Isolated attosecond pulses for atomic and molecular physics

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Real-time observation and **direct control** of *electronic motion* in atoms, molecules, nanostructures and solids

**Prerequisite**
- Generation of attosecond pulses
- Attosecond metrology

**Applications of attosecond pulses**
- Status and prospects of attosecond spectroscopy and control
Tracing the motion of electrons in atoms

Bohr-model of hydrogen atom: electron in the ground state moves in a circular classical orbit around the nucleus in \( \sim 150 \) as.

Attosecond resolution is required
Tracing the motion of electrons in atoms

1s-2s coherent superposition in hydrogen

$T \approx 402 \text{ as}$

Attosecond resolution is required
Sub-femtosecond Pulses

T = 0.1 fs @ 30 nm
T = 2.5 fs @ 750 nm

Light pulses in the XUV are required for high-order harmonic generation.
An intense ultrashort light pulse is focused on a gas jet. Odd harmonics of the visible light are generated up to the soft-X-ray region. The intensity is described by the equation $E_{\text{max}} = I_p + 3.17 U_p$.
Attosecond Source: High-order Harmonic Generation

Step 1: Ionization
Step 2: Motion after ionization
Step 3: Recollision

maximum photon energy: $h \nu_{\text{max}} \propto I \lambda_L^{-2}$
“Intrinsic” tools in Attosecond Technology

- Attosecond optical pulses always associated to attosecond electron pulses
  - electrons give access to spatial resolution:
    - electron wavelength (~1Å)
  - optics gives electron collision physics a systematic method for measuring dynamics

- Attosecond photon or electron pulses always synchronized to a visible pulse with controlled waveform
  - extension of conventional ultrafast spectroscopy and strong field coherent control from the cycle-averaged into the sub-cycle domain of visible light
Basic “laser” tools for attosecond technology

**Chirped-Pulse Amplification**

**Hollow-fiber compression**
Sub-6-fs high-peak power light pulses

**Ultrabroadband dispersion control with chirped mirrors**

**Carrier-envelope phase stabilization**
T.W. Hansh et al., 1997,1999
Carrier-Envelope Phase (CEP)

\[ E(t) = A(t) \cos(\omega_0 t + \psi) \]

- \( A(t) \): envelope
- \( \omega_0 \): carrier frequency
- \( \psi \): CEP
Isolated attosecond pulses

- Spectral selection of cutoff photons leads to generation of isolated attosecond pulses
- Requirements: sub-5-fs driving pulses (linear polarization)
Isolated attosecond pulses

- Spectral selection of cutoff photons leads to generation of one or two attosecond pulses
- Requirements: sub-5-fs phase-stabilized driving pulses (linear polarization)
Few-cycle linearly polarized pulses

- HHG in Neon: < 5 fs; stabilized CEP

→ Broad continuum only in the cut-off
Few-cycle linearly polarized pulses

- HHG in Neon: ~ 4 fs; stabilized CEP

Broad continuum
Temporal gating

Requirements: phase-stabilized driving pulses
Temporal gating schemes

- **Polarization gating:**
  - One- and two-color

- **Two-color gating:**
  - Intense IR pulses + intense visible (VIS) few-cycle pulses
  - Two IR pulses

- **Ionization gating:**
  - High-energy isolated pulses on target
Polarization gating

- Time-dependent polarization

Experimental results: Argon

- Pulse duration $\tau = 5$ fs; delay $\delta = 6.2$ fs; $\psi_0 < \psi < \psi_0 + 3\pi$

- Periodic change of amplitude and shape for $\Delta\psi = \pi$
- Continuous spectra from 30 eV to 55 eV for particular $\psi$
- CEP drives transition from double to single emission

Experimental results: Neon

- Pulse duration $\tau = 5$ fs; delay $\delta = 6.2$ fs; $\psi_0 < \psi < \psi_0 + 3\pi$

Strong periodic modulation of emission efficiency for $\Delta \psi = \pi$

Continuous spectra from 30 eV to 75 eV for all CEPs

Driving field: $\omega_1 + \omega_2$

$\omega_2 = 2 \omega_1 + \delta\omega$: spectrally detuned second harmonic

New periodicity of the electric field can lead to isolation of single attosecond pulses


Key parameters:
1. Central wavelength of the two components
2. Intensity of the pulses
3. Temporal overlap
4. Gas target position
Intense ultrashort two-color driver

**Intense IR pulses:** 1.45 μm, 20 fs, $I_{IR} = 2 \times 10^{14}$ W/cm$^2$

**Intense VIS pulses:** 0.8 μm, 13 fs, $I_{VIS} = 8.5 \times 10^{14}$ W/cm$^2$

$\tau = 0$: dramatic cutoff extension and continuum generation

outside overlapping region harmonic spectrum is dominated by VIS pulse

IR component: responsible for cutoff extension

VIS component: increase of conversion efficiency

Two-color vs one-color

Maximum photon energy with VIS: 100 eV
(high-conversion efficiency)

Maximum photon energy with IR: 140 eV
(low-conversion efficiency)

Maximum photon energy with VIS+IR: 160 eV
Ionization gating

\[ \psi = 0 \]

High-energy few-cycle pulses:

- complete depletion of neutral atom population on the pulse leading edge
- confinement of the XUV emission within a single event

Requirements:

- few cycle pulses
- peak intensity > saturation intensity
- CEP control
- low gas pressure
- spatial filtering after the gas cell
XUV spectra vs CEP

- Pulse duration $\tau = 5$ fs; peak intensity $2.3 \times 10^{15}$ W/cm$^2$; 2.5-mm xenon cell

- Periodic change of amplitude and shape for $\Delta \psi = \pi$

- CEP drives transition from double to single emission

- Measured pulse energy on target 2.1 nJ

Attosecond Metrology
Far from any resonance, attosecond electron wavepacket is a replica of the attosecond field
Characterization of the electron wavepacket
1) Initial electron momentum

\[ p_i = \sqrt{2mW_o} \quad W_o = \hbar \omega_{XUV} - I_p \]

2) Effect of streaking pulse

\[ \Delta p(t) = e \int_{t}^{+\infty} E_{IR}(t') dt' = eA(t) \]

3) Final electron momentum

\[ p_f(t) = p_i + \Delta p(t) \]

Electron energy:

\[ W(t) \approx W_o + \sqrt{8mW_o} eA(t) \]

Kitzler et al. PRL 88,173903 (2002)
Itatani et al. PRL 88,173904 (2002)
Attosecond streak camera

We \( A(t) \)

e \( A(t) \)

time

Kitzler et al. PRL 88,173903 (2002)
Itatani et al. PRL 88,173904 (2002)
Attosecond streak camera

eA(t)

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eA(t)

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Attosecond streak camera

eA(t)
Attosecond Metrology

- Cross-correlation with driving light pulse

→ Photoelectron spectra vs delay
Temporal characterization

- 100-nm Aluminum filter

Positive chirp

Retrieved Intensity profile and phase

$\tau = 280$ as
Temporal characterization

- Dispersion compensation by Aluminum foils
  - 300-nm Aluminum filter

  ➜ Good dispersion compensation
  ➜ Near-single cycle pulse

Retrieved Intensity profile and phase

Applications of Attosecond Pulses
Applications of Attosecond Pulses

- Status and prospects of attosecond spectroscopy and control
  - isolated atoms: a few examples (Kr, Ne, Xe, He)
  - simple diatomic molecules: 1 example (H₂/ D₂)
  - condensed matter: 1 example (tungsten crystal)
  - complex (bio)molecules and supramolecular assemblies
  - nanostructures

- Use of synthesized (waveform-controlled) pulses to steer electrons in molecules on the electronic time scale
**Charge migration in H$_2$/D$_2$**

- **Method**: measurement of angular asymmetries in momentum distributions of fragments resulting from dissociative ionization

- Excitation of D$_2$ with isolated attosecond pulses in the presence of few-cycle IR laser field
  - observation of electron localization following attosecond molecular photoionization

![Diagram showing charge migration](image-url)
Velocity Map Imaging

- dual microchannel plate
- extractor
- repeller, gas injection

- very high collection efficiency (up to 100%)
- energy & angular information
Excitation by isolated attosecond pulses

Several pathways lead to dissociative ionization (XUV spectrum between 20 and 40 eV)

- < 1 eV: direct dissociative ionization via 1sσg state
- 0 - 10 eV (primarily 2-7 eV): auto-ionization of doubly excited Q1 state to 1sσg
- > 5 eV: direct excitation of 2pσu

1 – 8 eV: auto-ionization of Q2 state to 2pσu and 1sσg
Isolated as pulse + few-cycle IR pulse

- D$^+$ kinetic energy distribution vs time delay

Bond softening induced by IR pulse (maximum when bound WP is at the outer turning point of the potential curve)

IR-induced ionization of Q$_1$ states producing 2p$\sigma_u$ state

increase of excitation cross-section of 2p$\sigma_u$ continuum due to IR-induced mixing of 2p$\sigma_u$ and 1s$\sigma_g$ states

Electron localization in \( \text{D}_2 \)

- Asymmetry parameter:
  \[
  A(E_k, \tau) = \frac{N_L(E_k, \tau) - N_R(E_k, \tau)}{N_L(E_k, \tau) + N_R(E_k, \tau)}
  \]

- Asymmetry extending from 2 eV up to 10 eV
- \( A(E_k, \tau) \) oscillates with the periodicity of IR laser
- Phase of asymmetry oscillations depends on \( E_k \)

Electron localization

- Left-right asymmetry: coherent superposition of *gerade* and *ungerade* states
  - Relative phase between the two states leads to left/right electron localization

\[
|2p\sigma_u^+\rangle = \frac{1}{\sqrt{2}} (|1s\sigma_u^+\rangle + |2p\sigma_u^+\rangle)
\]

\[
|r\rangle = \frac{1}{\sqrt{2}} (|1s\sigma_u^+\rangle - |2p\sigma_u^+\rangle)
\]

- IR can cause an asymmetry either by changing the wave function of the continuum electron (I) or by changing the wave function of the molecular ion (II)
Localization mechanism I

A. XUV excitation of $2p\sigma_u$ state and interaction of IR pulse with photo-electron: redistribution of the wave function over several angular momentum states

B. auto-ionization of $Q_1$ state (or direct ionization): formation of a dissociative WP on the $1s\sigma_g$ state with p-electron emission

- quantum interference of the two WPs: localization of bound electron
- mechanisms restricted to the XUV-IR overlapping region
IR-induced population transfer between a WP on $2pσ_u$ state and $1sσ_g$ state

→ requires high intensity of IR pulse during the dissociation of the molecule
From diatomic to complex (bio)molecules

- Attosecond-scale electronic dynamics in molecules affect chemical changes
  

- When *charge migration* is the crucial step, the time-scale relevant to chemistry is set by electronic motion
  - electron delocalization in aromatic molecules
  - photosynthesis
  - long-range electron transfer in biomolecules
  - biological energy conversion processes

- Molecular electronics and molecular photovoltaics
  Control of electronic current in ever smaller semiconductor nanostructures and molecular systems
Charge migration in small peptides

- Charge localization by sudden ionization of small peptides: the resulting hole is localized and is not stationary (the stationary orbitals of the cation are delocalized).

### Proposed Experimental Technique

Measure of kinetic energy distribution of photoelectrons released by a time-delayed sub-fs XUV pulse (250 as, 95 eV)

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