Real time tracing of valence-shell electronic coherences with attosecond transient absorption spectroscopy

A. Wirth [a], R. Santra [b,c], E. Goulielmakis [a,*]

[a] Max-Planck-Institut für Quantenoptik, Hans-Kopfermann-Str. 1, D-85748 Garching, Germany
[b] Center for Free-Electron Laser Science, DESY, Notkestrasse 85, 22607 Hamburg, Germany
[c] Department of Physics, University of Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany

ABSTRACT

The chemical properties of atoms, molecules and of more complex systems such as clusters, nanoparticles or condensed matter systems are determined by valence electrons. Real-time control of these properties requires the capability of tracing as well as of driving valence electrons on their native temporal scale of motion, that is, within tens to thousands of attoseconds. Here we detail the technique of attosecond transient absorption spectroscopy. It combines the extreme sensitivity of core-level spectroscopy with the unprecedented temporal resolution offered by the tools of attosecond technology. We use the technique to demonstrate real-time tracing and complete characterization of coherent electron motion triggered by single, double or multiple ionization of atoms exposed to intense, few-cycle pulses. Our work opens the door to high fidelity, time-domain studies and control of electron dynamics in the microcosm.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Progress in light technology over the last decade has widened the scope of ultrafast science to include tracing and real-time control of electronic dynamics [1,2] in atoms, molecules and condensed matter. Field control of intense few-cycle waveforms has enabled the reproducible generation of isolated extreme ultraviolet (EUV) attosecond pulses [3] and the establishment of novel methods for chronoscopy, such as the attosecond streak camera [4–9]. Owing to their unprecedented resolution [10,11], these tools have made possible the real-time tracing of ultrafast electron wavepackets and associated dynamics, triggered by direct or indirect pho-

toionization (e.g. Auger decay) of atoms [12], molecules [13] and condensed matter [14].

Valence electron motion can be initiated by the coherent population of valence electronic state manifolds of virtually any microscopic system—from a single atom to a complex protein—and results in the dynamic evolution of its electronic charge distribution. Because the chemical reactivity of atoms and molecules is closely linked to their electronic charge distributions [15], measurement and control of electron dynamics can open up new ways for steering chemical reactions on extreme time scales. Electron motion in atoms [16] or in molecules [13] has been recently accessed via bound and free wavepacket interferences, harmonic interferometry as well as angularly resolved ion momentum spectroscopy [17–19]. Here we demonstrate a more generic probe scheme with attosecond temporal resolution as well as broad

* Corresponding author.
  E-mail address: elgo@mpq.mpg.de (E. Goulielmakis).

dynamic range, capable to capture valence dynamics unfolding within tens of attoseconds or hundreds of femtoseconds, offering new possibilities for tracing electronic processes in complex molecular systems [20].

2. Attosecond transient absorption spectroscopy

2.1. The concept

Our approach is based on the well-established approach for probing structural changes at the valence shell of atoms, molecules or solids, namely the technique of core-level X-ray absorption spectroscopy [21–23]. Implemented with extreme ultraviolet pulses generated via high harmonic generation (HHG)—typically of femtosecond duration—this technique has been successfully employed to trace structural dynamics in solids [24], as well as the quantum-state resolved ionization of atoms[25] and molecules [26] triggered by femtosecond pulses in the NIR. Here we show that this technique can be endowed with attosecond resolution by employing EUV attosecond pulses *to probe* ultrafast electron dynamics initiated by a precisely controlled few-cycle light waveform. Variations of this technique, in the meanwhile implemented by other groups, have allowed access to the autoionization of atoms [27] as well as to the interference of transiently bound electron wave packets [28].

Fig. 1 illustrates triggering and probing of electron dynamics within the concept of attosecond transient absorption spectroscopy. An intense few-cycle laser pulse (red) liberates electrons from the 4p valence shell of krypton atoms to create singly, doubly or triply charged ions in the $4p^{-1}$, $4p^{-2}$ and $4p^{-3}$ manifolds of quantum states. An EUV pulse (purple) can promote the generated ions to the core–hole excited-state manifolds $3d^{-1}$, $3d^{-1}4p^{-1}$ and $3d^{-1}4p^{-2}$. Inner shell excitation is typically followed by Auger decay of the core–hole states. If the EUV pulse is transmitted through an ensemble of ionic specimen, resonant absorption will occur and will be manifested by sharp dips in the transmitted spectrum centered at the energy of the characteristic transitions of the ion. The linewidth is inversely proportional to the core–hole life time of the system. For krypton ions, the 3d Auger decay is on the order of T_{3d} ~7 fs resulting in line widths of ~88 meV [29]. In close analogy to femtosecond transient absorption spectroscopy, pioneered by Mathies and coworkers [30–33], quantum state populations as

well as coherent dynamics of the studied systems are imprinted on sample-transmitted spectra of the probe pulse that can be recorded as function of the pump–probe delay between the two pulses.

2.2. Basic instrumentation and the optical attosecond streak camera

The experimental setup used to supplement absorption spectroscopy with attosecond resolution is detailed in Fig. 2(a). Waveform reproducible quasi-monocycle laser pulses are focused (*f* = 50 cm) into a neon filled (~220 mbar) quasi-static gas cell to generate EUV pulses via the process of high harmonic generation [34]. The emerging, highly collimated EUV pulses are transmitted through a disc-like Zirconium (Zr) foil (150 nm) mounted on a thin pellicle (15 μm), while the near infrared (NIR) pulses—which are also making their way through the Ne cell—are transmitted around the margins of the Zr disc to create an annular beam. A module, comprised of a concave, multilayer-coated inner mirror and a silver coated concave annular sector (outer mirror), focuses (*f* = 12.5 cm) EUV and NIR fields into a Ne gas jet for streaking experiments or a quasi-static cell for transient absorption experiments (Kr or Xe for the experiments presented here). Streaking spectrograms recorded by this apparatus [8] allow not only the precise temporal characterization of the NIR electric field [6], but also the reconstruction of the EUV pulse characteristics utilizing a FROG based retrieval [35,36]. The intensity profile of an attosecond EUV pulse measured by the apparatus is displayed in Fig. 2(b).

The gas cell—used for transient absorption measurements—has diameter of <1.0 mm, substantially smaller than the >3 mm confocal parameter of the focused laser beam. The required gas density in the quasi-static gas cell for recording transient absorption spectra depends on the EUV photoabsorption cross-section. To quote a few useful numbers, a cross section of ~1 Mb and an atom density of $2.5 \cdot 10^{18}$ atoms/cm^3 (~100 mbar), yields an EUV absorption of >20% within the bandwidth of an absorption line. The estimation suggests robust signals which are essential for high fidelity measurements.

The transmitted attosecond pulse is focused by a concave mirror (ROC = −340 mm), placed at nearly grazing incidence (~64°) with respect to the incident beam, to create a vertical focus on the plane of the entrance slit of an EUV spectrometer. The spectrometer which is based on the Rowland-circle geometry, utilizes a ~2400 lines/mm concave grating to spectrally disperse the EUV beam on a single-stage microchannel plate (cesium iodide coated photocathode) followed by a phosphor screen and fiber-coupled, peltier-cooled CCD camera. We obtain a spectral resolution better than 350 meV at ~80 eV.

3. Charge state time-resolved ionization of atoms

One of the first experiments [37] that employed picoseconds EUV transient absorption on NIR strong-field generated ions aimed at the retrieval of the EUV pulse width by using the ionization via a strong field as the probe. With attosecond EUV probes considerably shorter than the NIR driver pulse, the technique affords access into the dynamics of strong field ionization and the accurate determination of the ionization gate which is the key parameter for affecting or even controlling the coherence of the ensuing electron dynamics in the valance shell, to be discussed in the next sections. Ionization dynamics can be elucidated by tracing absorption of an attosecond pulse in the presence of the strong field, namely within the time span where both pump and probe pulses overlap. The quantity that links the population of the absorbing species to the experimentally recorded signals is absorbance and is defined as: $A(E,\tau) = \ln(I_0(E,\tau)/I_{trans}(E,\tau))$, where $I_0(E,\tau)$ is the spectral density

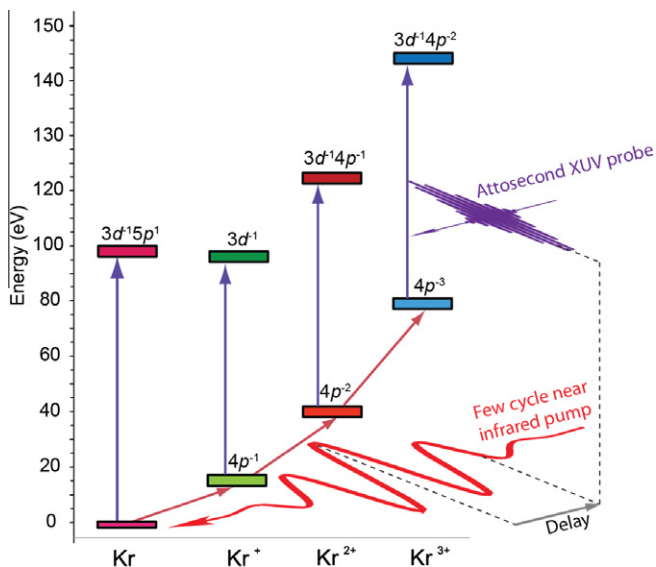**Fig. 1.** Probing krypton atoms and ions by attosecond absorption spectroscopy.