Attosecond science of complex molecules: perspectives at FELs

Session VI: attosecond experiments

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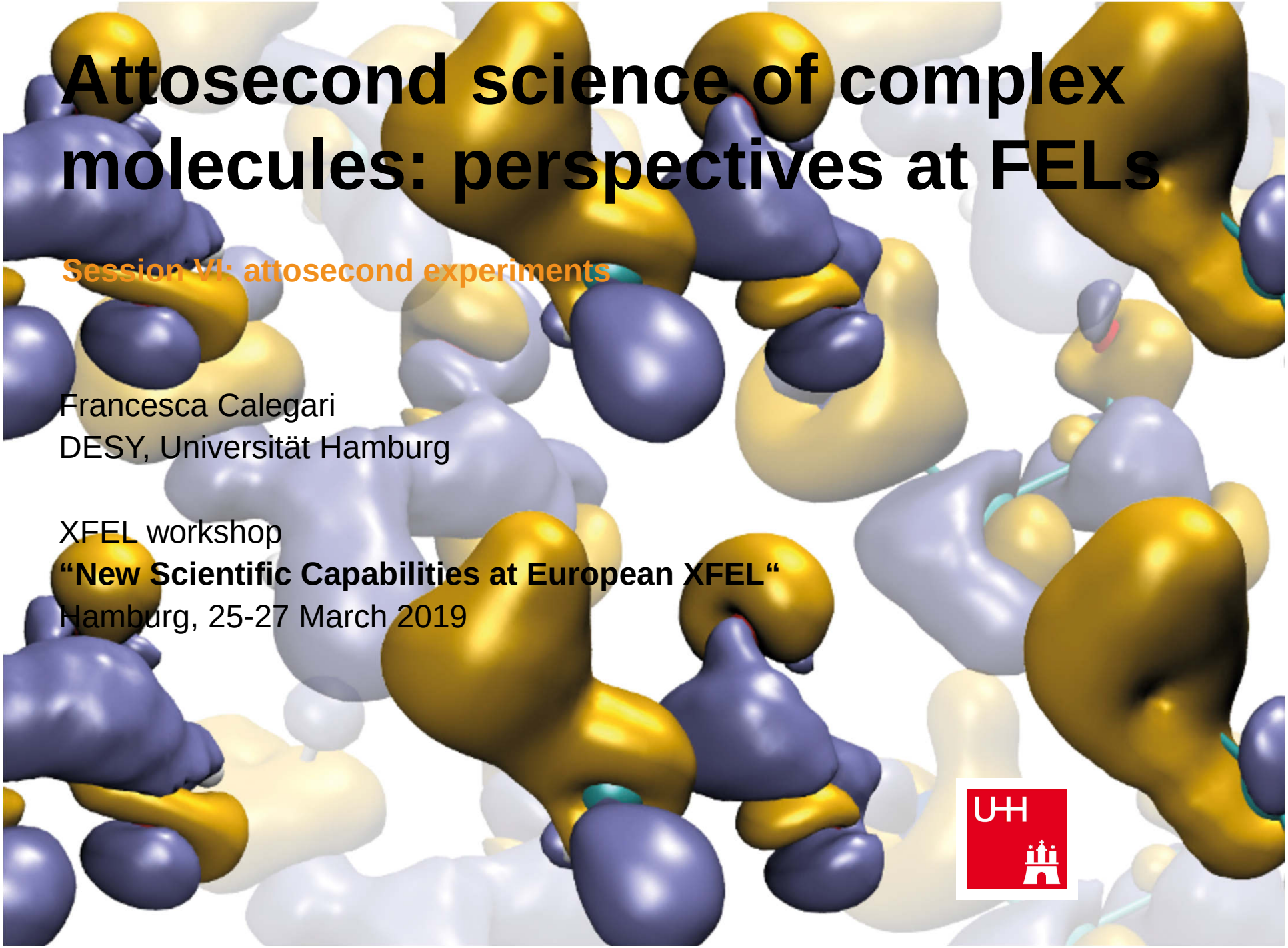
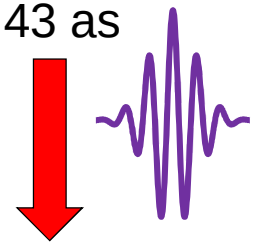
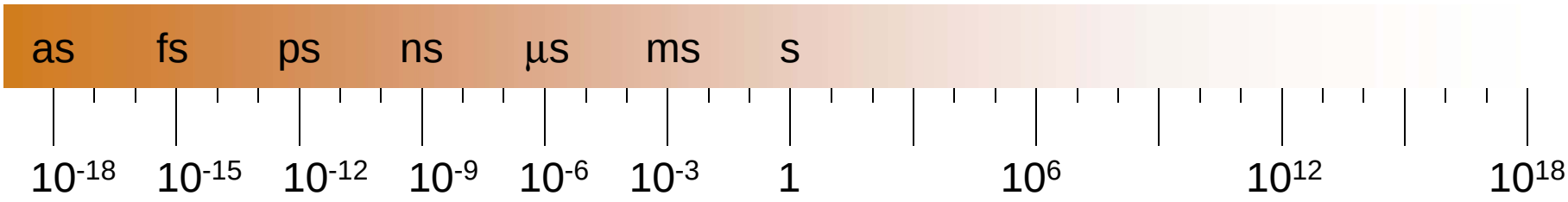
XFEL workshop
“New Scientific Capabilities at European XFEL“
Hamburg, 25-27 March 2019

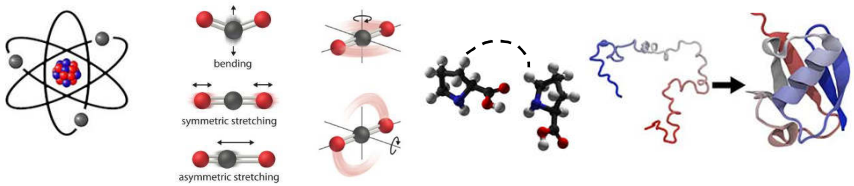


Time scales & molecular dynamics

Shortest
light pulse
43 as







Electron
time scale

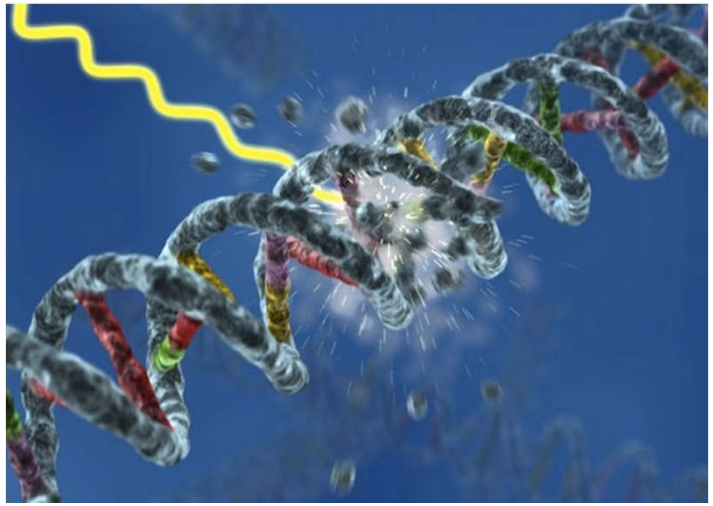
Atomic unit of time:
24 attoseconds

Electron orbit time
around the nucleus:
150 attoseconds

Ultrafast molecular dynamics

Ultrafast dynamics proven to be at the core of many photo-chemical and photo-biological processes

- Vision (isomerization of the retinal <100 fs)
- Photosyntesis (energy transfer <200 fs)
- DNA damage/photo-protection (ultrafast relaxation through conical intersections <100 fs)



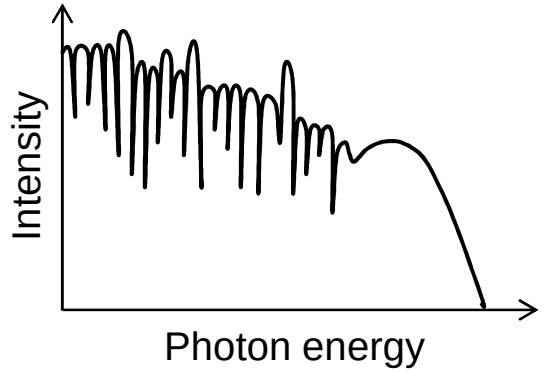
Role of electron dynamics in the photochemistry of complex molecules

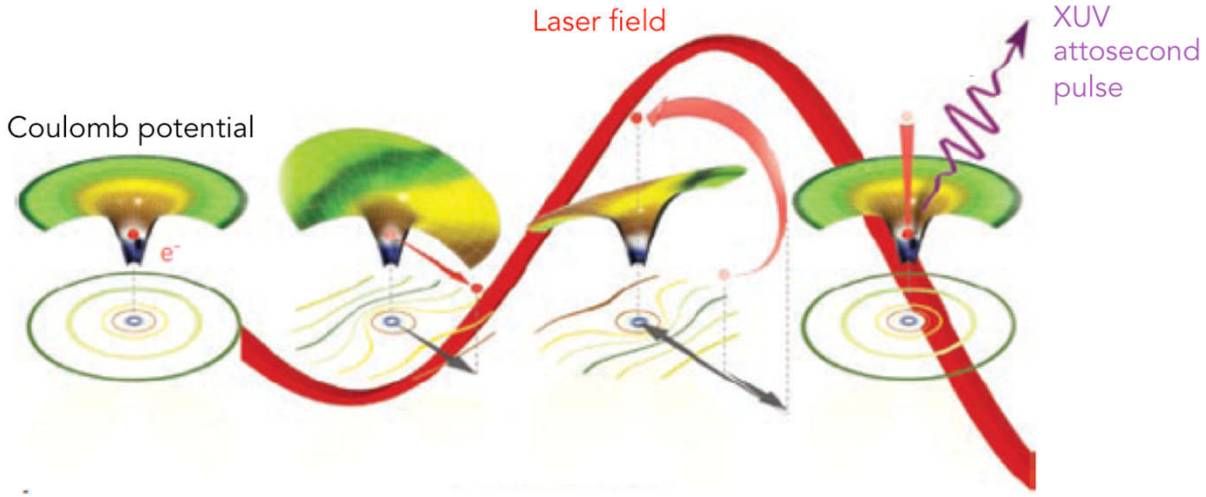
Watch and control new properties emerging at the level of electrons

HHG and attosecond pulse generation

Three-step model

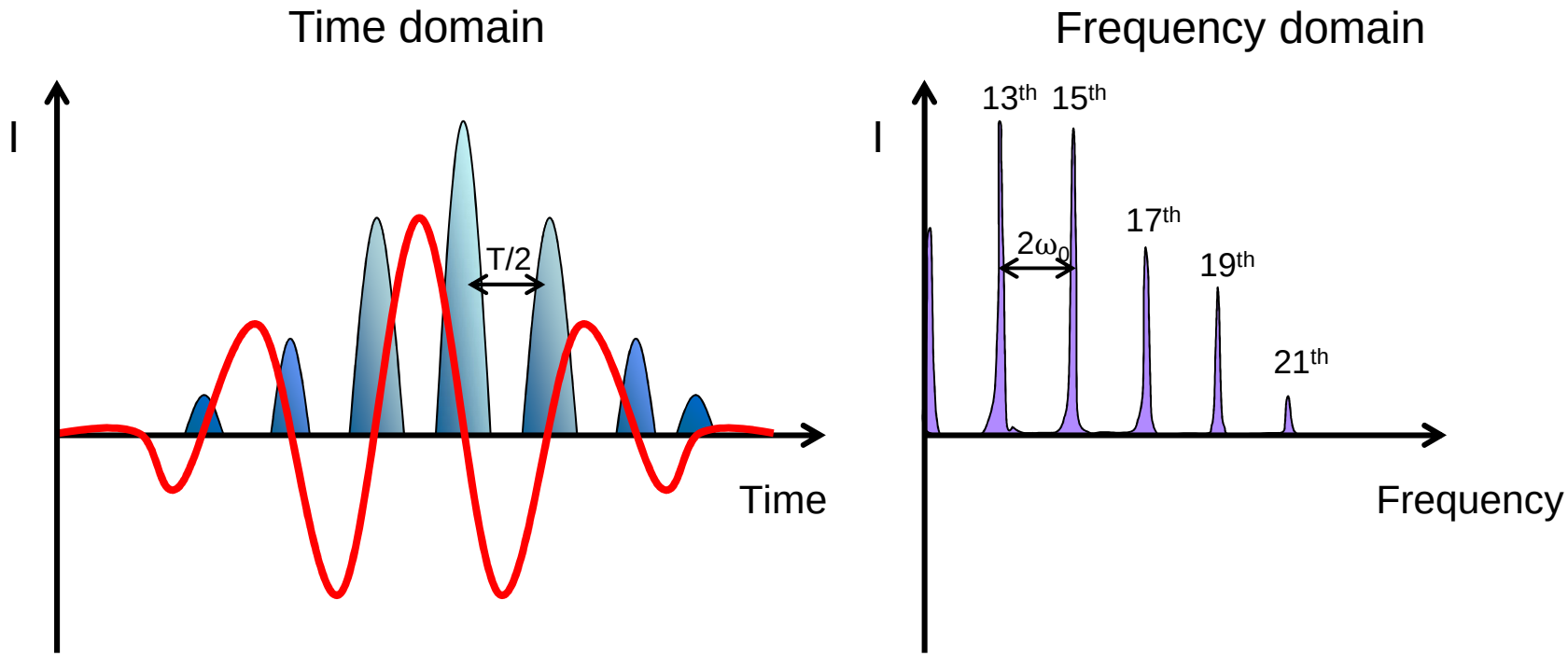
1. Tunnel ionization
2. Acceleration
3. Recollision





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

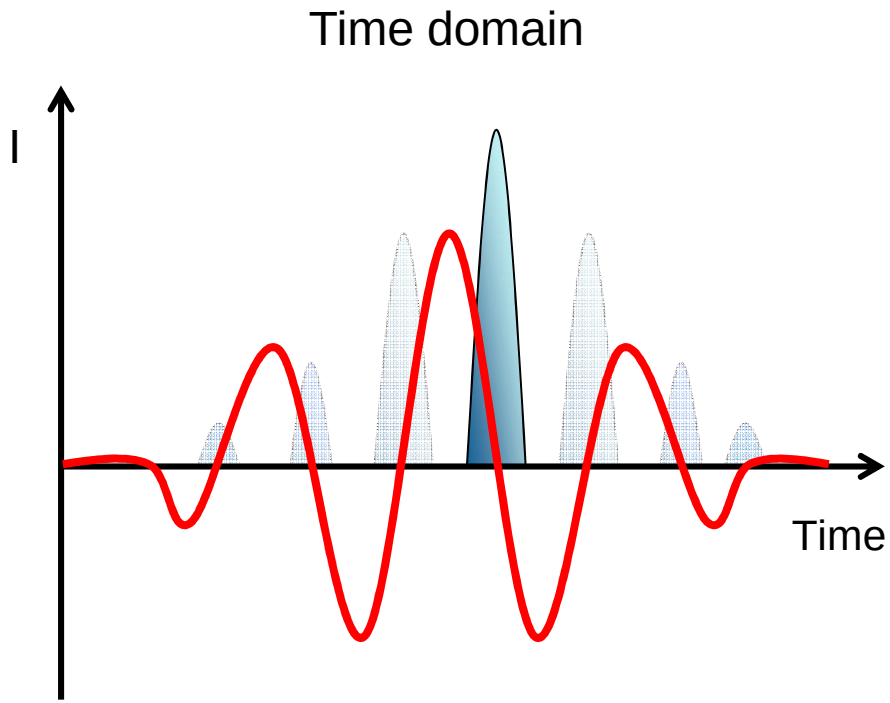
The attosecond pulse train

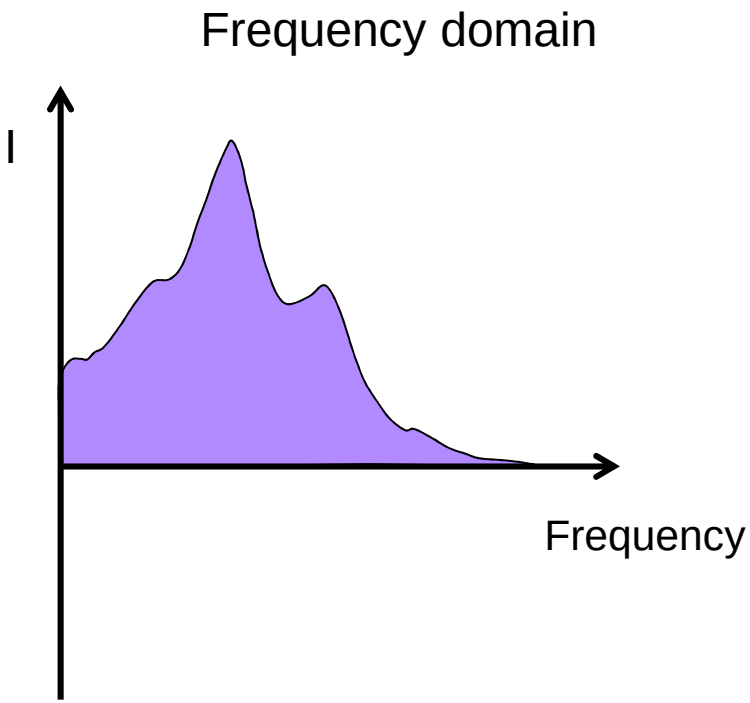


HHG every half cycle of the driving laser: attosecond pulse train

The interference between attosecond pulses separated T/2 gives rise to odd order harmonics of the fundamental frequency (spaced 2ω)

Isolated attosecond pulse





Gating methods on HHG
allow the generation of an isolated attosecond pulse

Shortest attosecond pulse 43 as!

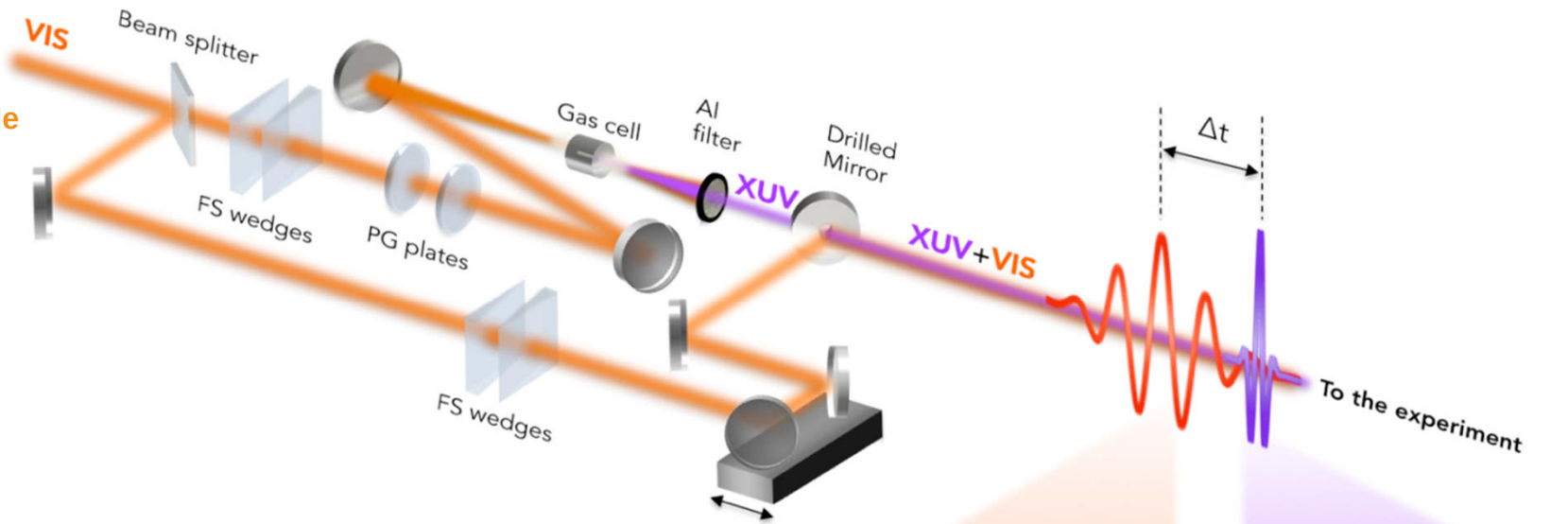
T Gaumnitz et al, Optics Express 25 (2017)

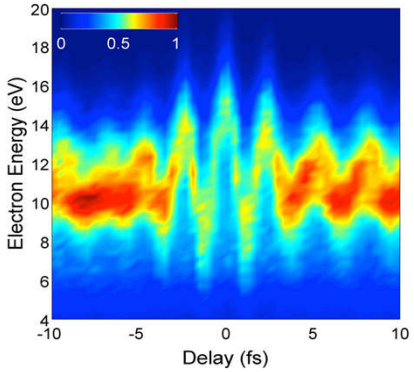
A single attosecond pulse corresponds to a broad continuous emission in the frequency domain

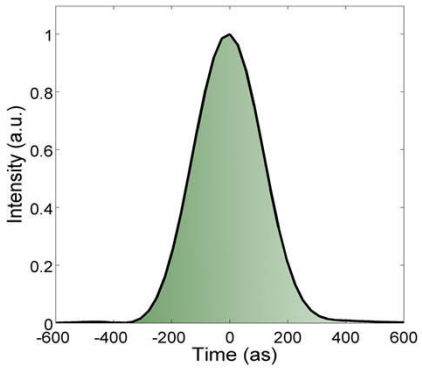
G. Sansone et al., Science 314, 443 (2006)
F. Calegari et al., J. Phys. B 45, 074002 (2012)
S. Gilbertson et al., Phys. Rev. A 81, 043810 (2010)
F. Ferrari et al., Nat. Photonics 4, 875 (2010)

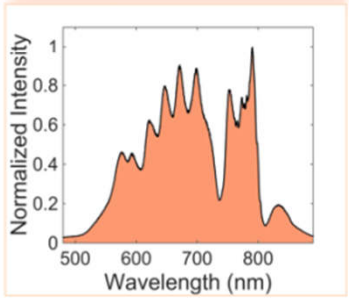
Attosecond pump probe setup

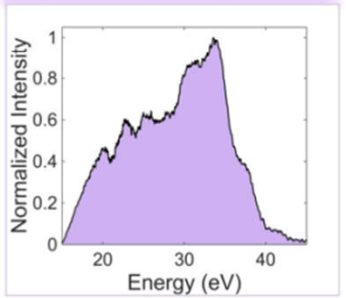
Few-fs
multi mJ
1 kHz
CEP-stable











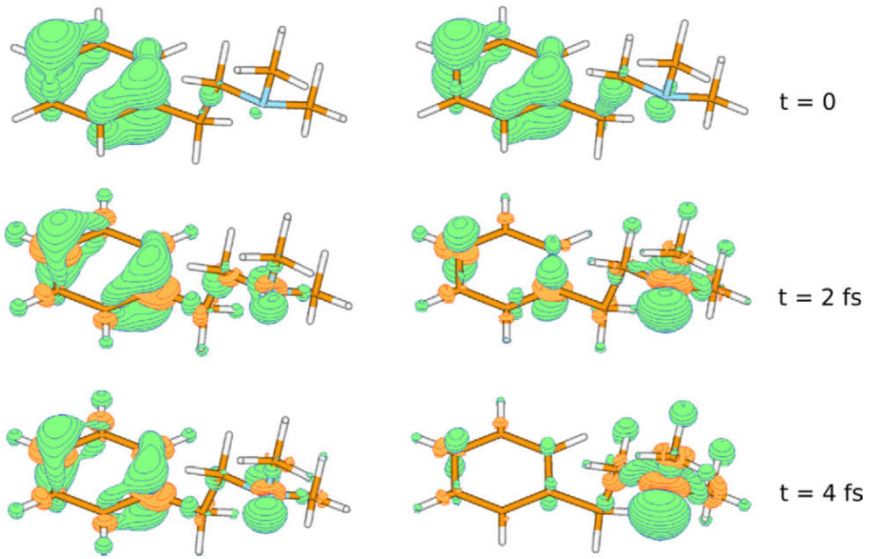
F. Calegari et al., *J. Phys. B: Atom. Mol. Opt. Phys.* ***49*** , 062001 (2016)

Advantages and disadvantages of table top sources

- Attosecond pulses generated in a broad spectral range (from VUV to soft-x)
- Very good pulse to pulse stability
- Attosecond synchronization with a second laser pulse
- Reproducibility of the experiment
- CEP stability and reproducible electric field

- Low conversion efficiency of the process → limited pulse energy (pJ-nJ)
- With current pulse energies in the soft-x no possibility for two color experiments (soft-x pump soft-x probe)
- Limited photon energy
- Not enough photon flux for imaging at high photon energies

Scientific case: charge migration



After ionization a hole is created

The hole can migrate from one end to the other of the molecule in attoseconds / few-femtoseconds

Process driven by electronic correlations

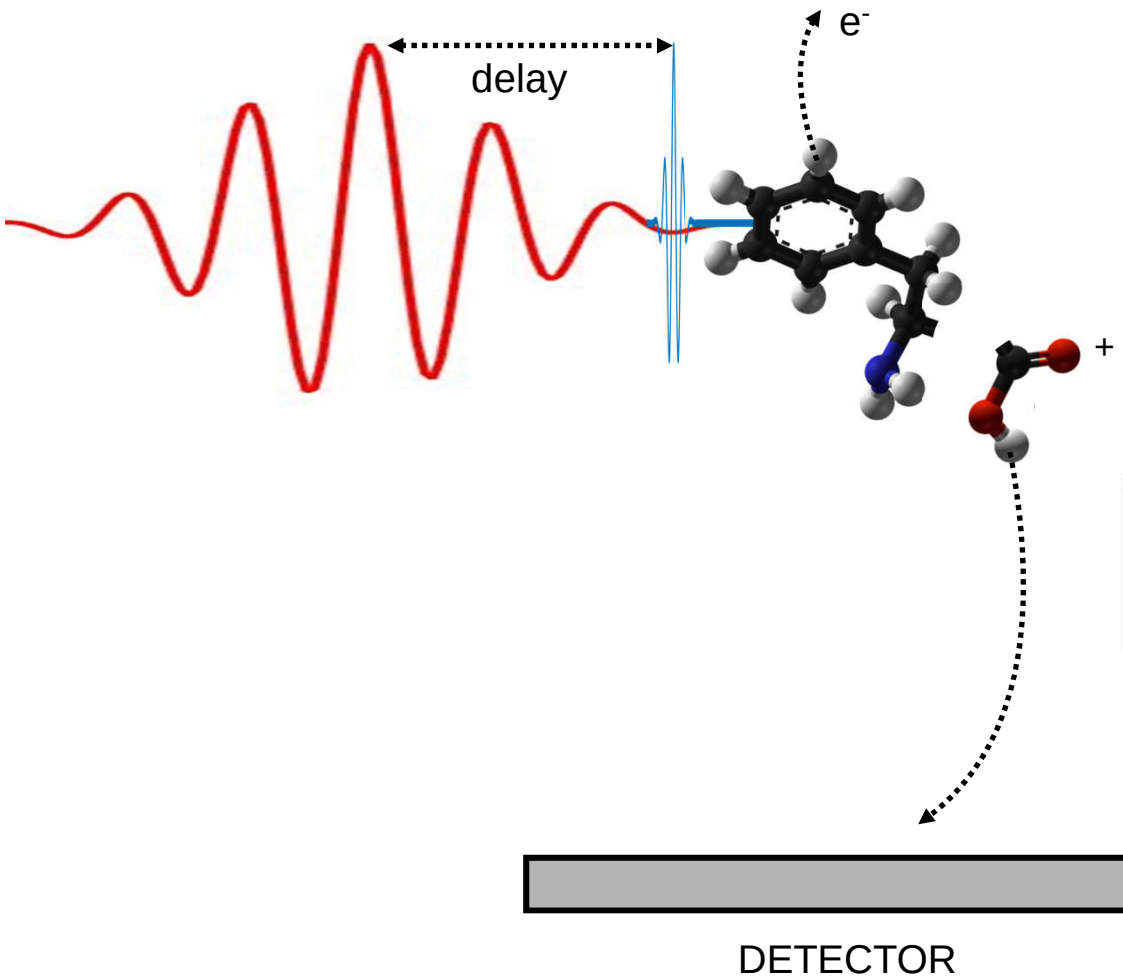
S. Lünnemann et al., Chemical Physics Letters 450, 232 (2008)
L. Cederbaum, J. Zobeley, Chem. Phys. Lett. 307, 205 (1999)
F. Remacle, R. Levine, PNAS 103, 6793 (2006)
A. Kuleff, L. Cederbaum, Chem. Phys. 338, 320 (2007)

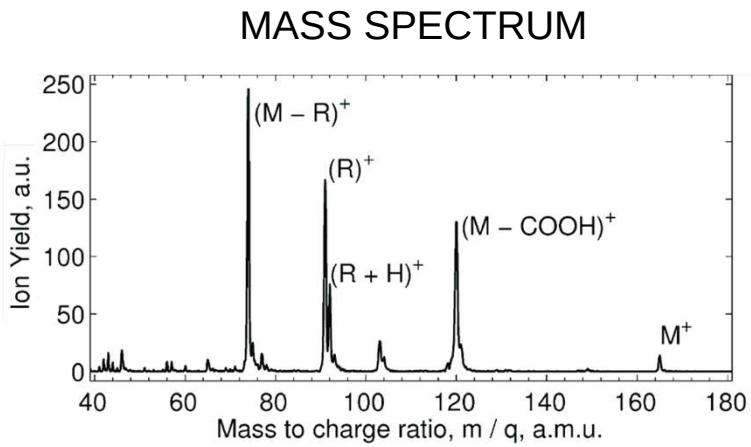
Is it possible to drive the charge on the attosecond/few-femtosecond time scale?

Can we control the fate of the molecule by acting on this extreme time scale?

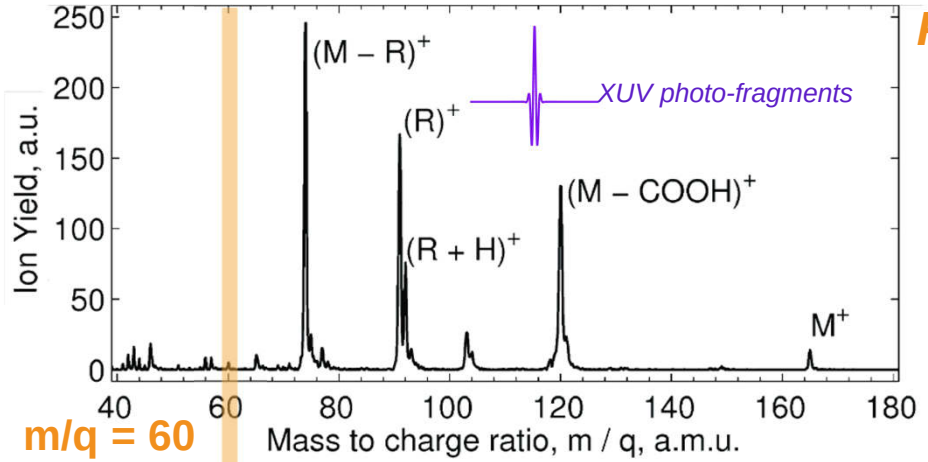
Experimental approach

Time resolved photofragmentation



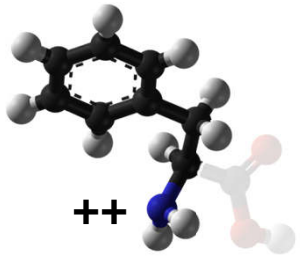


Mass spectra for aromatic amino acids



m/q = 60

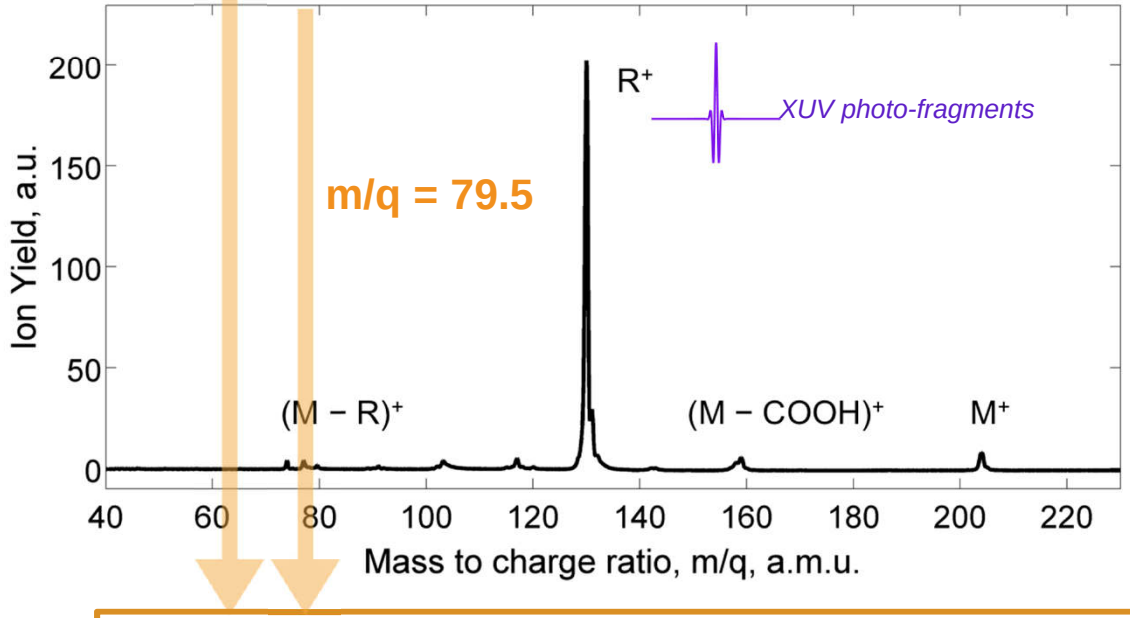
PHENYLALANINE



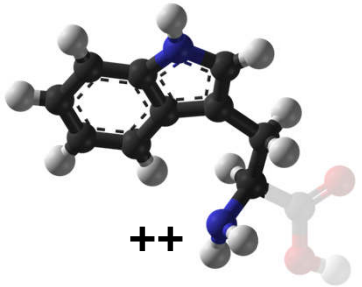
M⁺
Parent ion

(M – COOH)⁺
Immonium ion

R⁺
Side chain



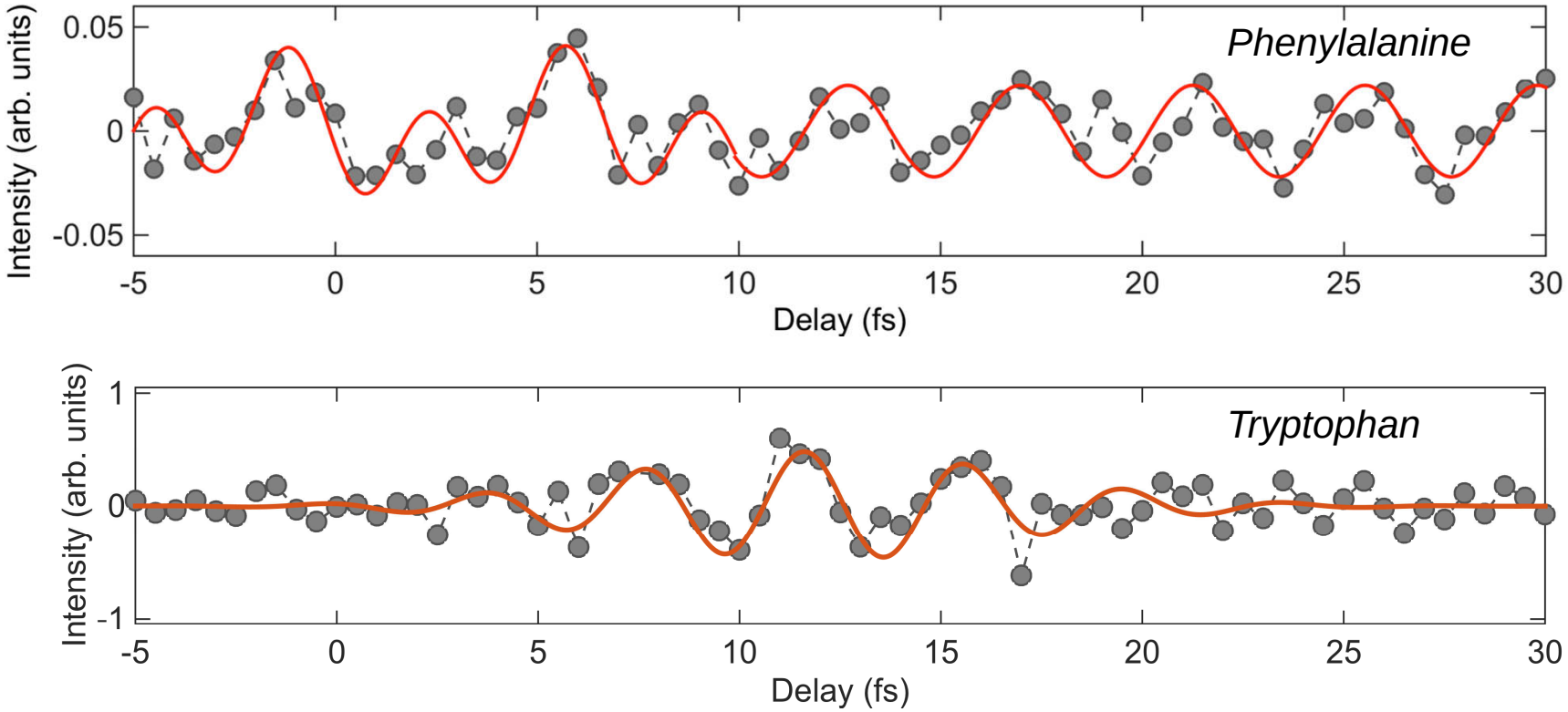
TRYPTOPHAN



(M-COOH)$^{++}$ = Doubly charged immonium ion

Time dependent dication yield

Dication yield after subtraction of the 25-fs decay



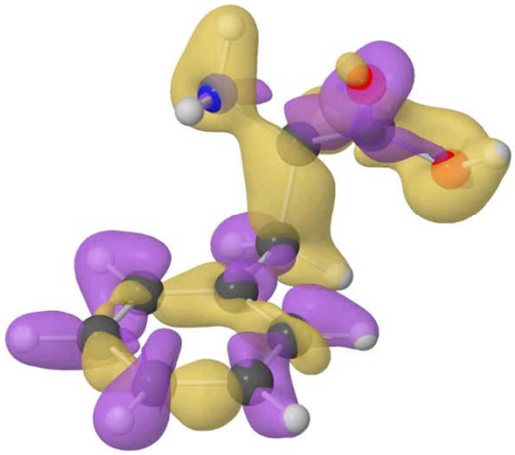
F. Calegari et al., Science 346, 336 (2014)
F. Calegari et al., IEEE JSTQE 21, 2419218 (2015)
M. Nisoli et al., Chem Rev 117 10760 (2017)

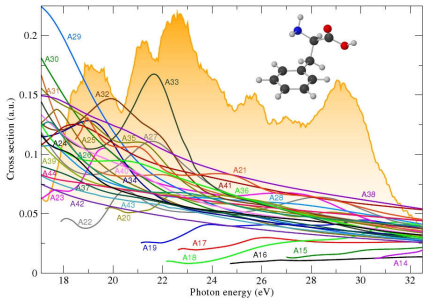
Sub 4.5 fs oscillations:
Electron dynamics?

Theoretical model

Evolution of electronic wave packet evaluated by standard time-dependent density matrix formalism

PHENYLALANINE

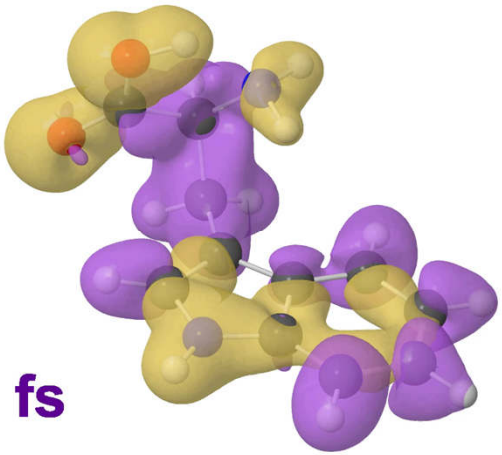




0.00 fs

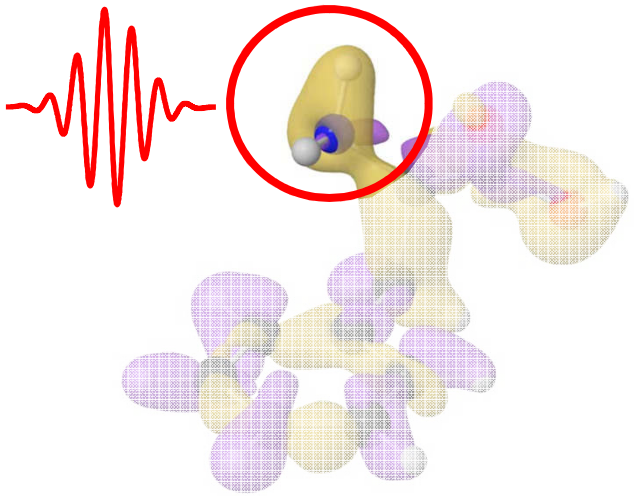
Complex hole dynamics for both Phenylalanine and Tryptophan

TRYPTOPHAN



0.00 fs

Probing charge density variations



0.00 fs

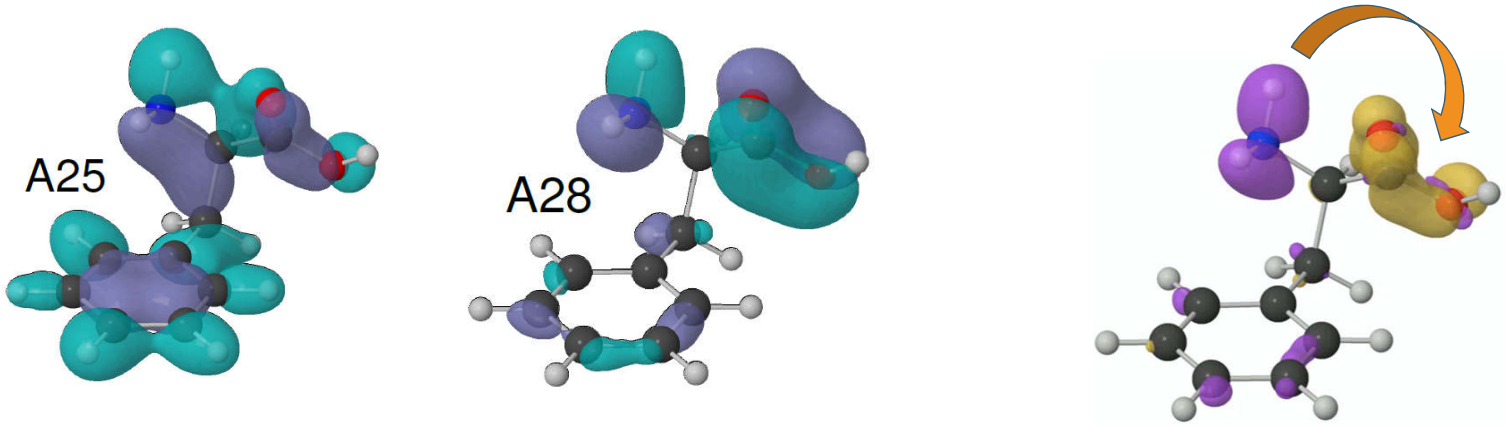
The IR probe pulse is more likely to be absorbed on the amino site of the molecule and it creates the doubly charged ion

Fast charge density variations on the amino site produce fast yield variations in the doubly charged ion

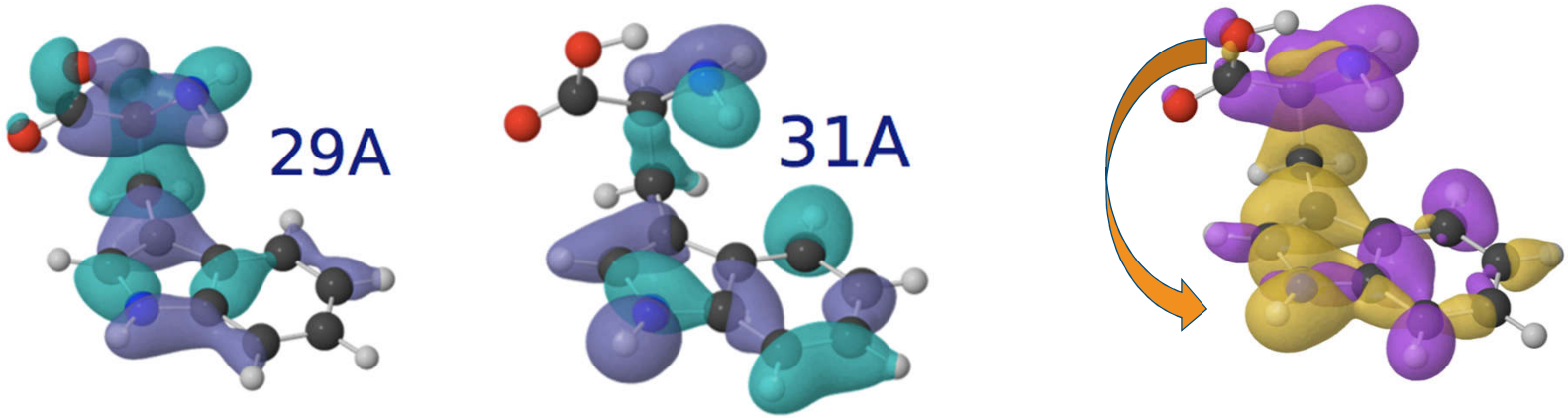
Visualization of the electron density variations around a functional group in real-time

Charge migration between two functional groups

Phenylalanine: superposition of A25 and A28: migration from amine to carboxyl



Tryptophan: superposition of A29 and A31: migration from amine to indole



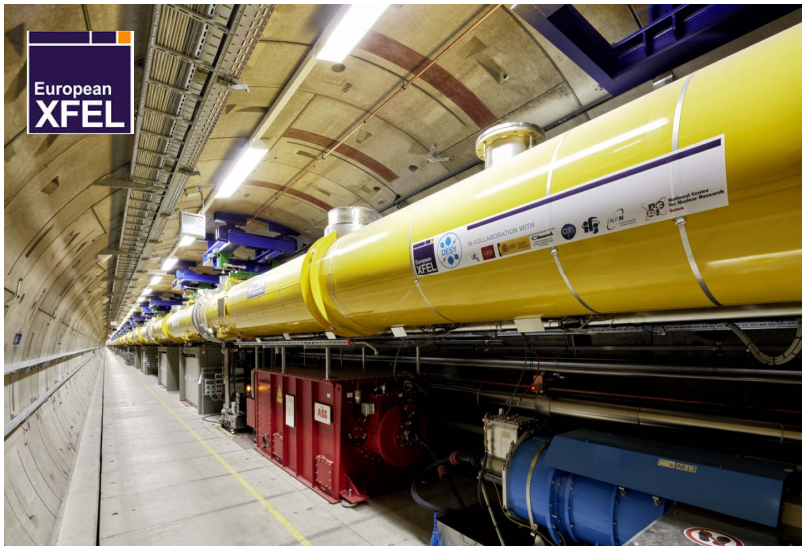
New perspectives at FELs

Attosecond science at
Free Electron Lasers (FELs)

S Serkez et al, *J. Opt.* 024005, 20 (2018), review article

New perspectives for short pulse durations @ European XFEL

At present attosecond pulses are generated at LCLS



LCLS II – charge migration

Charge migration as one of the science drivers for LCLS II (see next talk)

Fundamental Dynamics of Energy and Charge

Charge migration, redistribution and localization even in simple molecules are not well understood at the quantum level, and these processes are central to complex processes like photosynthesis, catalysis and bond formation/dissolution that govern all chemical reactions. Indirect evidence points to the importance of quantum coherences and coupled evolution of electronic and nuclear wave functions in many molecular systems.

However, it hasn't been possible to directly observe these processes to date, and they are beyond the description of conventional chemistry models. High-repetition-rate soft X-rays from LCLS-II will enable new techniques that will directly map charge distributions and reaction dynamics at the scale of molecules. New nonlinear X-ray spectroscopies offer the potential to map quantum coherences in an element-specific way for the first time.

New perspectives at FELs

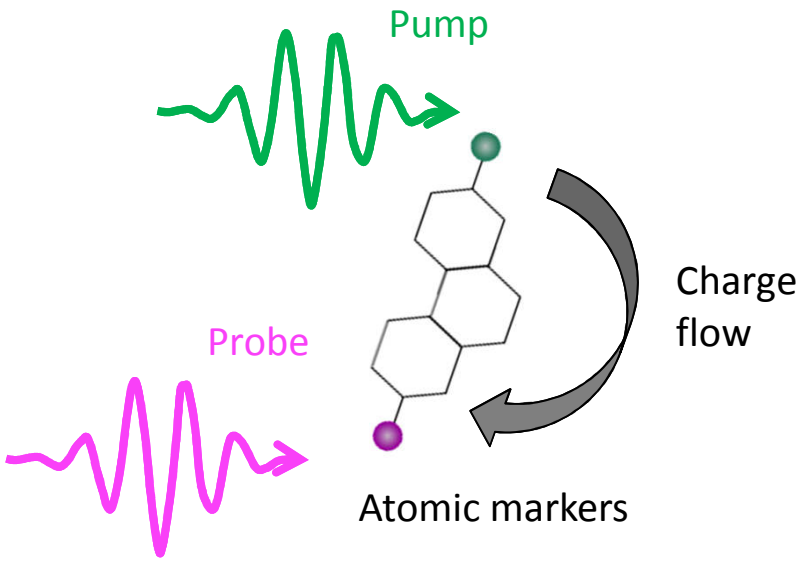
What are the advantages and disadvantages of attosecond FEL?

- Bright emission
- High photon energy
- Two-color experiments in the soft-x/x-ray
- Synchronization with a second laser pulse
- Possibility for diffractive imaging

- SASE does not allow for pulse reproducibility
- Need for single shot detection
- Attosecond synchronization with an external laser?

New perspectives at FELs

Initiate and track quantum coherences with site specificity



A two color experiment would allow for initiating the charge migration on a specific atomic site and track it on a different atomic site

K edges of C,N,O (soft-x)
K edges of metals (x ray)

Metallic markers can be used to track the charge

Charge migration in metallic complexes

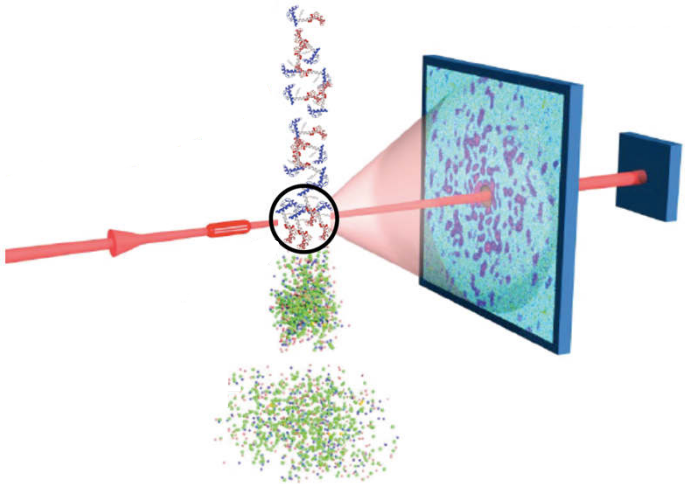
New perspectives at FELs

Initiate and track quantum coherences with site specificity

A FEL offers the possibility to use different spectroscopy techniques

- Time resolved photo-electron and photo-ion spectroscopy
- Time resolved absorption spectroscopy
- Time resolved imaging

Attosecond pulses @ FELs allows to act on the system on the same time scale (or even faster) then shake-up, shake-off and auger processes → a new level of control on the system



Few fs Pulses at FLASH – first Results

Single spike SASE

- Single mode: the minimum radiation pulse duration (SASE):

$$\tau\ (\text{FWHM}) = \frac{M\ \lambda_r\ L_{sat}(\lambda_r, \gamma)}{5\ c\ \lambda_u}$$

M number of modes

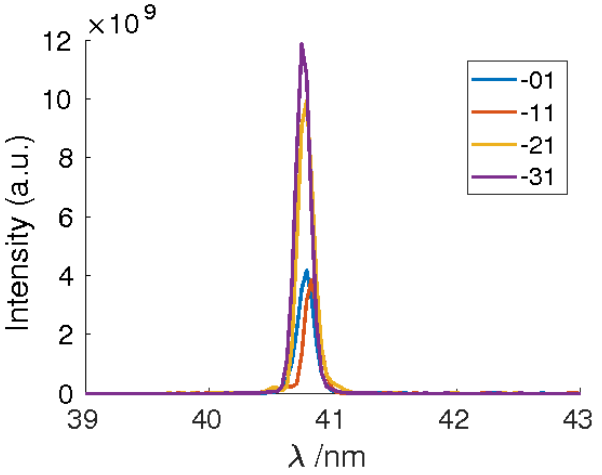
L_{sat} saturation length

λ_r radiation wavelength

λ_u undulator period

Juliane Rönsch-Schulenburg

Example: For 41 nm XUV radiation at FLASH2

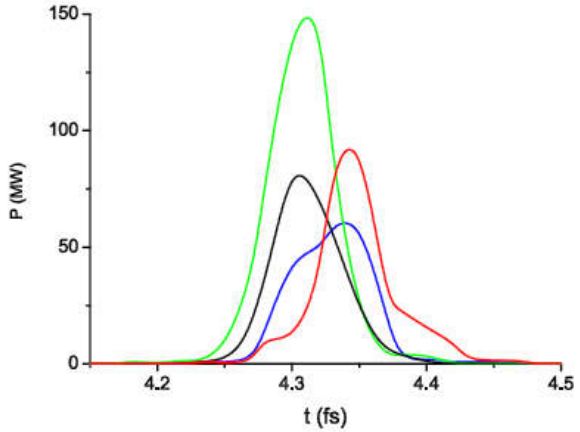


maximum fluctuation: 97%
→ number of modes: 1.05
FEL pulse duration: 14 fs (FWHM)

Attosecond Science with FLASH2020+

Novel lasing schemes

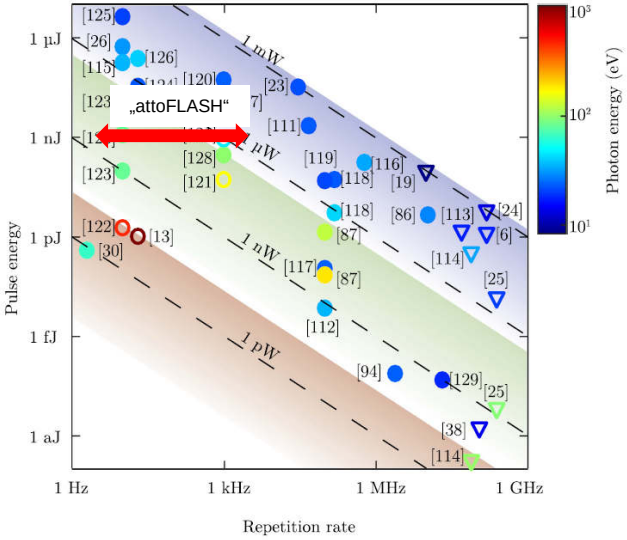
Wavelength 5 nm
pulse length 50-70 asec (FWHM)
pulse energy 5 nJ
contrast above 98%



E. Schneidmiller, M. Yurkov

With XFEL attosecond pulses @ higher photon energies?

Scaling of XUV HHG laser sources



C.M. Heyl et al., J. Phys. B: At. Mol. Opt. Phys. 50 (2017) 013001

The attosecond science group @ DESY









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