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From Femtochemistry to Attochemistry?

The formation or breaking of bonds between atoms typically happens on a femtosecond timescale (1 femtosecond corresponds to 10^{-15} seconds). Towards the end of the 20th century, the development of femtochemistry has made it possible to study the processes in a chemical reaction in real time. In a femtochemistry experiment, a femtosecond pump pulse initiates a reaction, and a second femtosecond probe pulse interrogates the system at different time delays, enabling the observation of a chemical reaction while it is taking place. For his pioneering work, Ahmed Zewail was awarded with the Nobel Prize in Chemistry in 1999.

While femtochemistry enables the observation of atomic motion, electron dynamics take place on even faster timesc=ales in the attosecond domain (1 attosecond corresponds to 10^{-18} seconds). The development of attosecond science at the beginning of the 21st century therefore raised expectations that the concept of femotochemistry may be transferred to the attosecond timescale, meaning that one attosecond pump pulse initiates electron dynamics in a system and that a second attosecond probe pulse interrogates this system at different time delays. However, it soon became obvious that the ability to perform attosecond-pump attosecond-probe spectroscopy (APAPS) is a very challenging goal.

To understand why this is the case, it is important to consider how attosecond pulses are generated. Most often a process known as high-harmonic generation (HHG) is used, where an infrared (IR) femtosecond driving laser pulse is focused into a gas or solid-state target. While this results in frequency up-conversion to the extreme-ultraviolet (XUV) or X-ray regions of the electromagnetic spectrum, the conversion efficiencies are very low (typically < 10^{-4}).

Since it is difficult to generate intense attosecond pulses, weak attosecond pulses have been used in combination with femtosecond infrared (IR) pulses in the vast majority of attosecond pump-probe experiments. By using the oscillation period of the IR pulse as a clock, exciting insights into electron dynamics on extremely fast timescales have been obtained in atoms, molecules, liquids, solids and at the nanoscale. There are, however, clear limitations of this approach: (1) The IR laser fields used in these experiments are often strong enough to distort atomic and molecular potentials. These strong laser fields may therefore change or mask the dynamics of interest. (2) The femtosecond duration of the IR pump or probe pulse limits the temporal resolution, and (3) IR pulses typically only interact with valence-shell electrons.

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In spite of the success of attosecond science up to now, its full potential may only unfold when creating the ability to perform attosecond-pump attosecond-probe spectroscopy, in analogy to how a typical femtochemistry experiment is carried out. Pioneering work on the generation of intense attosecond pulses, which are a requirement for APAPS experiments, has been carried out by the groups of Charalambidis in 2011 [1] and Midorikawa in 2013 [2]. Their approach relied on the up-scaling of the XUV pulse energy obtained via HHG. To this end, they used large setups and laser systems with high IR pulse energies, allowing them to generate a large driving laser focus and thereby to increase the volume from which high harmonics can be generated. Following tight focusing of the generated XUV pulses, they were able to achieve sufficiently high XUV intensities which enabled them to perform auto-correlation measurements in atomic and molecular samples. In these experiments, two copies of the XUV pulses were generated, and two-photon absorption was studied as a function of the time delay between the two XUV pulses. The XUV pulse durations were estimated from these measurements as 1.5 femtoseconds [1] and 500 attoseconds [2]. The first result refers to a short attosecond pulse train, while the second result refers to an isolated attosecond pulse.

At the Max-Born-Institut (MBI) we were recently able to demonstrate an attosecond-pump attosecond-probe capability. Using an HHG beamline with a length of 18 meters, up-scaling of the XUV intensity to a value of 7 x 10^{14} W/cm^2 was achieved. This enabled the study of highly nonlinear ionization of Ar and resulted in charge states as high as Ar^{5+}, requiring the absorption of at least 10 XUV photons [3]. In a delay-dependent experiment, the formation of doubly-charged Ar^{2+} and triply-charged Ar^{3+} ions was studied with attosecond time resolution [4]. The results are presented in Fig. 1, where the red and blue curves show the Ar^{2+} and Ar^{3+} ion yields as a function of the time delay between two short attosecond pulse trains. While the Ar^{2+} ion yield exhibits a small dependence on the time delay, the Ar^{3+} ion yield shows clear oscillations with a period of about 1.3 femtoseconds. This oscillation period is a consequence of the fact that one attosecond burst is generated during each half cycle of the driving laser. In the current study, driving laser pulses at a wavelength of 800 nanometers were used, corresponding to an oscillation period of 2.67 femtoseconds. Taking into account that the formation of Ar^{2+} requires the absorption of two XUV photons [3], the results presented in Fig. 1 demonstrate that these two XUV photons are absorbed sequentially rather than simultaneously. In contrast, the clear oscillations observed in the Ar^{3+} ion yield demonstrate that at least two XUV photons are simultaneously absorbed, which is a consequence of the high XUV intensity that was used in this experiment. Following the results in [1, 2], the MBI is the third place in the world where an APAPS capability was demonstrated.

A disadvantage of the experiments reported in [1, 2, 4] is that large setups and highly specialized laser systems were used, which are further limited to low repetition rates (10-100 Hertz). This may explain why so far only a very few results on APAPS have been reported. In contrast, attosecond experiments, in which an XUV pulse is combined with an IR pulse, are typically performed using laser systems at repetition rates in the kilohertz range, which provide a much higher stability and can improve the statistics in these experiments. Recently, we developed a compact source of intense XUV pulses, where up-scaling of the XUV intensity was achieved by generating high harmonics far away from the IR driving laser focus [5]. Using this concept, we were able to demonstrate the first APAPS experiment at a kilohertz repetition rate [6]. In contrast to the previously reported autocorrelation measurements, a two-color scheme was realized, where different spectral bands were selected for the pump and the probe beam from the broadband XUV spectrum. This result was achieved in a compact setup, which has requirements that are similar or even lower when compared to a standard attosecond experimental setup. Therefore, our approach may be applied in many laboratories around the world, and may lead to a situation where APAPS unfolds its full potential.

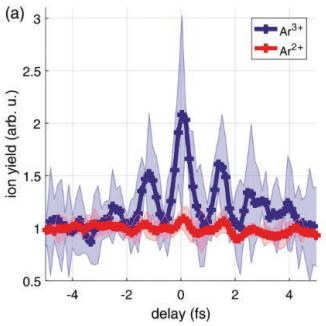

Fig. 1: Attosecond-pump attosecond-probe spectroscopy, showing Ar^{2+} (red curve) and Ar^{3+} ion yields (blue curve) as a function of the time delay between two short attosecond pulse trains. In this experiment, the XUV peak intensity was modified by changing the time delay between the two pulses, enabling control over the efficiency of a simultaneous two-photon absorption process. The results show that Ar^{2+} is predominantly formed by sequential two-photon absorption, while the formation of Ar^{3+} involves the simultaneous absorption of at least two XUV photons. Reprinted with permission from Ref. [4] © The Optical Society.

In addition to the progress in the development of table-top APAPS, an exciting new development is the demonstration of attosecond pulses at the X-ray free-electron laser LCLS in Stanford [7]. Using this machine, which has an extension of several kilometers, the generation of attosecond pulses with unprecedented intensities has become a reality. This makes it possible to perform APAPS experiments at shorter wavelengths (< 10 nanometers) in the (soft) X-ray region, and first APAPS results have recently been reported [8]. In the future, APAPS may also become possible at other free-electron lasers including the European XFEL in Hamburg/Schenefeld.

The recent development of APAPS capabilities both in the XUV spectral range using table-top light sources and in the X-ray regime at large-scale facilities permits the investigation of fundamental processes on extremely short timescales, which are not easily accessible by other pump-probe techniques. Among these, charge migration in biologically relevant molecules is of high interest [9], and its observation in real time may become possible using APAPS. Another area where APAPS may play an important role are multi-electron correlation processes, which manifest themselves e.g. via extremely fast Auger-Meitner and interatomic/intermolecular decay processes. As happened in the past when applying new techniques, the application of APAPS may further lead to surprising and interesting findings that we do not yet anticipate.

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As a child Bernd Schütte developed an interest in astronomy, being fascinated by the extreme length and time scales of the universe. During his undergraduate studies at TU Dresden and Lund University (Sweden) he came in contact with the other extreme, studying ultrafast dynamics on atomic spatial scales. He was fascinated by the ability to observe and control these dynamics using extremely short laser pulses. Consequently, he performed his PhD work on ultrafast dynamics at the University of Hamburg, where he investigated Auger-Meitner decay processes. In 2011 Bernd Schütte received his PhD and joined the Max-Born-Institut (MBI) in Berlin as a PostDoc, where he developed an intense XUV beamline and studied ultrafast processes in nanoplasmas. He continued this work during his stay at the Imperial College in London from 2014-2016. Afterwards he returned to the MBI and became group leader in 2020, where he and his team develop and apply attosecond-pump attosecond-probe spectroscopy.