

Attosecond time-resolved absorption spectroscopy in the water window

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Attosecond transient-absorption spectroscopy (ATAS) has the potential to address fundamental open questions in photochemistry and photophysics. With the broad high-harmonic spectrum, achieved using an intense mid-infrared (MIR) femtosecond source, transient-absorption spectroscopy measurements can be performed at the carbon K-edge [1,2]. In this work, we present the soft X-ray (SXR) high-harmonic source with a cutoff energy of 450 eV, and we demonstrate the first time-resolved results from our experimental setup showing the capability to resolve the fast electronic and structural dynamics in the broad class of organic molecules.

Our experimental setup consists of a commercial 1 kHz Ti:Sa laser system used to pump an optical-parametric amplifier to generate millijoule pulses centered at 1.8 μm and subsequently broadened in an argon-filled hollow-core fiber [3] and compressed with bulk material, delivering sub-two-cycle MIR pulses (~ 10.5 fs). The MIR beam is coupled into a Mach-Zehnder interferometer. In one of its arms, the MIR beam is focused to a helium-filled finite gas cell, in which the high-harmonic generation process occurs, thereby producing an attosecond SXR pulse [4]. The SXR beam is then focused by a toroidal mirror into the target ethylene gas. The transmitted photons are detected with a CCD-camera based spectrometer. The relative delay between pump and probe pulses is introduced by a delay stage integrated into the other optical path of the interferometer, i.e., the optical path of the MIR pump beam. The MIR beam is focused into the sample target where it is recombined with the SXR beam.

The focus of the discussion will be on the fast electronic relaxation dynamics ever measured by extending ATAS to the carbon K-edge. We selectively launch both adiabatically and non-adiabatically evolving wave packets in the electronic ground (D0) and first excited (D1) states of ethylene cation. The electronic D1 \rightarrow D0 relaxation is found to take place with a short time constant of 6.8 ± 0.2 fs. The electronic-state switching at conical intersections is directly visualized in ATAS owing to a spectral separation of the D1 and D0 absorption bands caused by electron correlation. Moreover, the technique simultaneously allows observing the structural dynamics of the ethylene via characteristic oscillations of the positions of the absorption bands. Our experimental results show that the electronic relaxation in the prototypical organic chromophore can take place within less than a single vibrational period and thus, demonstrate the capability of the ATAS technique to resolve the fast electronic and structural dynamics in the broad class of organic molecules.

[1] Y. Pertot, C. Schmidt, M. Matthews, A. Chauvet, M. Huppert, V. Svoboda, A. von Conta, A. Tehlar, D. Baykusheva, J.-P. Wolf, and H. J. Wörner, "Time-resolved X-ray absorption spectroscopy with a water window high-harmonic source," *Science* **355**, 264-267 (2017).

- [2] C. Schmidt, Y. Pertot, T. Balciunas, M. Matthews, K. Zinchenko, H. J. Wörner, “High-order Harmonic source spanning up to Oxygen K-edge based on Filamentation Pulse Compression,” *Opt. Express*, **26**, 9, 11834–11842 (2018).
- [3] F. Silva, S. M. Teichmann, S. L. Cousin, M. Hemmer and J. Biegert, “Spatiotemporal isolation of attosecond soft X-ray pulses in the water window,” *Nat. Commun.* **6**, 6611 (2015).
- [4] T. Gaumnitz, A. Jain, Y. Pertot, M. Huppert, I. Jordan, F. Ardana-Lamas, and H. J. Wörner, “Streaking of 43-attosecond soft-X-ray pulses generated by a passively CEP-stable mid-infrared driver,” *Opt. Express* **25**, 27506-27518 (2017).