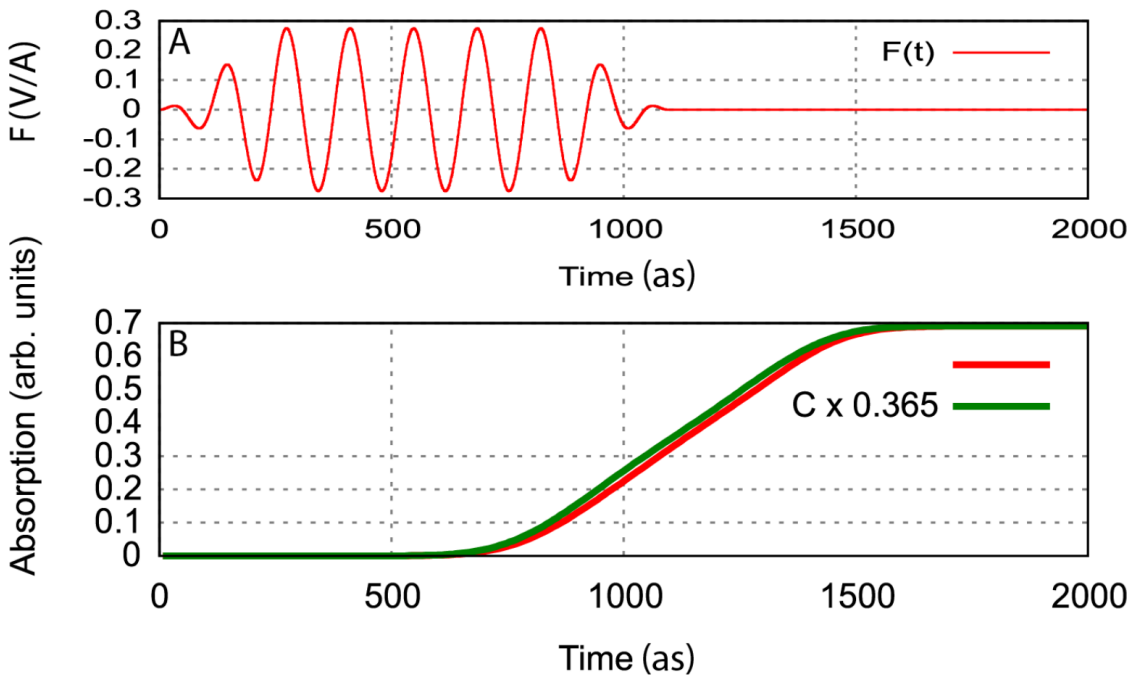


Large delay between electrons emitted from C and O sides

Orientation-dependent delay in CO - theory

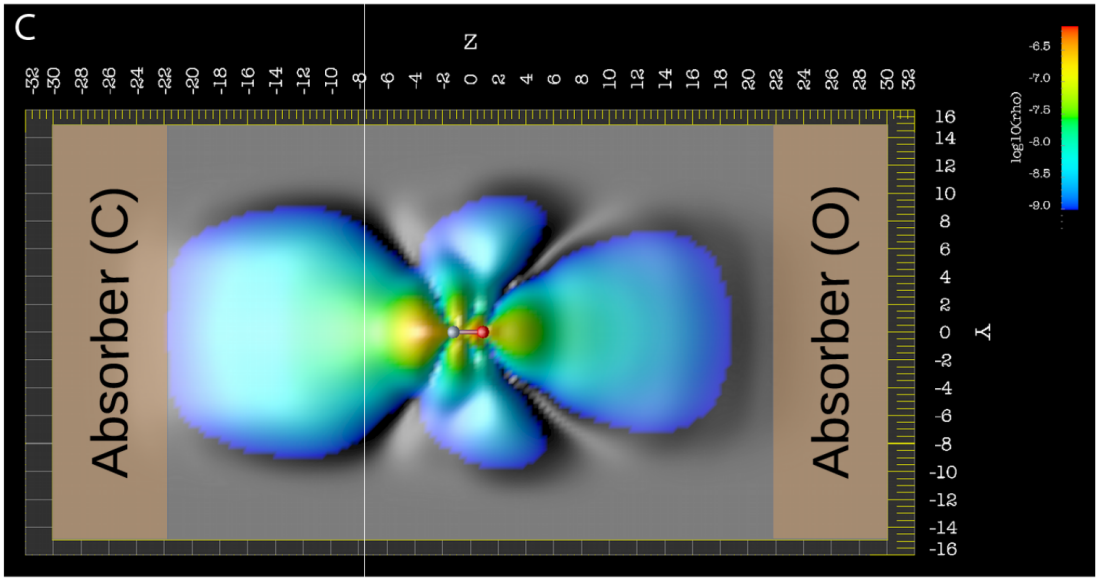
Vos *et al.*, *Science* **360**, 1326–1330 (2018)

Numerical experiment – time dependent resolution in ionic states



Attosecond pulse (electric field)

Electron signal measured on C and O side



Snaphsot of electron density at t=650as

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics – camphor ($C_{10}H_{16}O$)

Autoionization dynamics

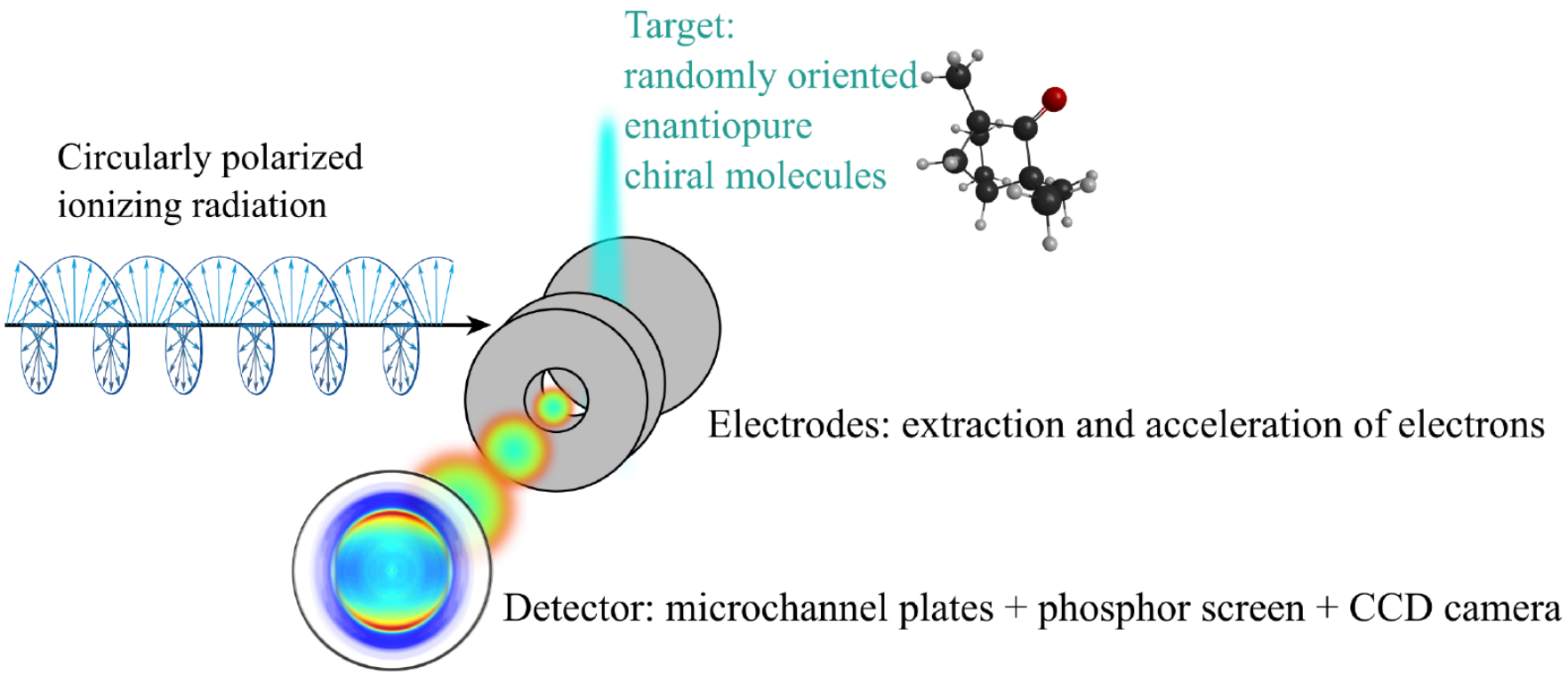
Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Photoionizing chiral molecules

B. Ritchie, PRA 13, 1411 (1976)
N. Bowering et al., PRL 86, 1187 (2001)



Photoionizing chiral molecules

B. Ritchie, PRA 13, 1411 (1976)
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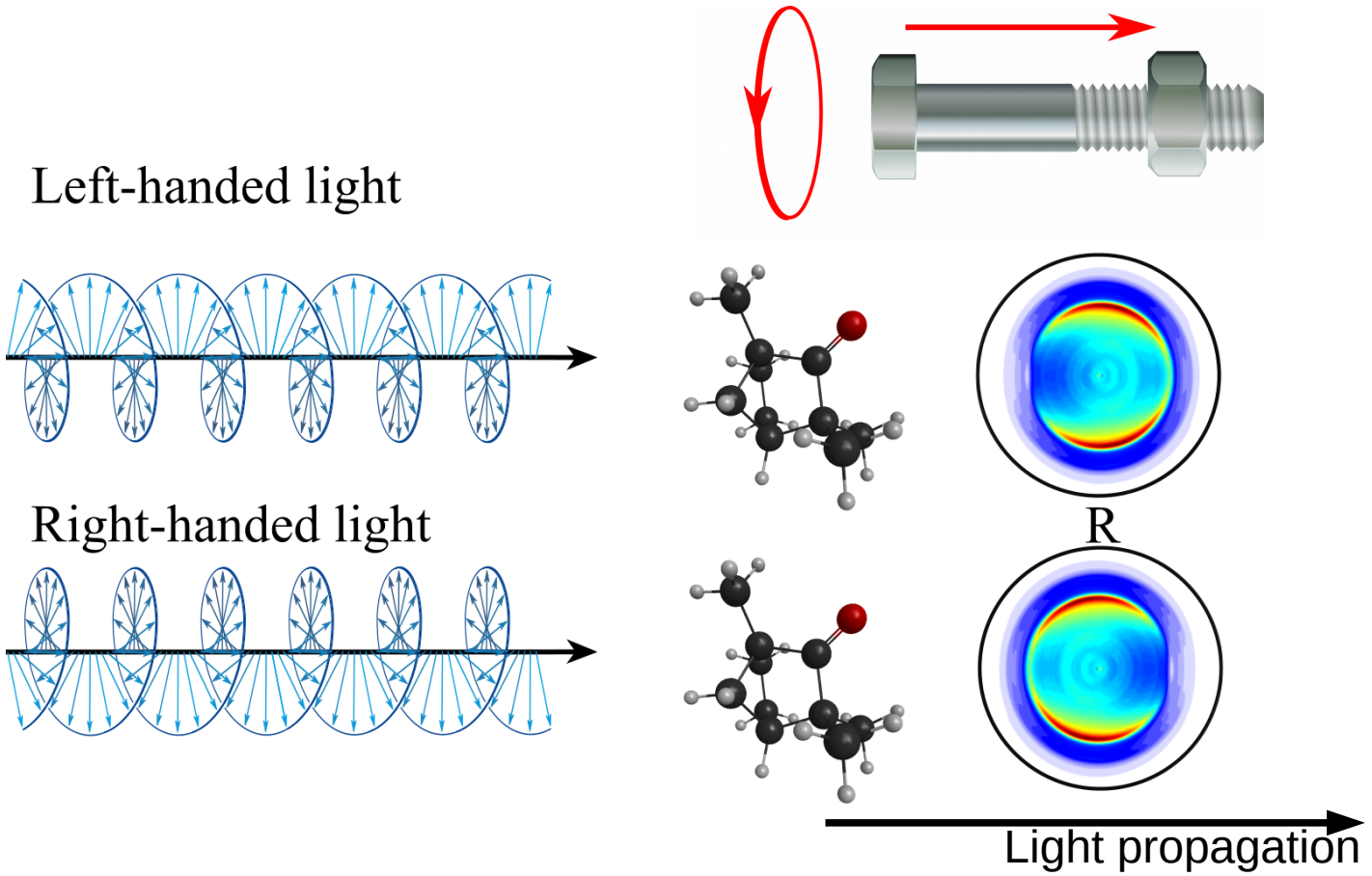


PhotElectron Circular Dichroism – PECD :Pure electric dipole effect

→ much stronger than most other CDs

Up to 37 % measured

For a review see L. Nahon et al., J. Elec. Spec. Rel. Phen. 2014, 322 (2015)

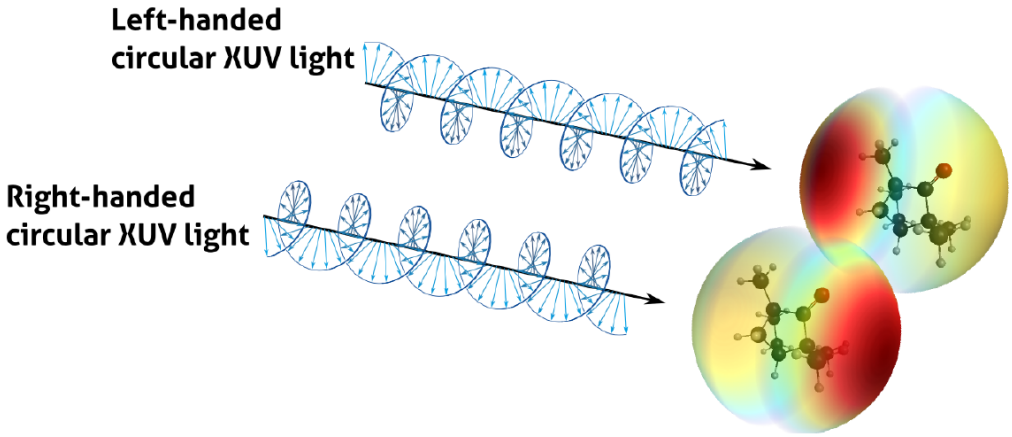
Physical origin of PECD

Quantum mechanically : asymmetric scattering of the outgoing electrons

Combined influence of circular laser field and chiral potential

Highly sensitive to scattering phases

→ Wigner delays ?



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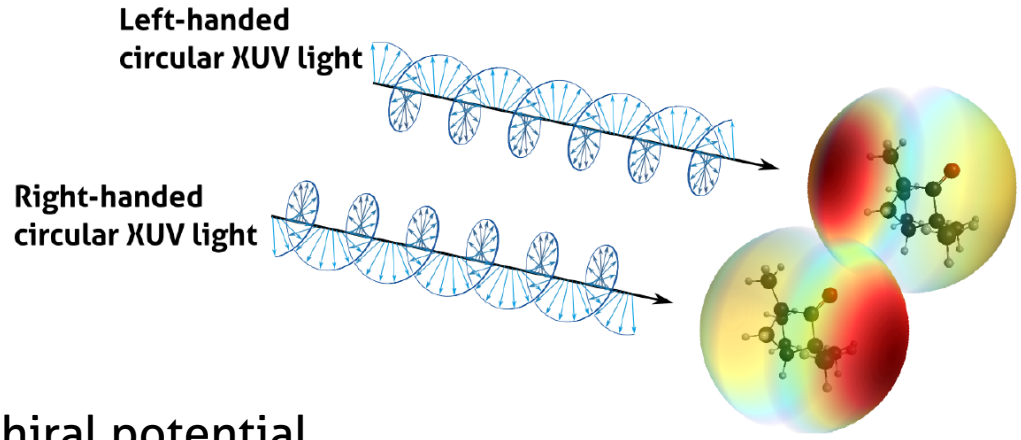
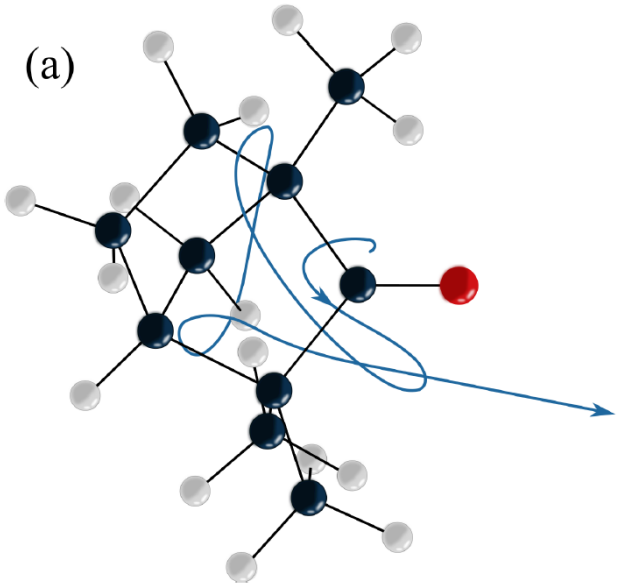


Classical interpretation ?

Calculation of electron trajectories in the chiral potential,
under the influence of the circularly polarized ionizing field.

S. Beaulieu et al., New J. Phys. 18, 102002 (2016)



Dynamical origin of PECD (scattering) → must be measurable by attosecond metrology

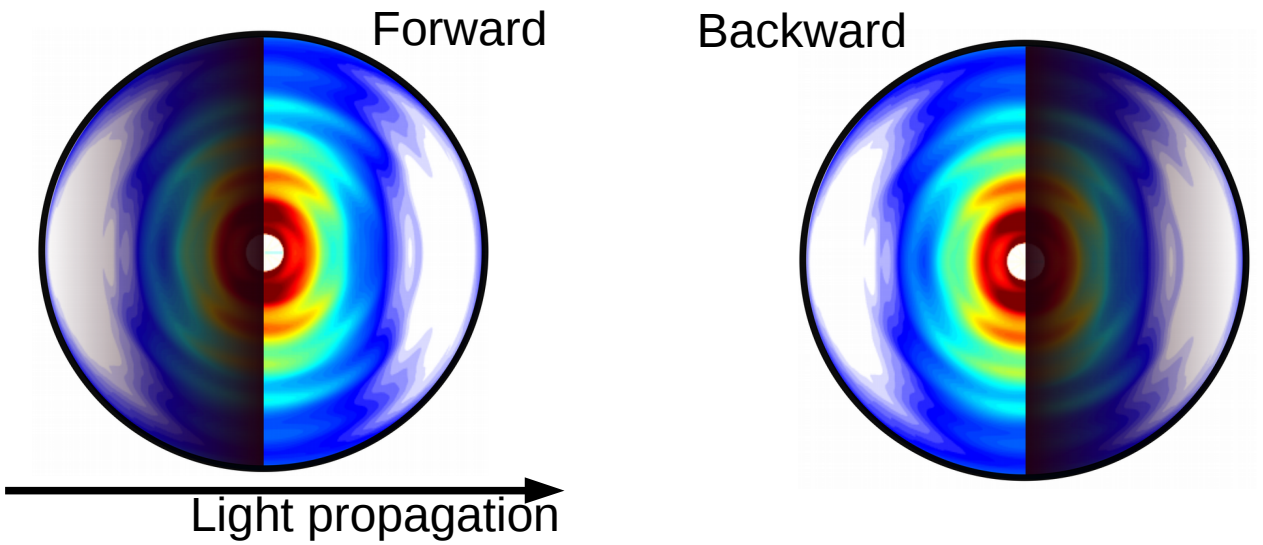
Attosecond chiral photoionization

Attosecond-resolved photoionization of chiral molecules

S. Beaulieu,[1,2]* A. Comby,[1] A. Clergerie,[1] J. Caillat,[3] D. Descamps,[1] N. Dudovich,[4] B. Fabre,[1] R. Géneaux,[5] F. Légaré,[2] S. Petit,[1] B. Pons,[1] G. Porat,[4] T. Ruchon,[5] R. Taïeb,[3] V. Blanchet,[1] Y. Mairesse[1]

Science **358**, 1288–1294 (2017)

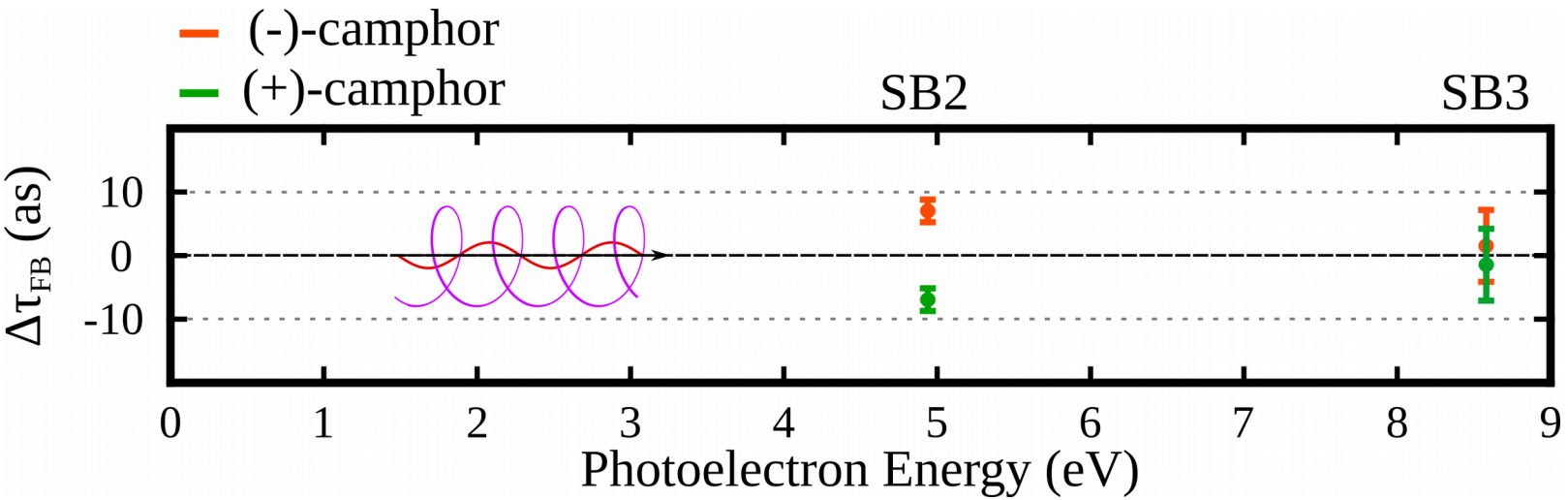
Measurement of the sideband phase in the forward and backward direction :



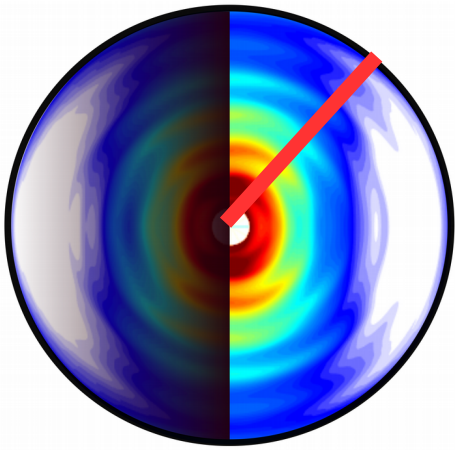
Differential delay : $\Delta\tau^{FB}$

Differential measurement

Beaulieu *et al.*, *Science* **358**, 1288–1294 (2017)

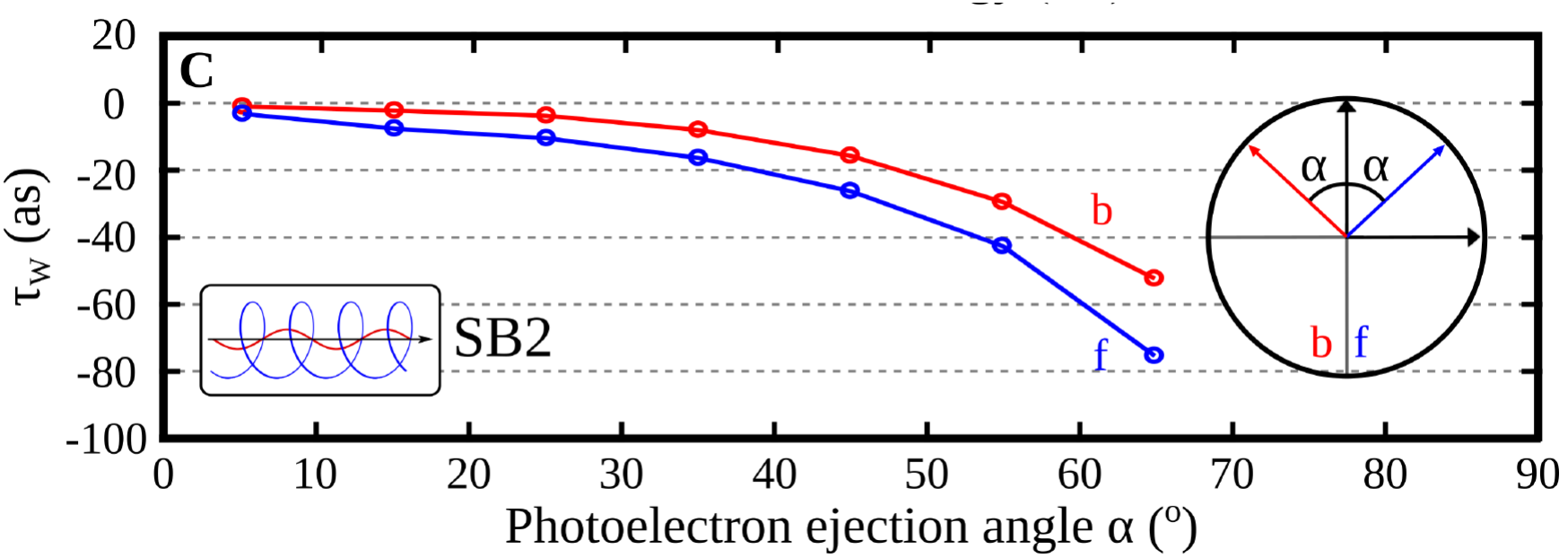


7 ± 2 as delay at 5 eV
between electrons ejected forward and backward



Angle-resolved delays

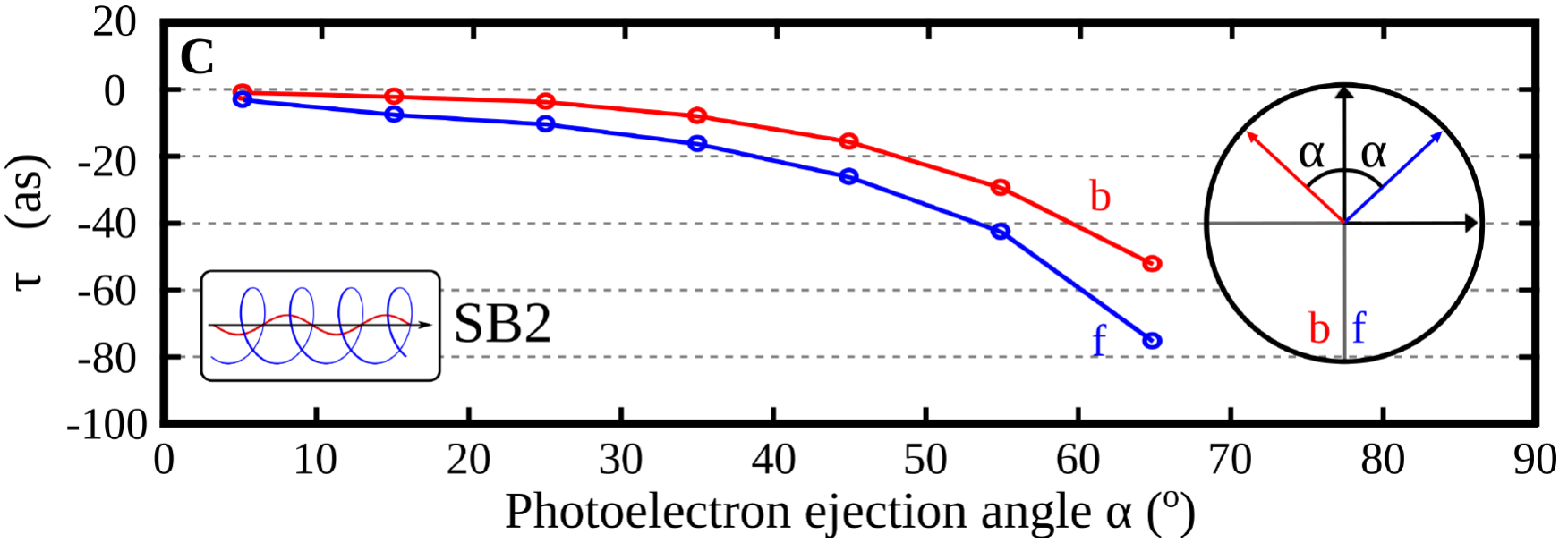
Beaulieu *et al.*, *Science* **358**, 1288–1294 (2017)

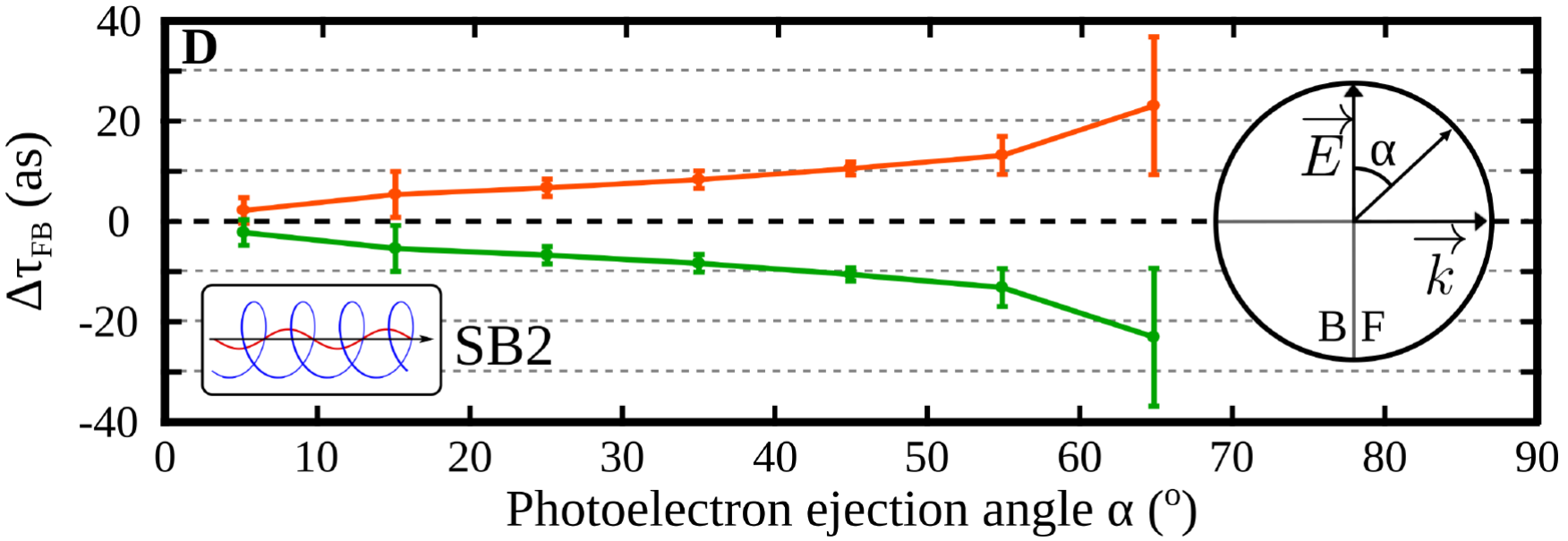


The Wigner delay depends on the ejection direction of the electron

Angle-resolved delays

Beaulieu *et al.*, *Science* **358**, 1288–1294 (2017)





The angle-resolved differential Wigner delay reaches 24 attoseconds

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics

Autoionization dynamics - principle

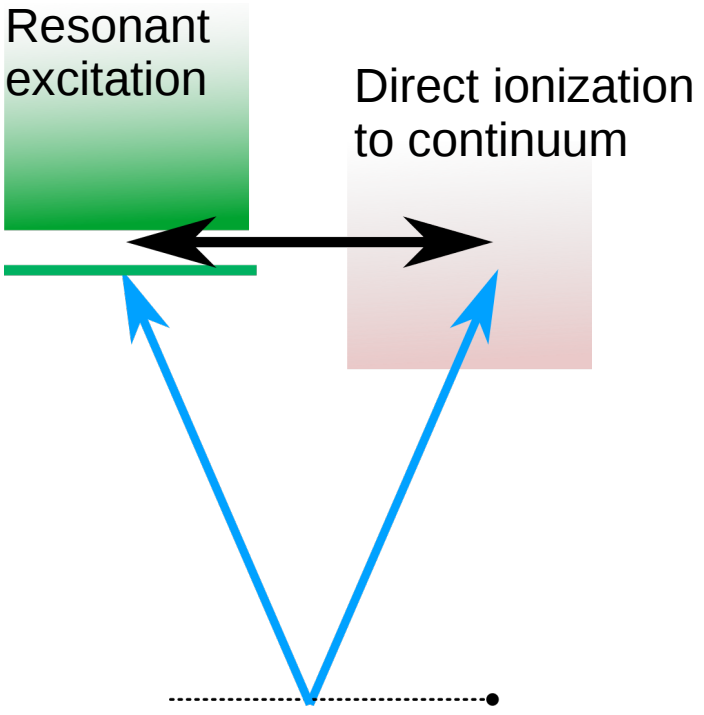
Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Photoionization through a Fano resonance

Ionization through a discrete resonant state coupled to a continuum (autoionizing state)



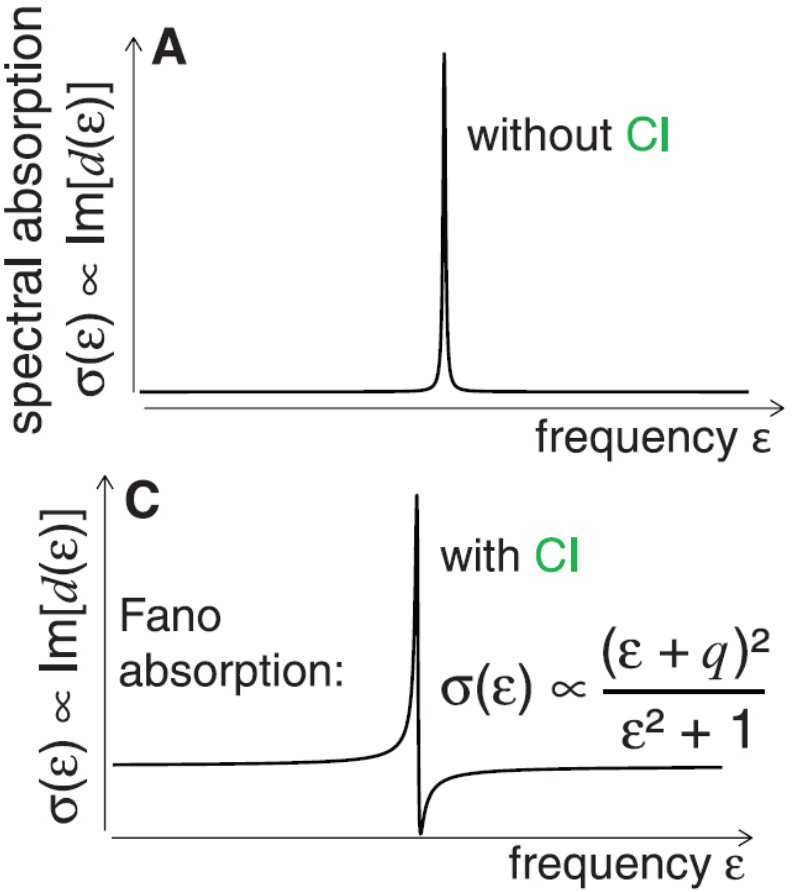
The interference of direct and resonant pathways produces characteristic lineshapes

→ **Fano profiles** *U. Fano, Phys. Rev. 6, 1866 (1961)*

Photoionization through a Fano resonance

Ionization through a discrete resonant state coupled to a continuum (autoionizing state)

Interference between direct (continuum) and resonant ionization
→ Characteristic cross section :



(CI=Configuration Interaction)

The autoionizing state decay is a dynamical process
→ **complex temporal structure of the wavepacket**

Photoionization through a Fano resonance

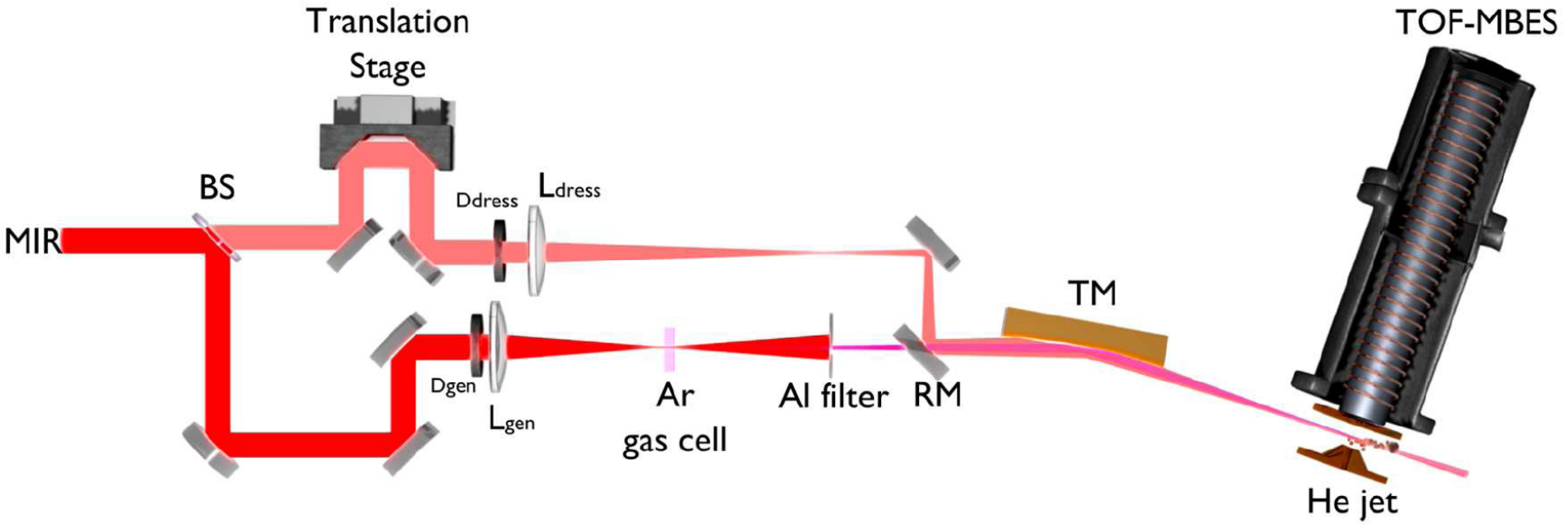
CHEMICAL PHYSICS

Attosecond dynamics through a Fano resonance: Monitoring the birth of a photoelectron

V. Gruson,[1*] L. Barreau,[1*] Á. Jiménez-Galan,[2] F. Risoud,[3] J. Caillat,[3] A. Maquet,[3] B. Carré,[1] F. Lepetit,[1] J.-F. Hergott,[1] T. Ruchon,[1] L. Argenti,[2†] R. Taïeb,[3] F. Martín,[2,4,5‡] P. Salières[1‡]

734 11 NOVEMBER 2016 • VOL 354 ISSUE 6313 sciencemag.org SCIENCE

Specificity of the setup : tunable laser (NOPA), set at 1295 nm



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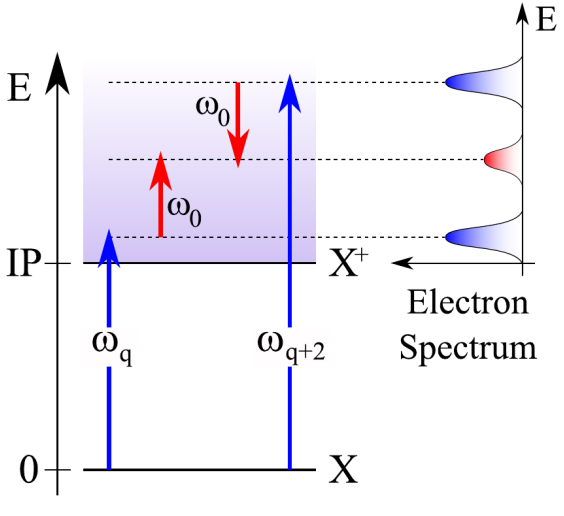
sciencemag.org SCIENCE 11 NOVEMBER 2016 • VOL 354 ISSUE 6313

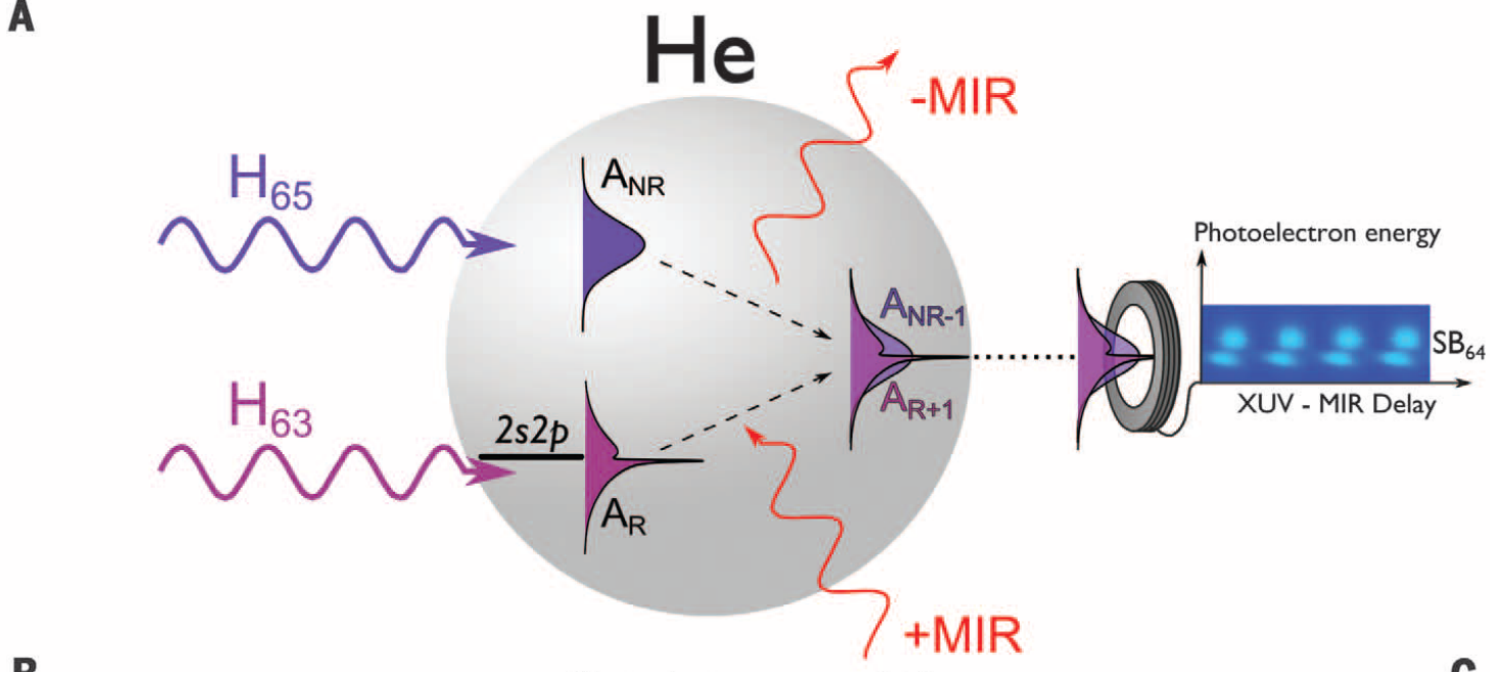
Spécificity of the setup : tunable laser (NOPA), set at 1295 nm

H63 hits the 2s2p state in the He continuum → Fano lineshape

RABBIT : sideband 64

→ Mesurement of the phase going through the autoionizing state (H63) or not (H65)
Spectrally-resolved measurement → spectrally-resolved ionization phase





RABBIT signal

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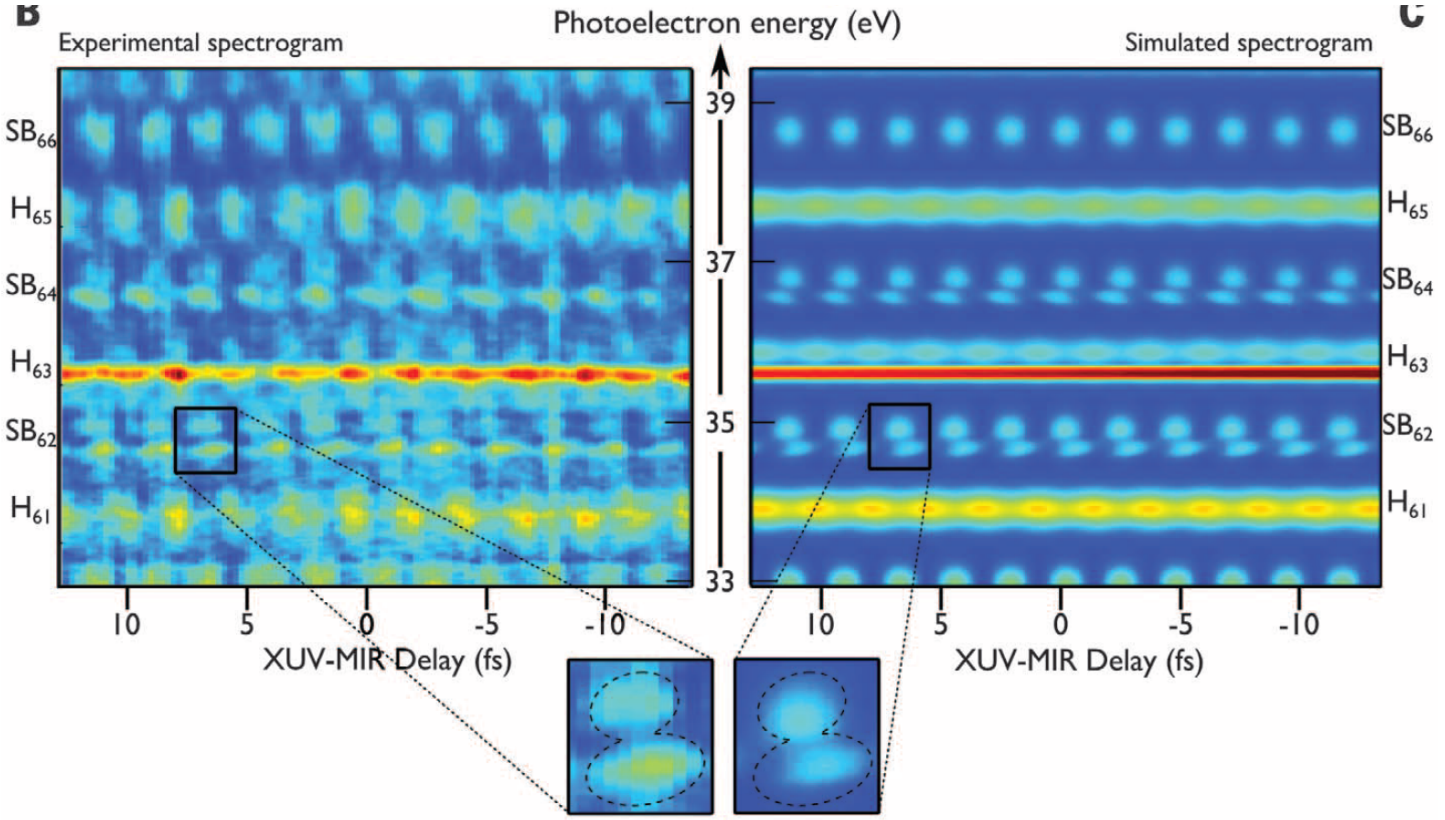
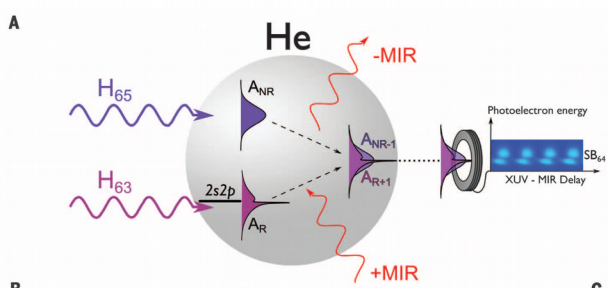
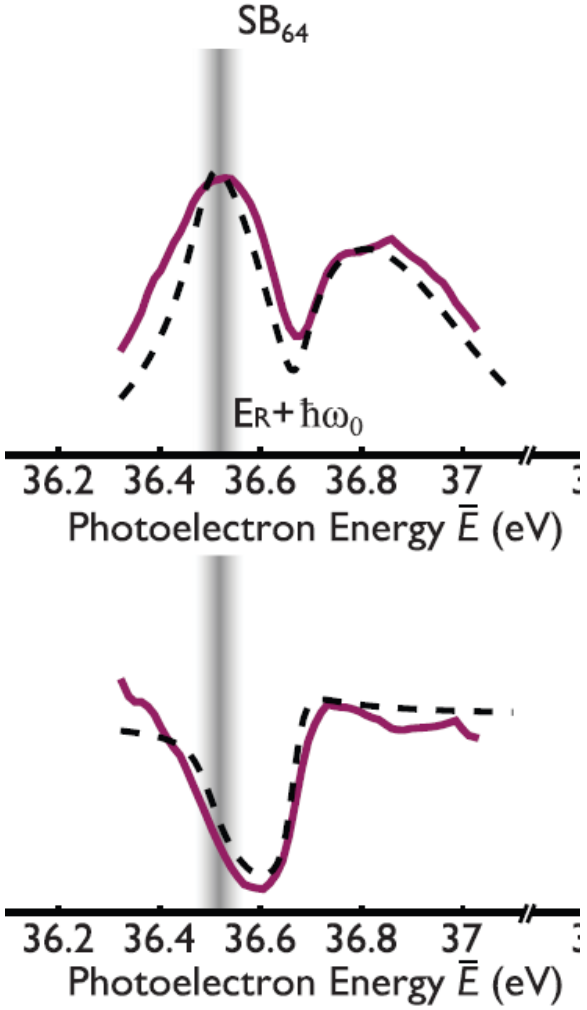


Results

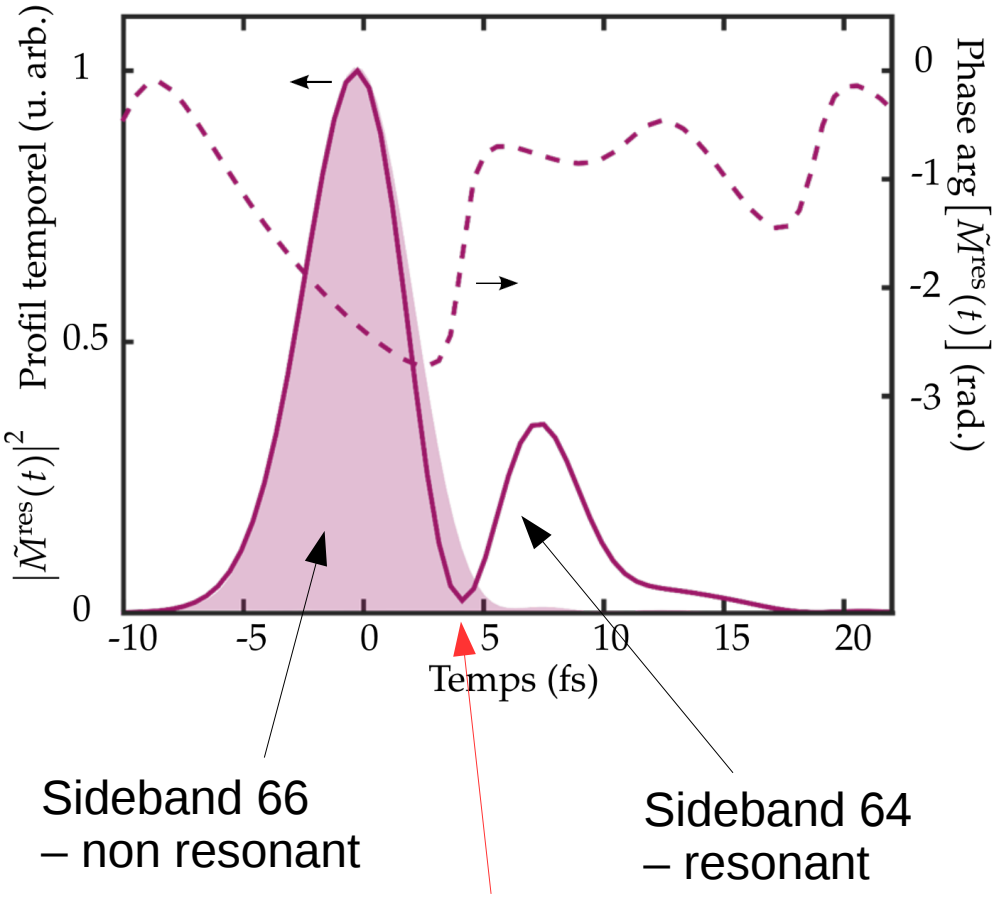


Spectum and spectral phase

Temporal profile of the electron wavepacket



Fourier Transform



Sideband 66 – non resonant

Sideband 64 – resonant

Destructive interference between direct and resonant ionization

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics

Autoionization dynamics - camphor

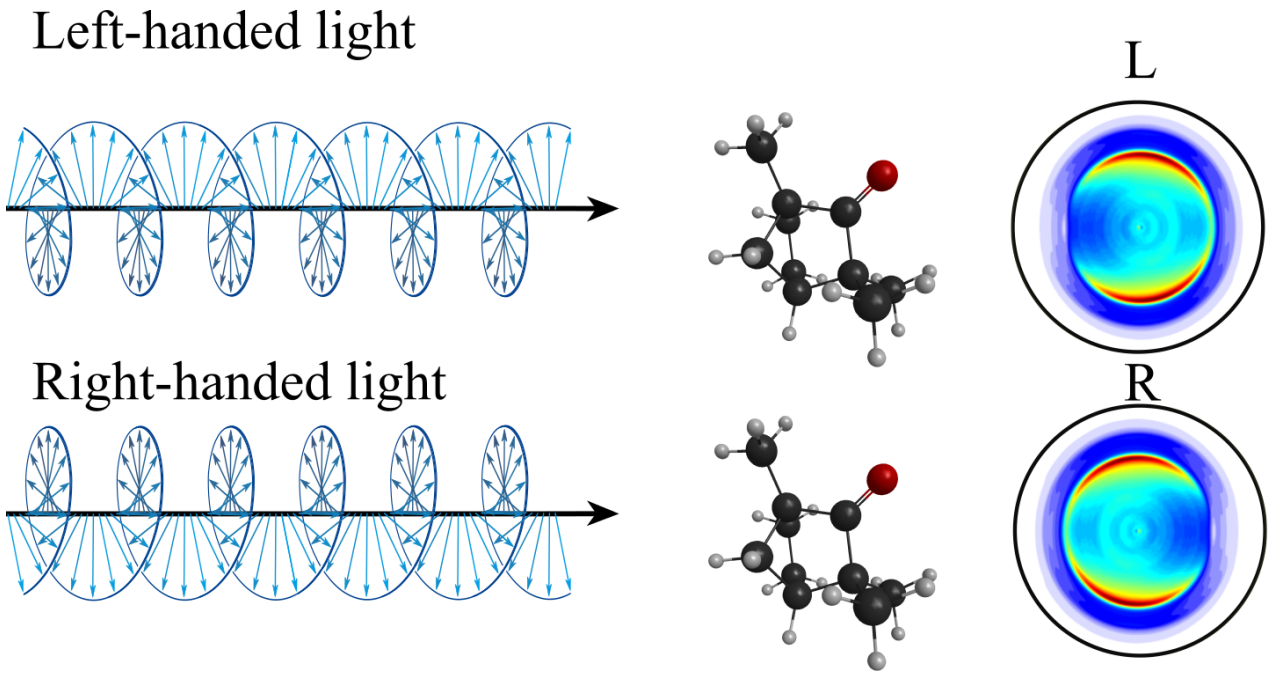
Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

Laser-induced electron diffraction

Resonant photoionization of chiral molecules

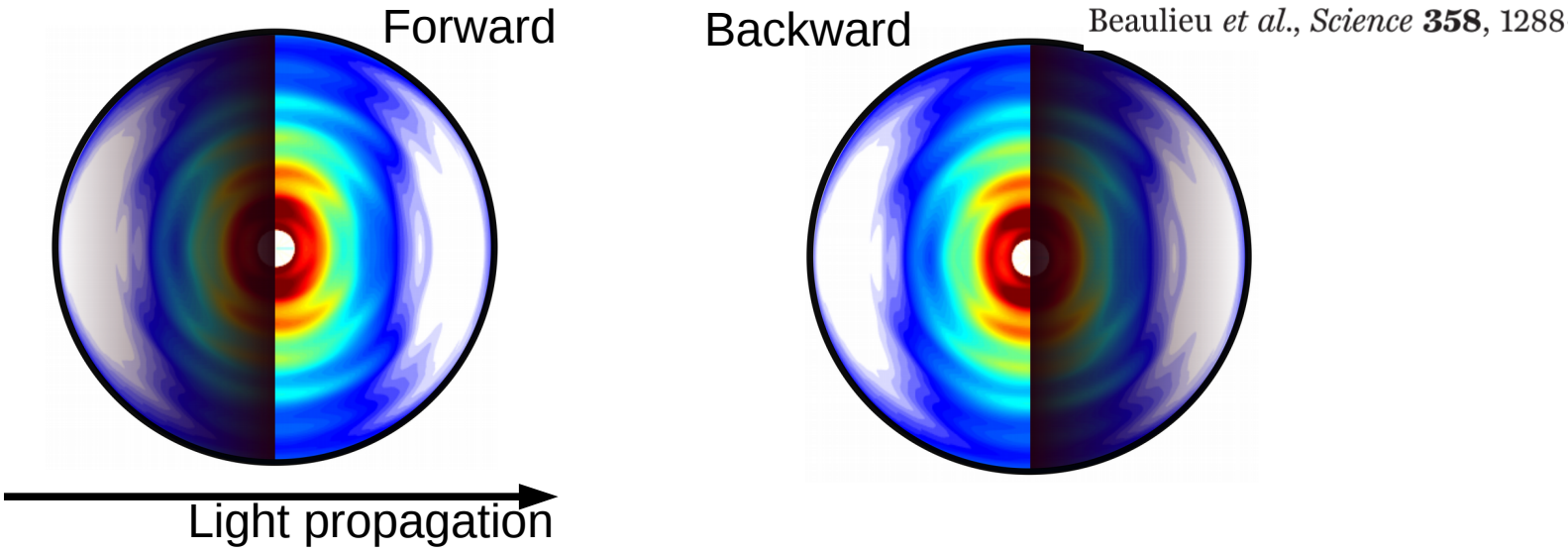
What happens if we resonantly ionize camphor molecules using circularly polarized light ?
Is the autoionization process forward/backward asymetric ?

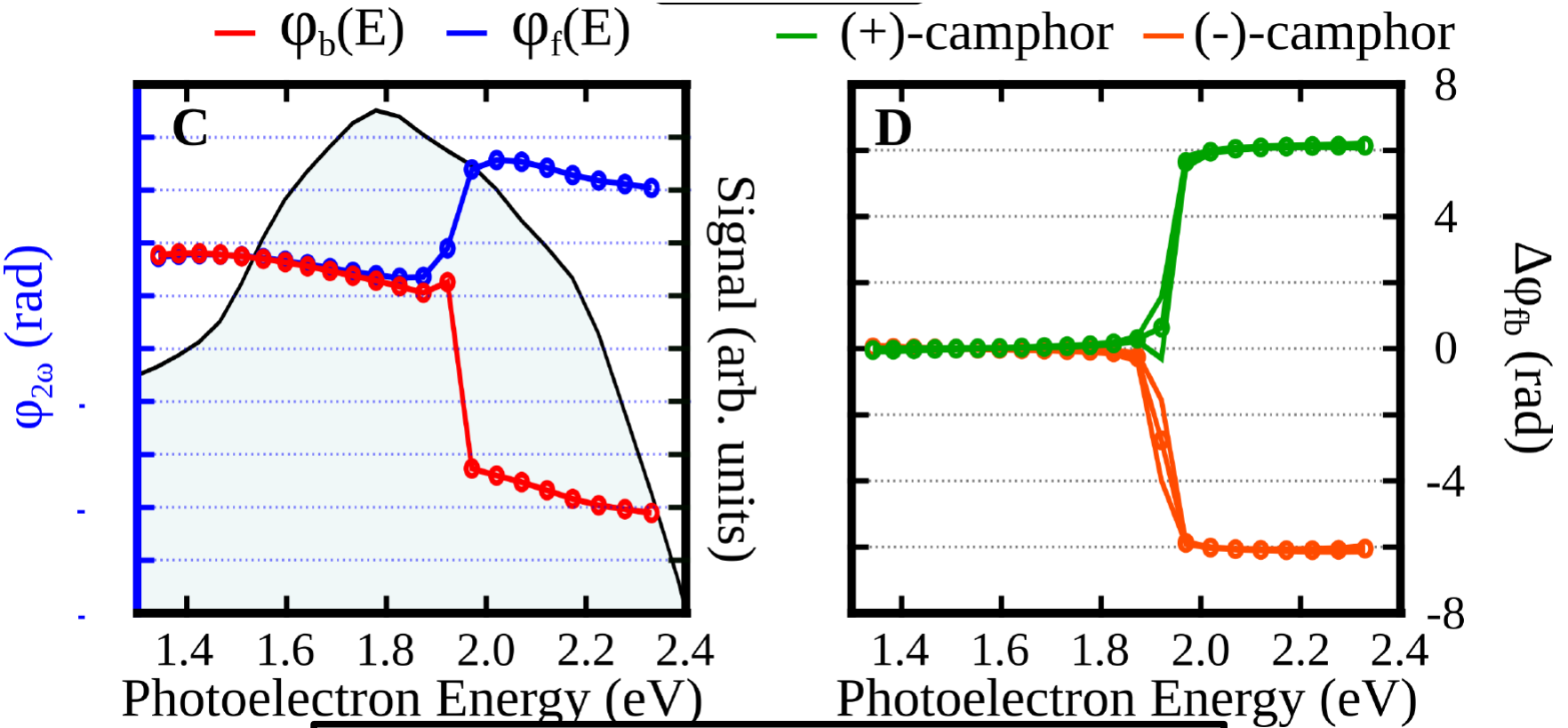


Measurement of the phase electrons ejected forward and backward

Resonant chiral photoionization

Beaulieu *et al.*, *Science* **358**, 1288–1294 (2017)



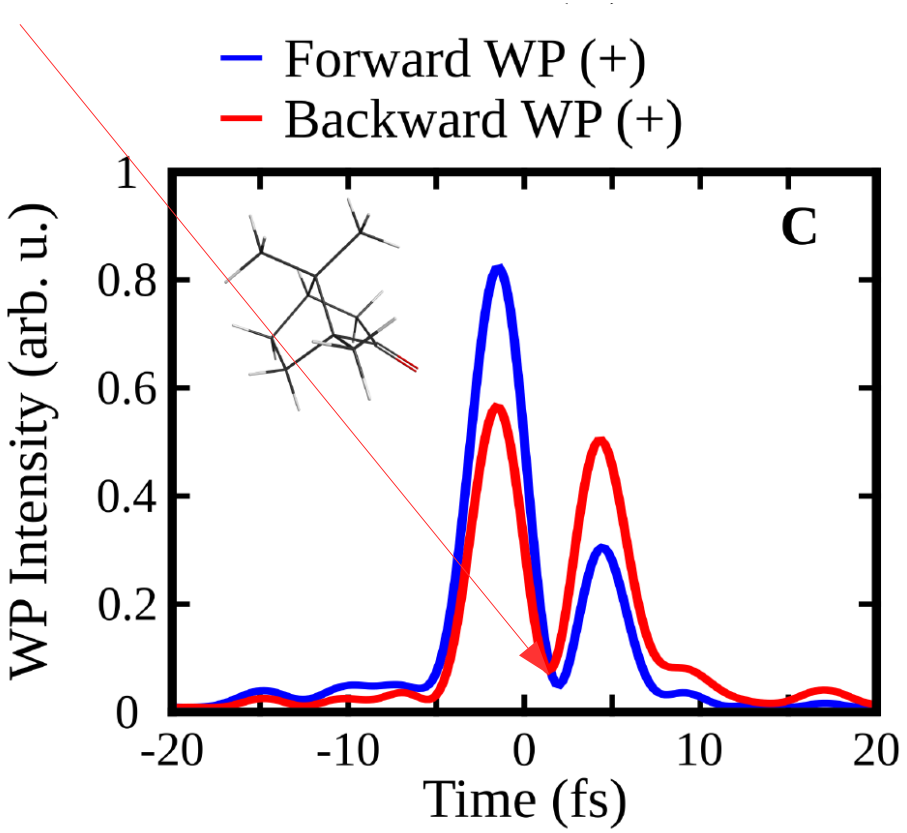


Chiral character of the autoionization process

Electron wavepackets

Beaulieu *et al.*, *Science* **358**, 1288–1294 (2017)

Destructive interference between
direct and resonant ionization

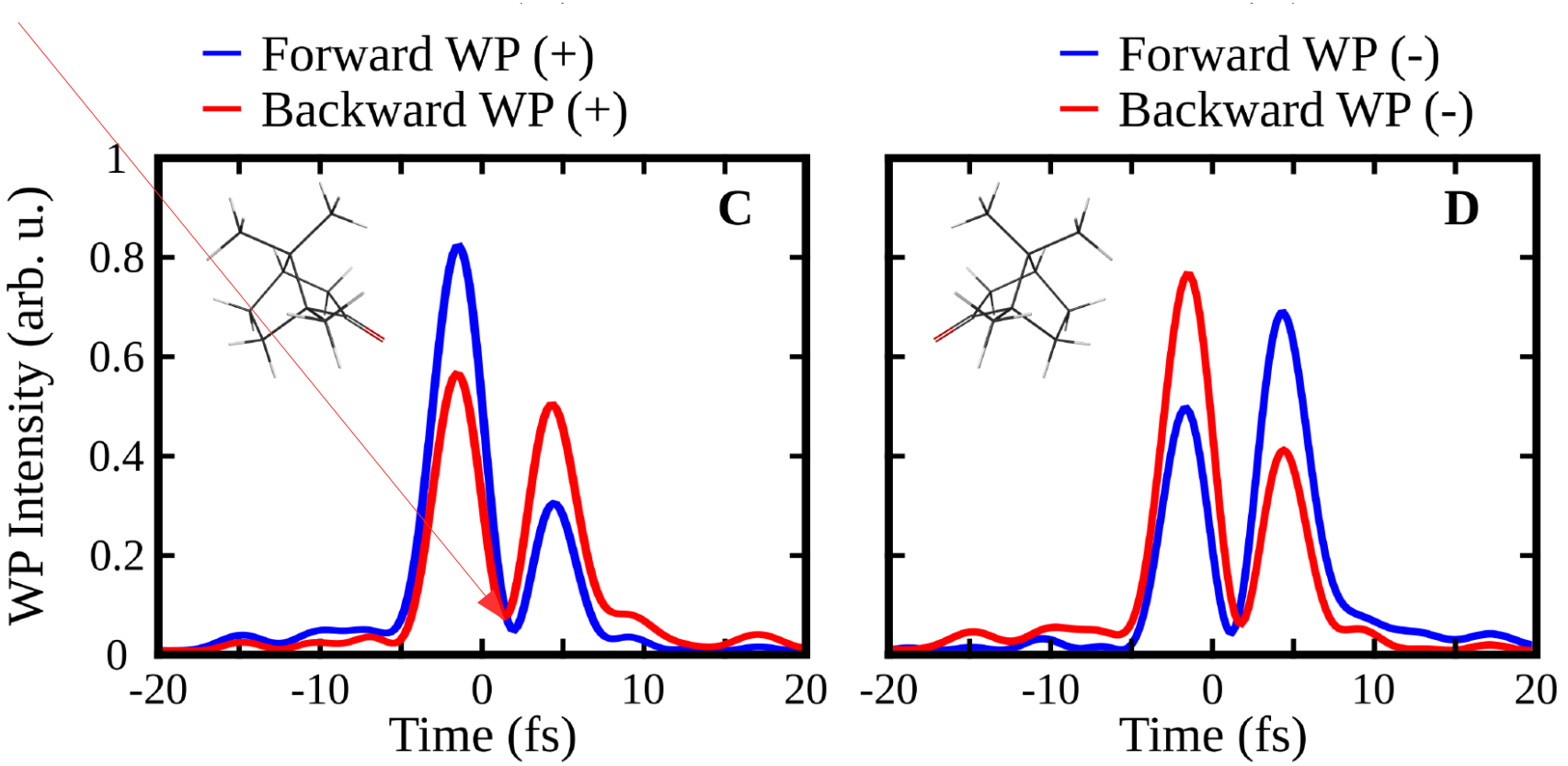


Strong asymmetry of the autoionizing wavepackets

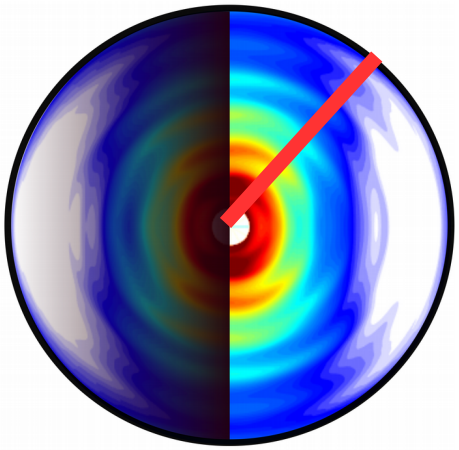
Electron wavepackets

Beaulieu *et al.*, *Science* **358**, 1288–1294 (2017)

Destructive interference between
direct and resonant ionization

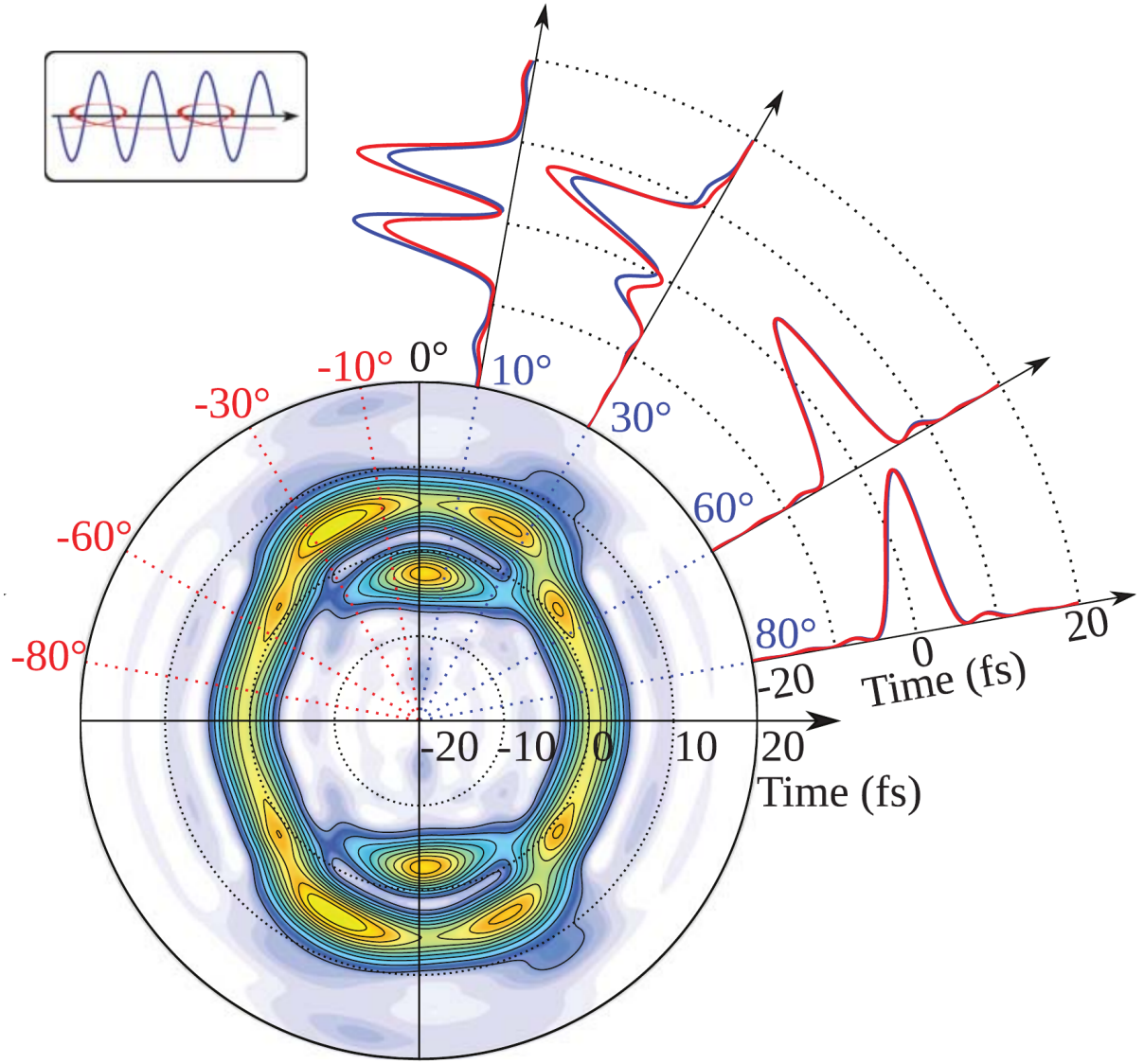


Strong asymmetry of the autoionizing wavepackets
Reverses with enantiomer – genuine chiral effect



Angle-resolved electron wavepackets

Beaulieu *et al.*, *Science* **358**, 1288–1294 (2017)



Angular mapping of the autoionization dynamics

Conclusions on photoionization delay measurements

Photoionization is not instantaneous

Photoionization delays have been measured in atoms, molecules, and surfaces

Attosecond pulse trains provide simultaneously high temporal and high spectral resolution

→ Perfect tool for molecules

Coincidence electron-ion imaging is a very powerful tool

Autoionization dynamics can be measured in the temporal domain

Photoionization delays depend on
- ionized orbital
- vibrational excitation of the ion
- electron ejection direction with respect to the laser polarization
- electron ejection direction with respect to the molecule

→ Very sensitive probe of photoionization

Generation of attosecond pulses

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Laser-induced electron diffraction

Influence of an intense laser field on XUV molecular photoionization

PRL **111,** 033001 (2013) PHYSICAL REVIEW LETTERS week ending 19 JULY 2013

Probing Time-Dependent Molecular Dipoles on the Attosecond Time Scale

Ch. Neidel, J. Klei, C.-H. Yang, A. Rouzée, and M. J. J. Vrakking*
Max-Born Institut, Max-Born Strasse 2A, 12489 Berlin, Germany

K. Klünder, M. Miranda, C. L. Arnold, T. Fordell, A. L'Huillier, M. Gisselbrecht, and P. Johnsson
Department of Physics, Lund University, P.O. Box 118, SE-221 00 Lund, Sweden

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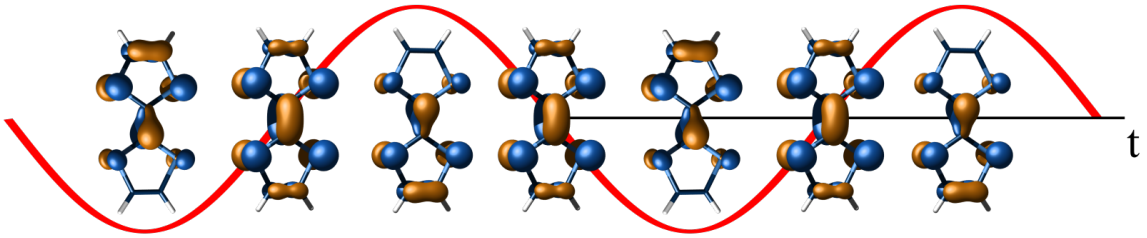
P.-G. Reinhard
Institut für Theoretische Physik, Universität Erlangen, Staudtstrasse 7, D-91058 Erlangen, Germany

V. Despré, M. A. L. Marques, and F. Lépine†
Institut Lumière Matière, Université Lyon 1, CNRS, UMR 5306, 10 Rue Ada Byron, 69622 Villeurbanne Cedex, France
(Received 21 March 2013; published 18 July 2013)

Idea : an intense laser field induces a polarization of molecules, following the fields oscillations



Influence of an intense laser field on XUV molecular photoionization

PRL **111,** 033001 (2013) PHYSICAL REVIEW LETTERS week ending 19 JULY 2013

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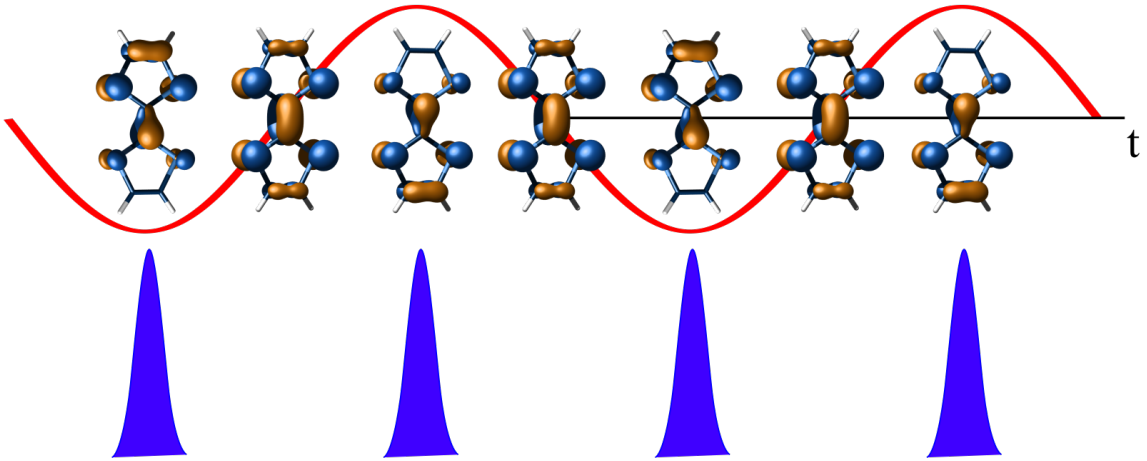
Idea : an intense laser field induces a polarization of molecules, following the fields oscillations

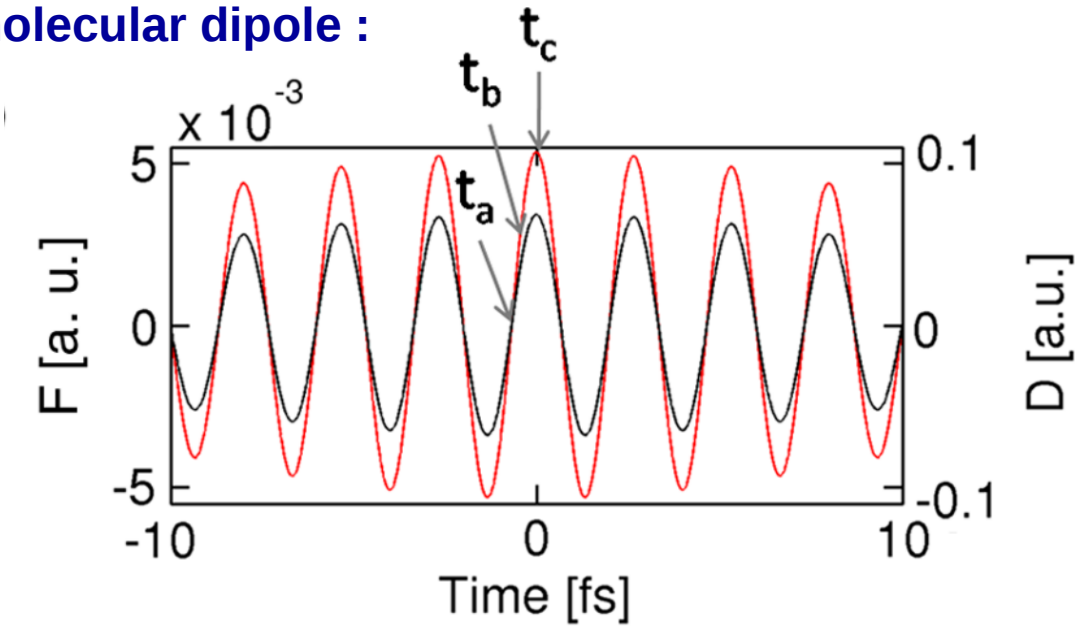
Can this be probed by attosecond photoionization ?



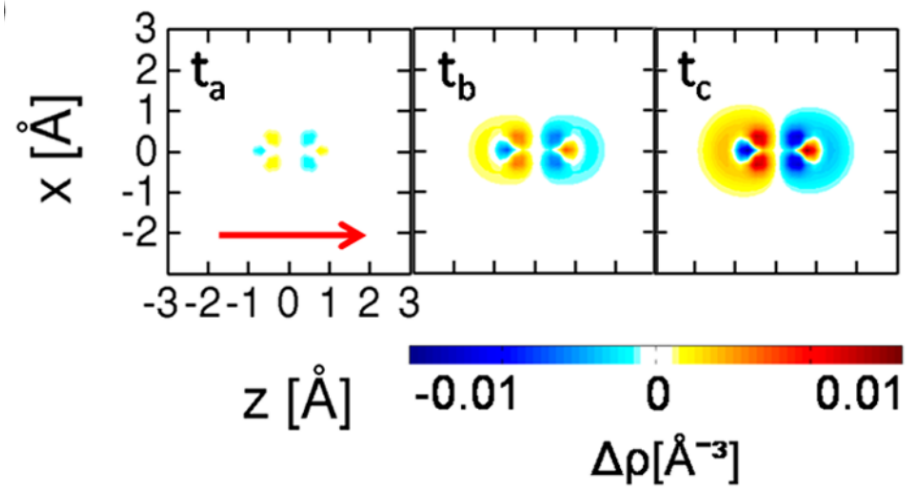
Molecular dipole in N2

PRL **111,** 033001 (2013)

Temporal evolution of molecular dipole :

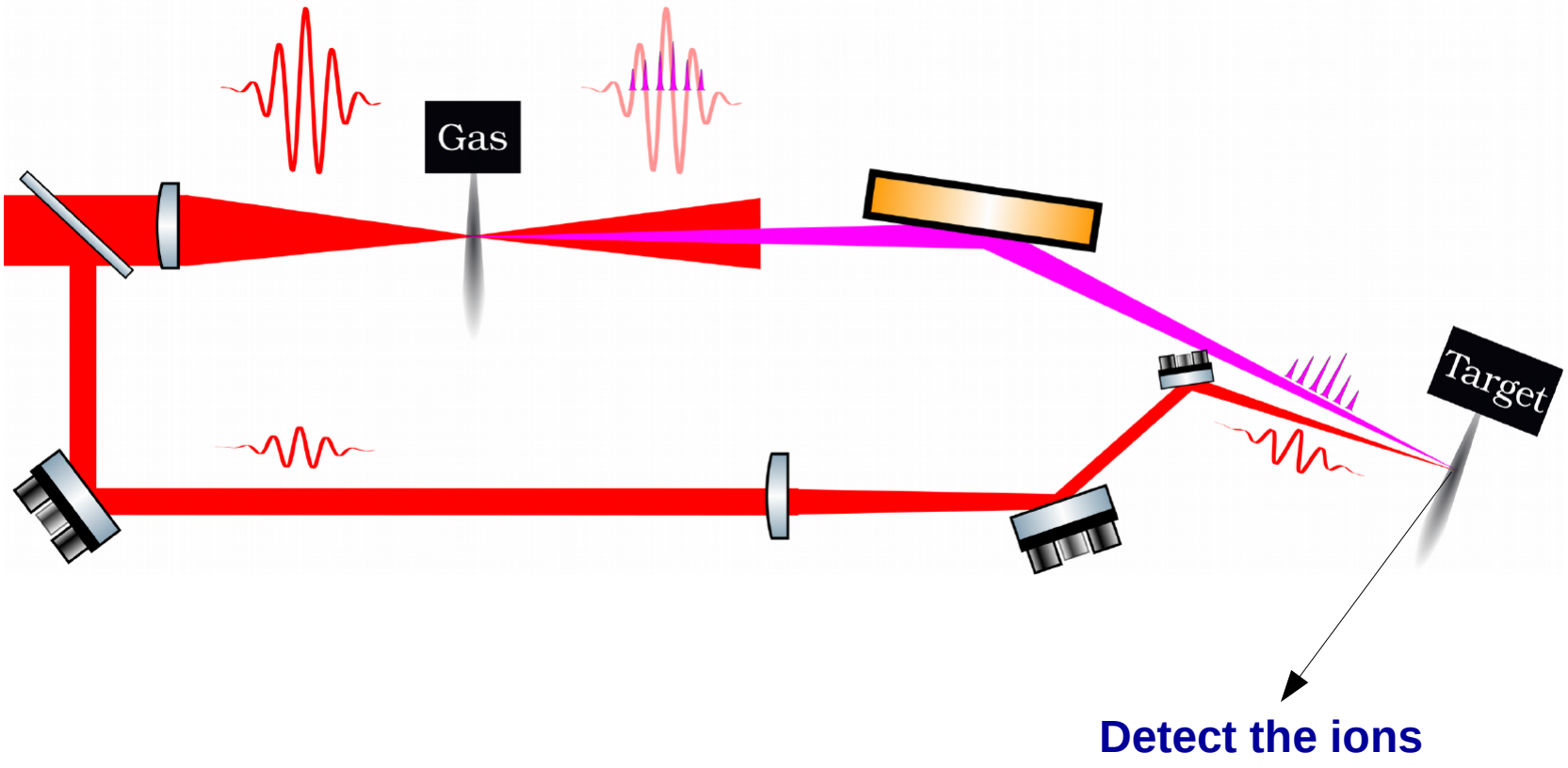


Field-induced distorsion of the electron wavefunction



Principle of the measurement :

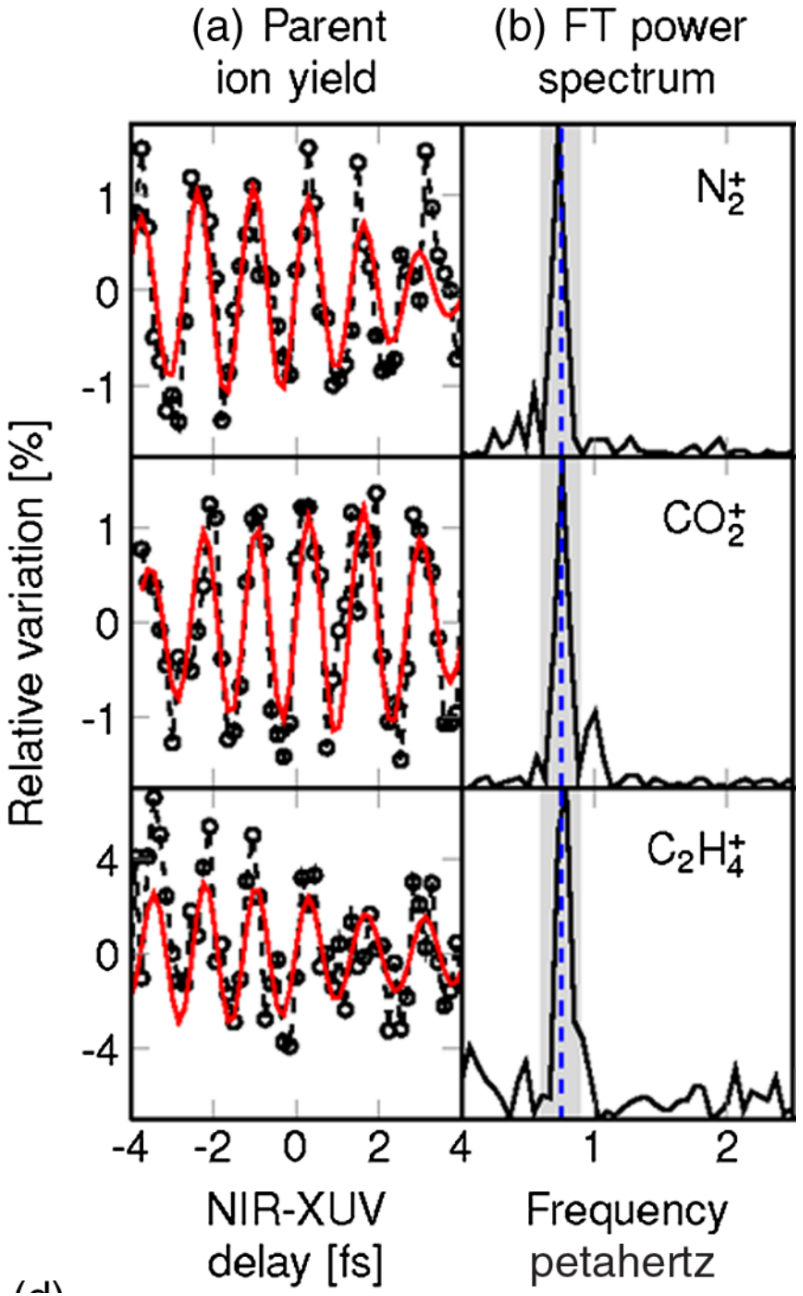
PRL **111,** 033001 (2013)



Experimental results

PRL **111,** 033001 (2013)

Pump : IR field.
Probe : attosecond pulse train



Clear oscillations of the XUV photoionization probability following the attosecond dynamics of the bound electrons

Larger modulations in more polarizable species

Observable ?

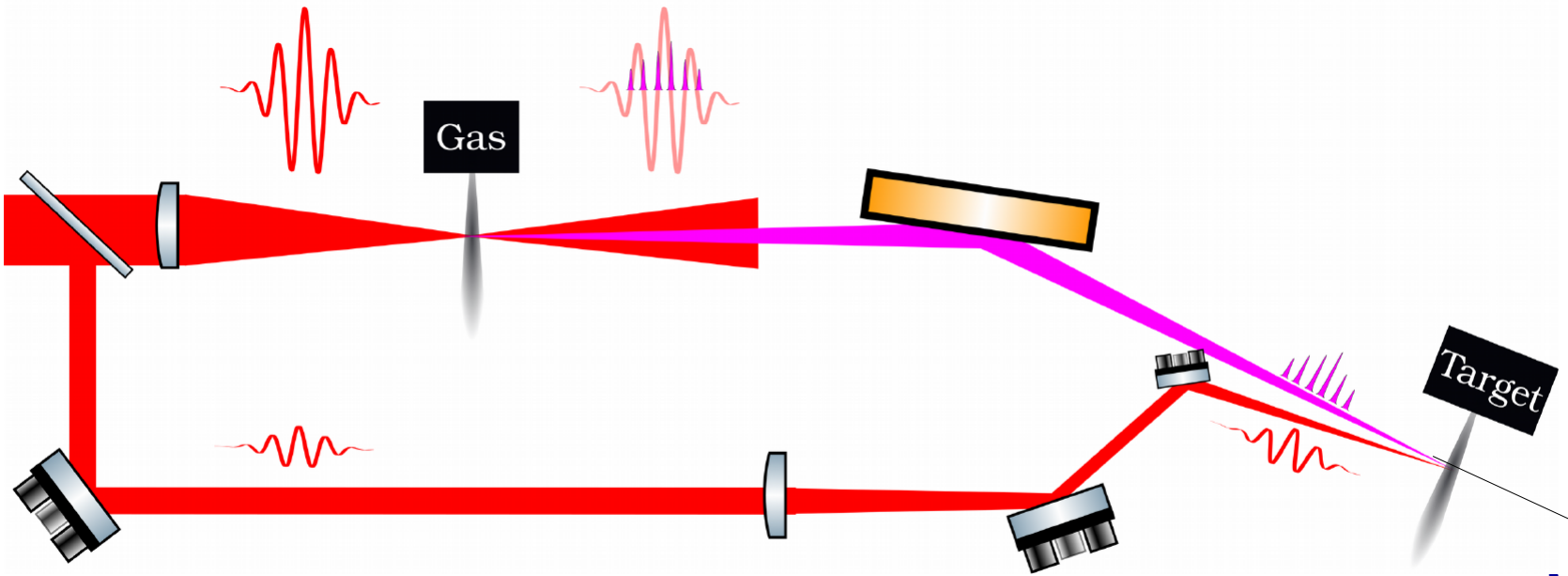
Ion signal : low dimensionality observable

Electron spectrum ?

Issue : the presence of the laser field strongly affects the electron spectrum
(the laser accelerates the ionized electrons)
→ Difficult to disentangle the effect of the IR on bound and ionized electrons

XUV absorption spectrum ?

Energy-resolved → could provide more spectroscopic information than the ion signal
Absorption by core levels → element specific → site specific



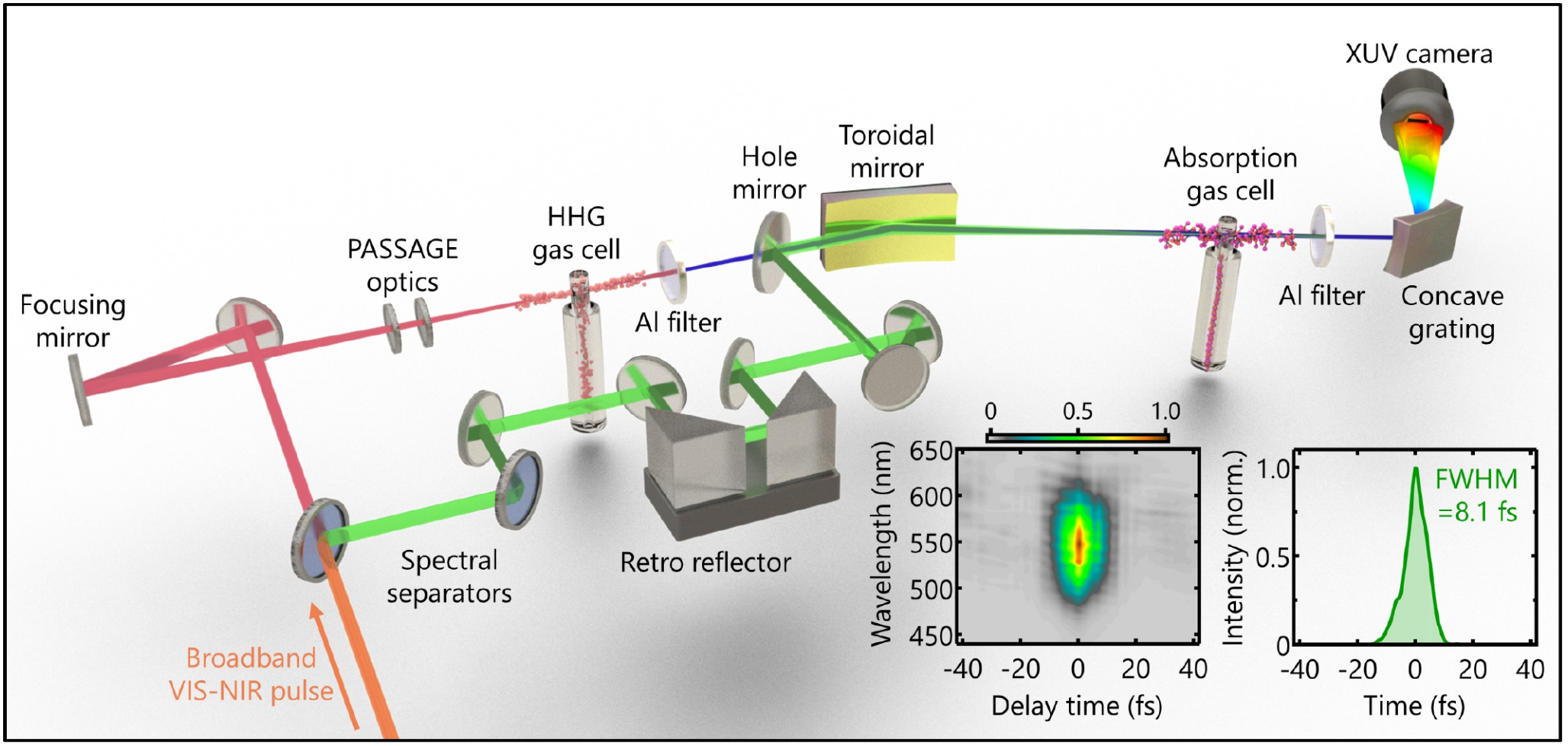
Measure the XUV spectrum

Typical attosecond transient absorption spectroscopy setup

Direct mapping of curve-crossing dynamics in IBr by attosecond transient absorption spectroscopy

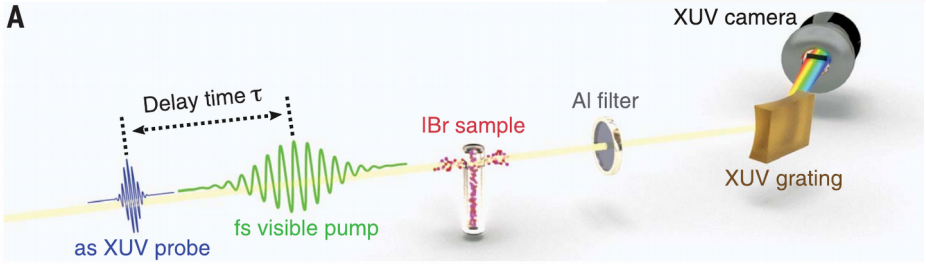
Yuki Kobayashi[1]*, Kristina F. Chang[1], Tao Zeng[2], Daniel M. Neumark[1,3]*, Stephen R. Leone[1,3,4]*

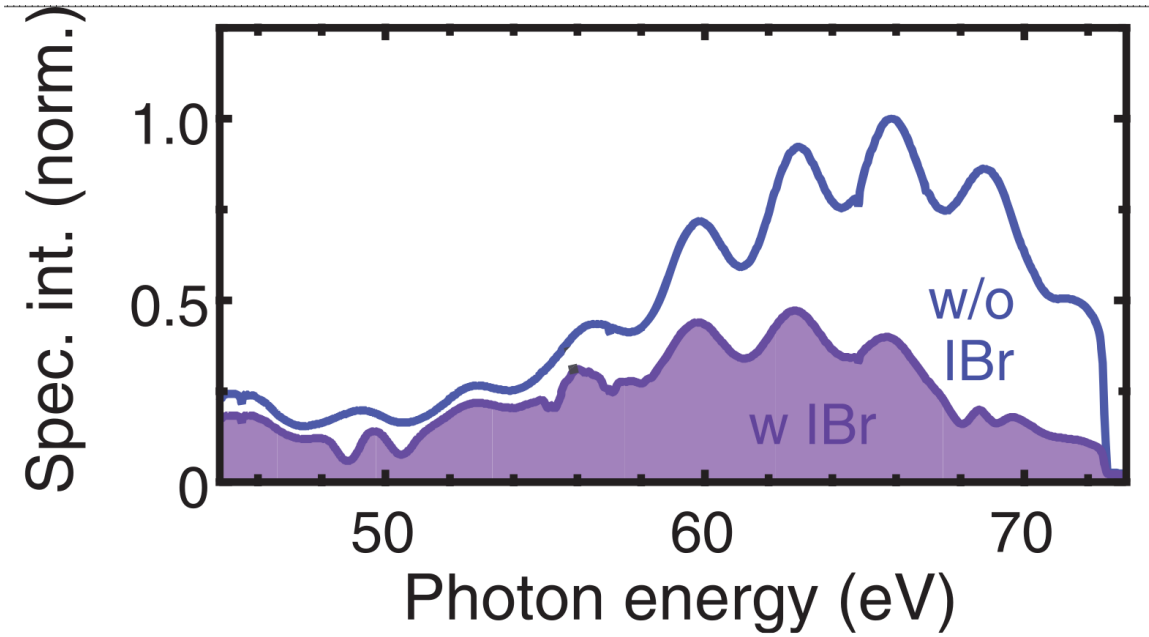
Kobayashi *et al.*, *Science* **365**, 79–83 (2019)



Measurements in IBr

Kobayashi *et al.*, *Science* **365**, 79–83 (2019)



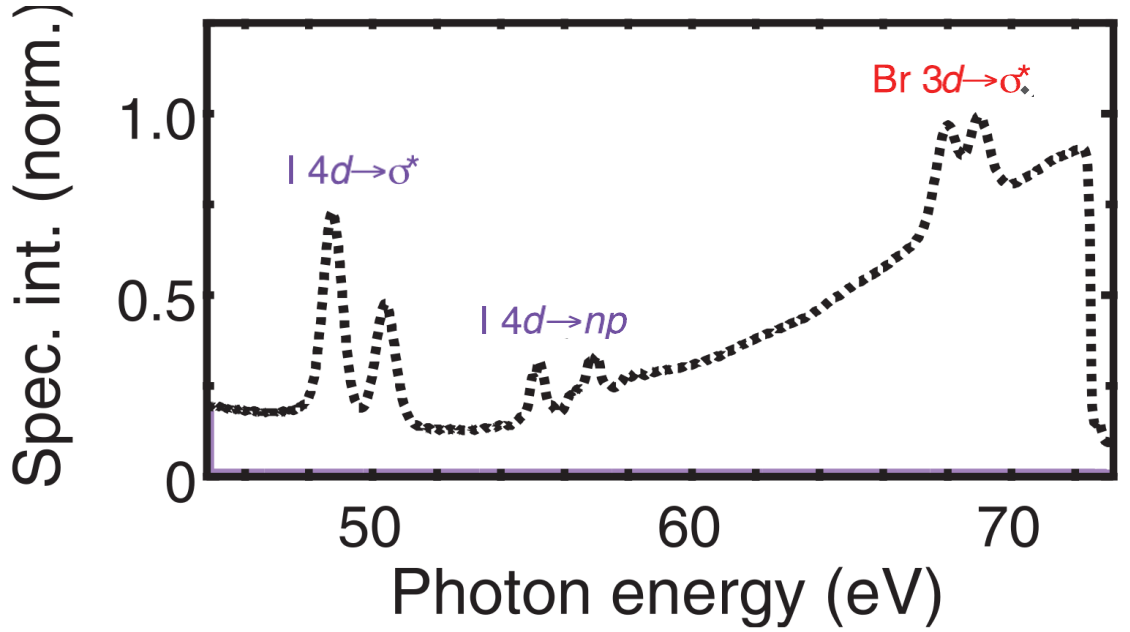


Absorption spectrum :

Lines due to core transitions :

Core to valence ($\rightarrow \sigma^*$)

Core to Rydberg ($\rightarrow$ np)

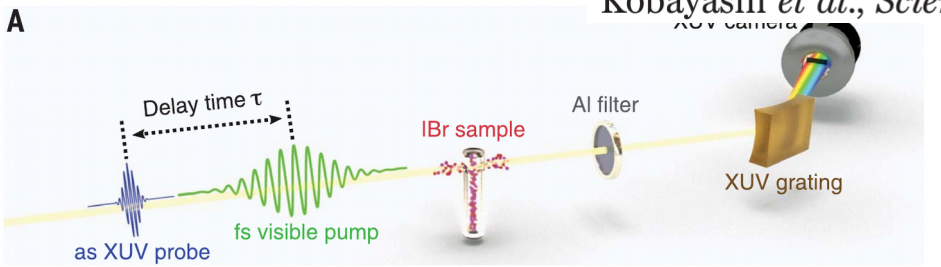


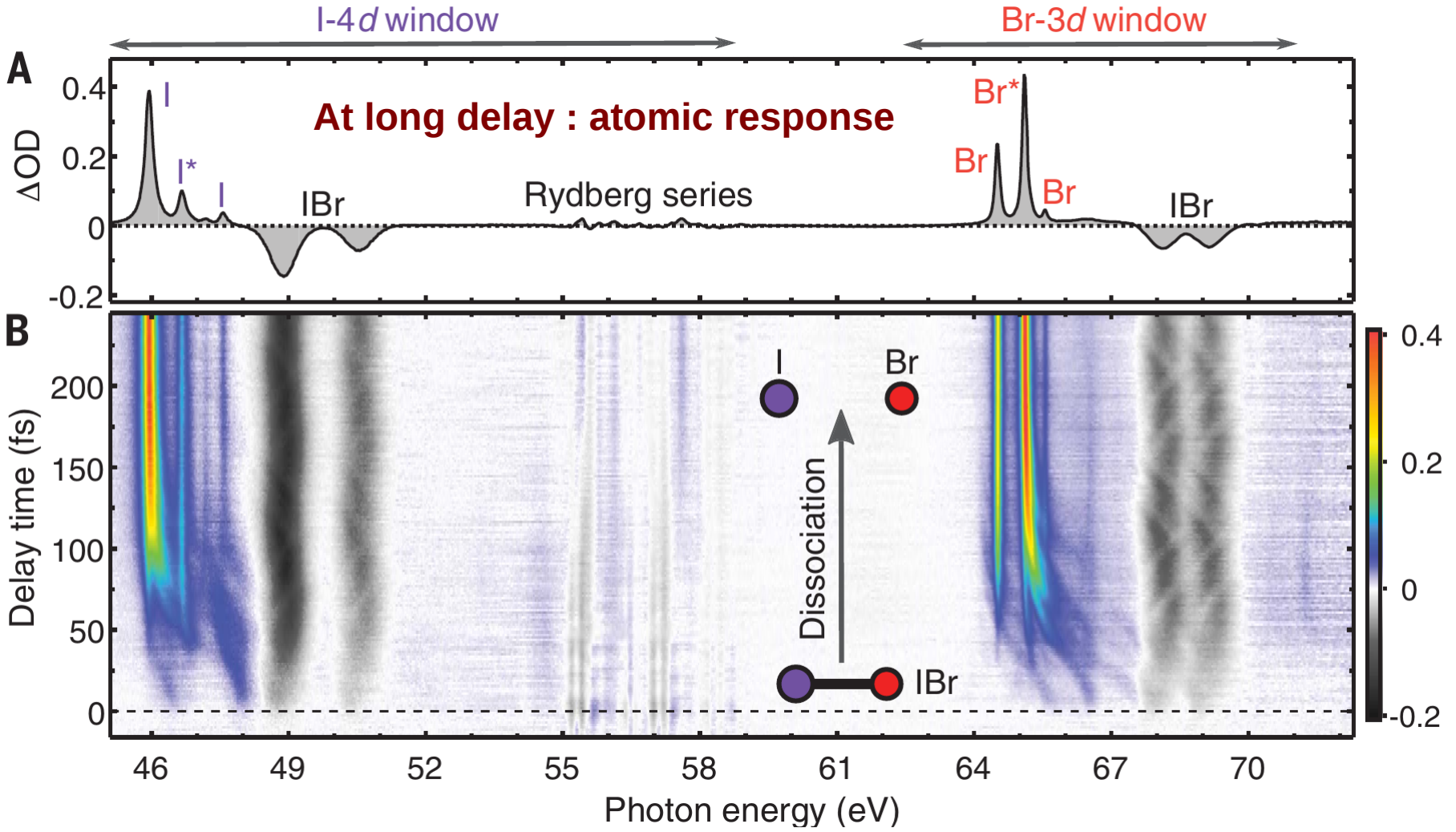
Element-specific lines in the absorption spectrum

Measurements in IBr - femtosecond

Kobayashi *et al.*, *Science* **365**, 79–83 (2019)

Pump : photodissociates Ibr
Probe : absorption of XUV pulse





The changes in the absorption spectrum reflect the dissociation dynamics

Measurements in CH3I - attosecond

THE JOURNAL OF PHYSICAL CHEMISTRY Letters
Letter
Cite This: J. Phys. Chem. Lett. 2019, 10, 265−269
pubs.acs.org/JPCL

State-Resolved Probing of Attosecond Timescale Molecular Dipoles

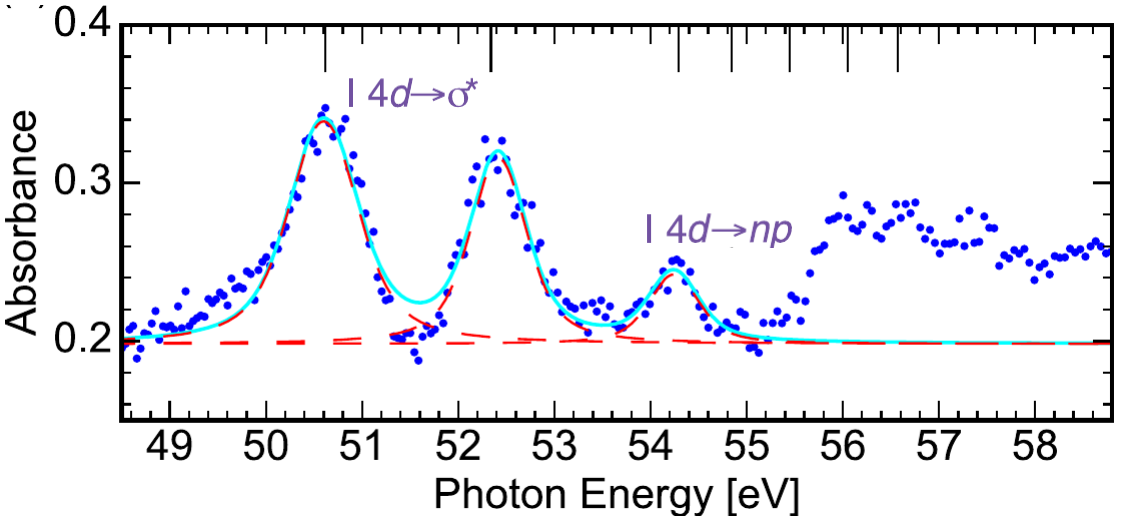
L. Drescher, G. Reitsma, T. Witting, S. Patchkovskii, J. Mikosch,* and M. J. J. Vrakking

Max-Born-Institut für nichtlineare Optik und Kurzzeitspektroskopie, Max-Born-Strasse 2A, 12489 Berlin, Germany

Absorption spectrum of CH3I:

Lines due to core transitions :

- Core to valence (→σ*)
- Core to Rydberg (→ np)



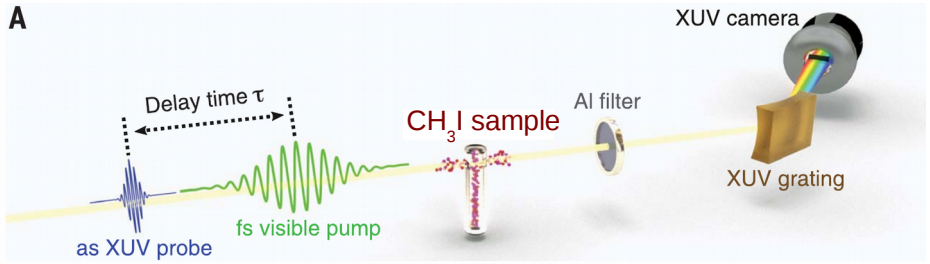
J. Chem. Phys. **145**, 011101 (2016)

Measurements in CH3I - attosecond

J. Phys. Chem. Lett. 2019, 10, 265−269

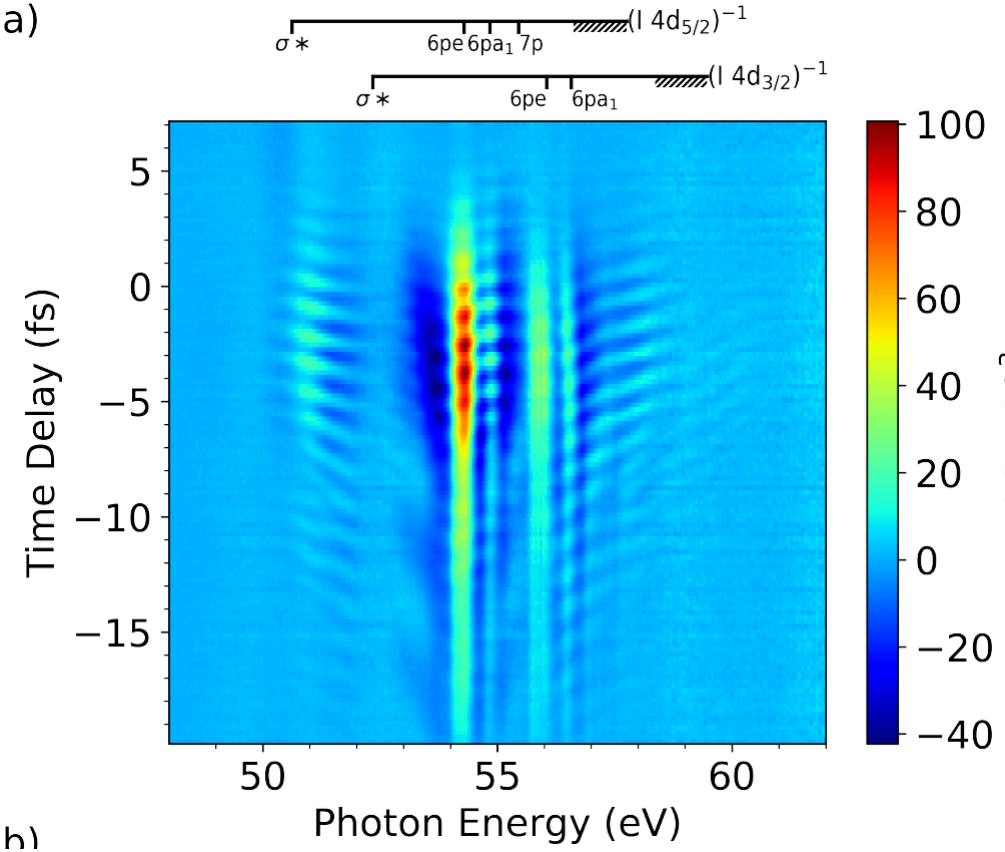
Pump probe scan around delay zero

→ Influence of the laser field on the attosecond XUV absorption



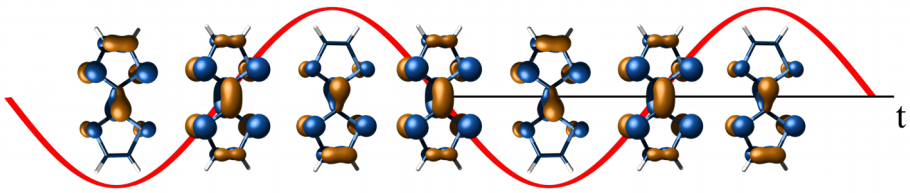
Experimental results :

(a)



(b)

Oscillation of the absorption signal at twice the laser frequency

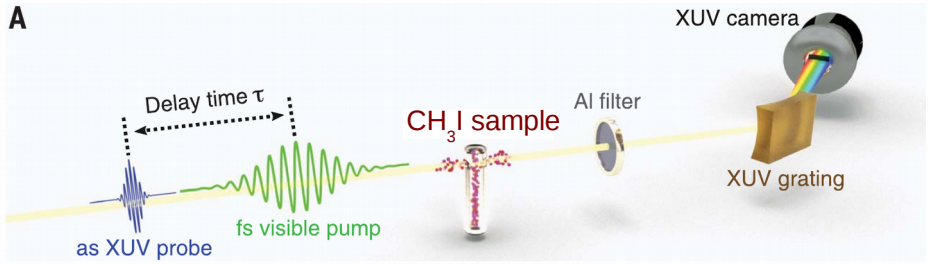


Measurements in CH3I - attosecond

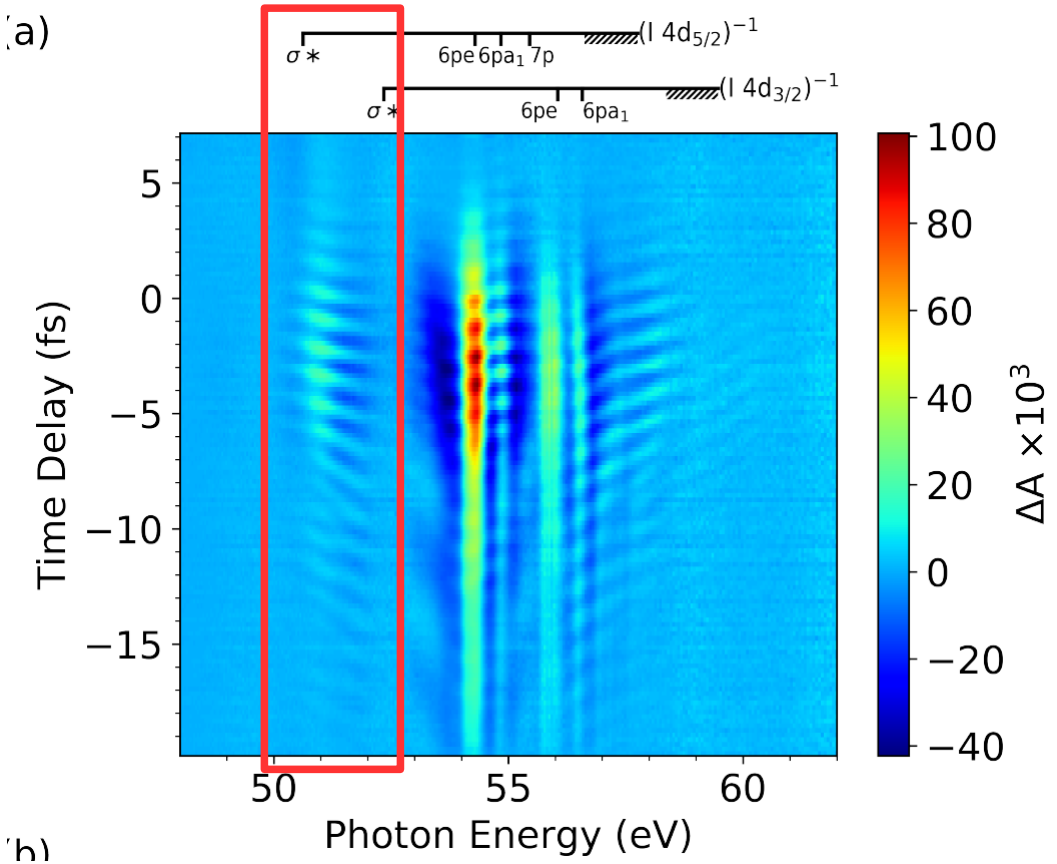
J. Phys. Chem. Lett. 2019, 10, 265−269

Pump probe scan around delay zero

→ Influence of the laser field on the attosecond XUV absorption



Experimental results :



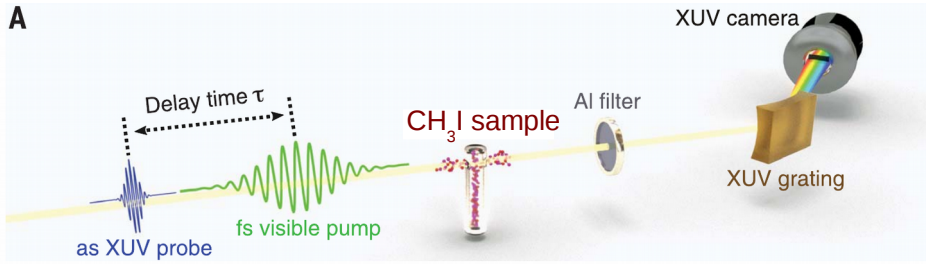
Valence excitation :
Weak influence of the IR field

Measurements in CH3I - attosecond

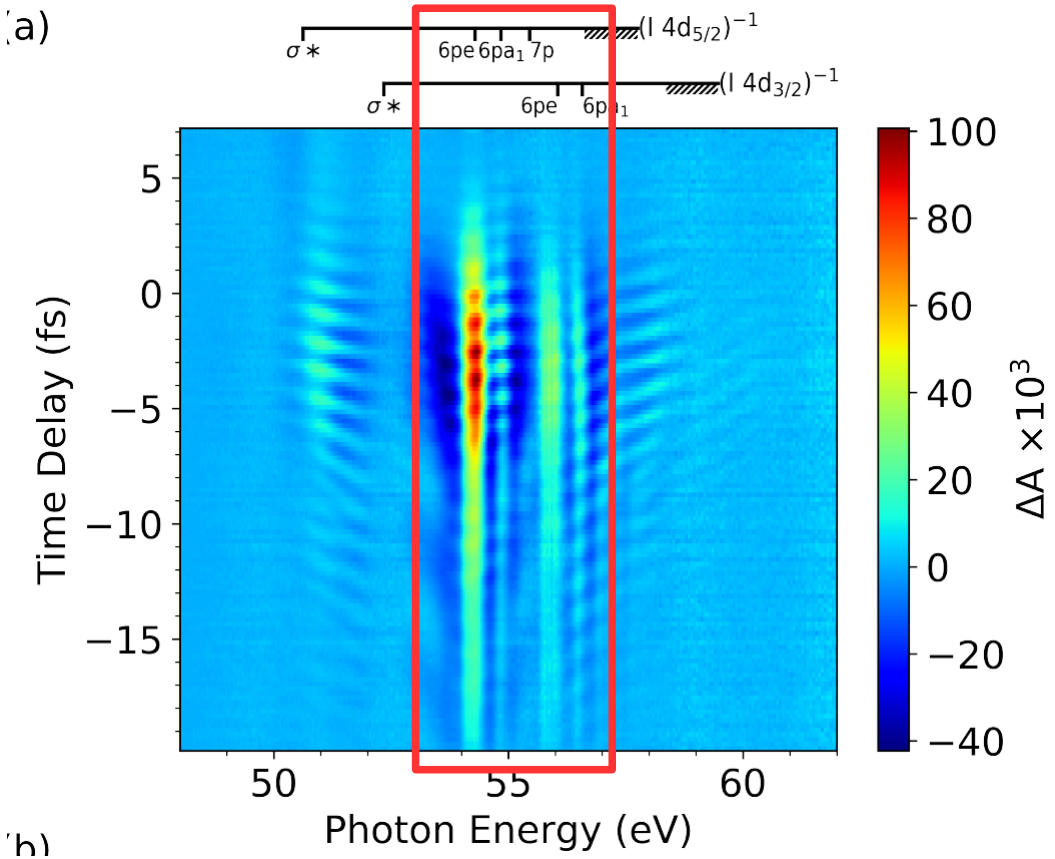
J. Phys. Chem. Lett. 2019, 10, 265−269

Pump probe scan around delay zero

→ Influence of the laser field on the attosecond XUV absorption



Experimental results :



Valence excitation :
Weak influence of the IR field

Rydberg excitation :
Strong influence of the IR field

Interpretation :
Higher polarizability of Rydberg states

Conclusions on ATAS

Attosecond pulses are broadband → can reach several absorption edges simultaneously

- Useful even for femtosecond dynamics
- Challenge : increase the photon energy to reach other edges
- Recently : several experiments in the water window (300-500 eV)

ATAS enables high spectral resolution with attosecond resolution

First attosecond ATAS experiments in molecule confirm the potential of the technique to track electronic dynamics.

Generation of attosecond pulses

An XUV pump-XUV probe measurement :
Nonlinear XUV Fourier transform spectroscopy in N2

Photoionization by an attosecond pulse

Charge migration

Electron escape dynamics

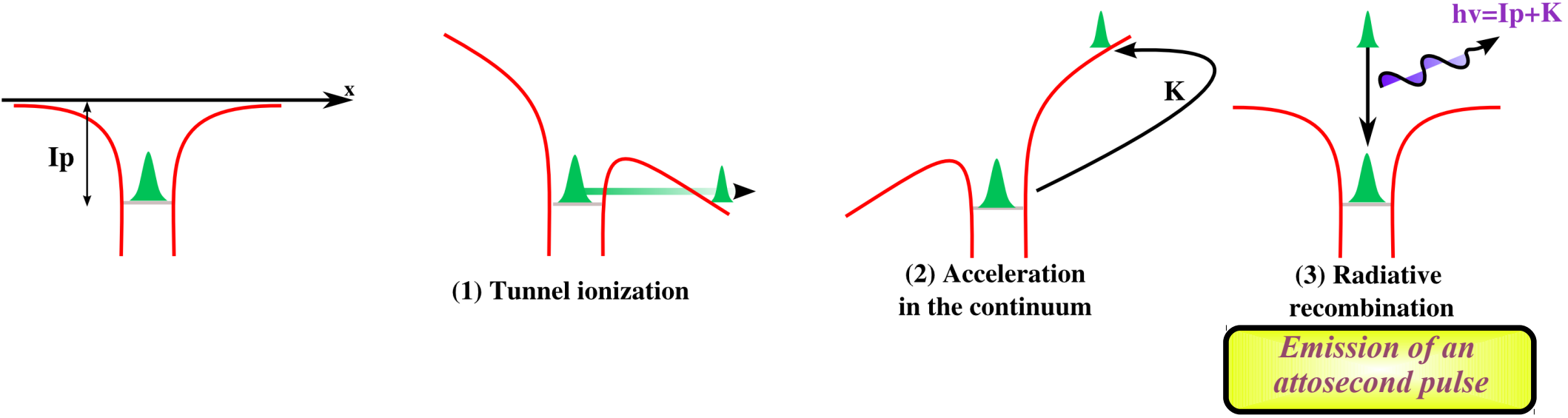
Autoionization dynamics

Attosecond transient absorption spectroscopy

High-harmonic spectroscopy

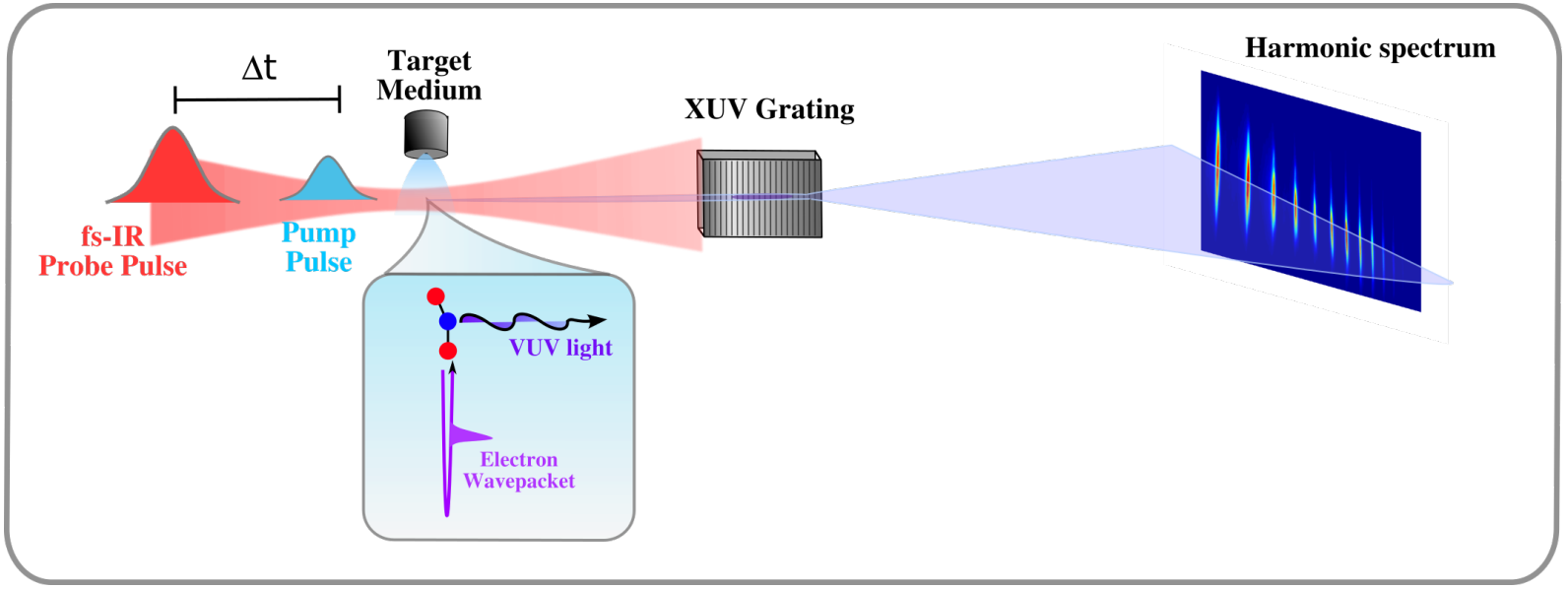
Laser-induced electron diffraction

High order harmonic generation mechanism

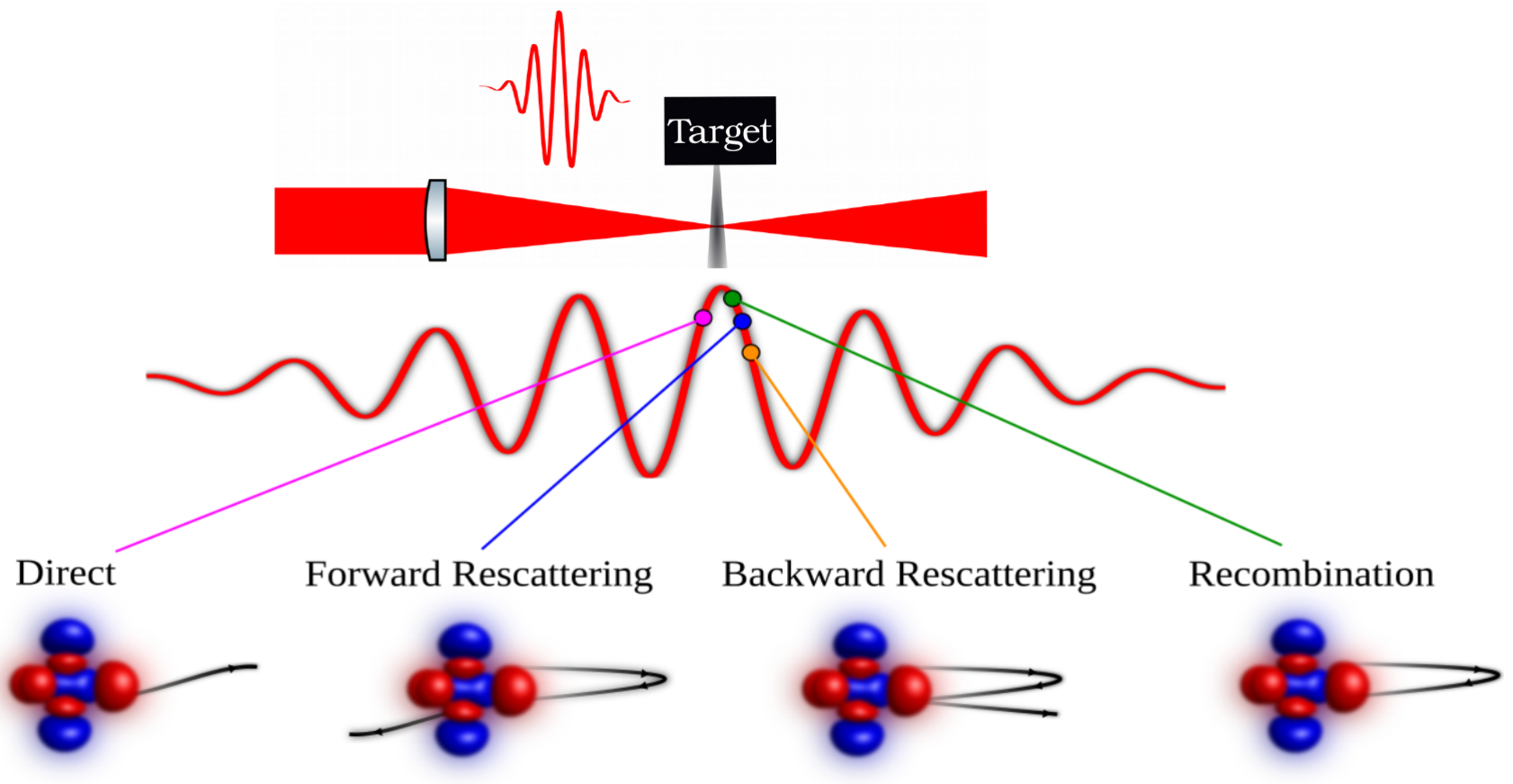


The XUV emission is caused by radiative recombination of an attosecond electron wavepacket

→ **The XUV radiation can directly be used as a probe of molecular structure and dynamics**



Strong fields to probe attosecond molecular dynamics



Above Threshold Ionization

P. Agostini et al., Phys. Rev. Lett. 42, 1127 (1979)

Laser-induced electron diffraction
Photoelectron holography

M. Meckel et al., Science 320, 1478 (2008)
C.I. Blaga et al., Nature 483, 194 (2011)
Y. Huismans et al., Science 331, 61 (2011)

High-order harmonic generation

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

Further readings

REVIEWS OF MODERN PHYSICS, VOLUME 81, JANUARY–MARCH 2009

Attosecond physics

Ferenc Krausz

Department für Physik, Ludwig-Maximilians-Universitat, Am Coulombwall 1, D-85748 Garching, Germany and Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Strasse 1, D-85748 Garching, Germany

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REVIEW OF SCIENTIFIC INSTRUMENTS **83**, 071101 (2012)

Invited Review Article: Technology for Attosecond Science

F. Frank,[1,a)] C. Arrell,[1,b)] T. Witting,[1] W. A. Okell,[1] J. McKenna,[1] J. S. Robinson,[1,c)] C. A. Haworth,[1] D. Austin,[2,d)] H. Teng,[1,e)] I. A. Walmsley,[2] J. P. Marangos,[1] and J. W. G. Tisch[1]

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Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **49** (2016) 142001 (25pp)
doi:10.1088/0953-4075/49/14/142001

Topical Review

Charge migration induced by attosecond pulses in bio-relevant molecules

Francesca Calegari[1], Andrea Trabattoni[2], Alicia Palacios[3], David Ayuso[3], Mattea C Castrovilli[1], Jason B Greenwood[4], Piero Decleva[5], Fernando Martín[3,6,7] and Mauro Nisoli[1,2]

nature photonics
FOCUS | REVIEW ARTICLES
PUBLISHED ONLINE: 28 FEBRUARY 2014 | DOI: 10.1038/NPHOTON.2014.25

Attosecond molecular dynamics: fact or fiction?

Franck Lépine[1], Misha Y. Ivanov[2] and Marc J.J. Vrakking[2]*

IOP Publishing
Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **45** (2012) 183001 (32pp)
doi:10.1088/0953-4075/45/18/183001

TUTORIAL

Introduction to attosecond delays in photoionization

J M Dahlström[1], A L'Huillier[2] and A Maquet[3,4]

OPEN ACCESS
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Journal of Physics B: Atomic, Molecular and Optical Physics
J. Phys. B: At. Mol. Opt. Phys. **49** (2016) 132001 (22pp)
doi:10.1088/0953-4075/49/13/132001

Topical Review

Development of high harmonic generation spectroscopy of organic molecules and biomolecules

J P Marangos

NATURE REVIEWS | PHYSICS

Attosecond imaging of molecules using high harmonic spectroscopy

*Peng Peng, Claude Marceau and David M. Villeneuve **