Attosecond soft-X-ray spectroscopy in the gas and liquid phases

Hans Jakob Wörner

Laboratory of Physical Chemistry, ETH Zurich, Switzerland
hwoerner@ethz.ch

Attosecond time-resolved spectroscopy has the potential to address fundamental open questions in chemical sciences. Although the first two decades of research have led to very important advances towards this goal, the techniques of attosecond spectroscopy still need to overcome two gaps. The first gap is the complexity gap, i.e. the challenge of applying attosecond spectroscopy to complex molecules. A promising approach to overcome the complexity gap consists in exploiting the element-, site- and spin-sensitivity of X-ray spectroscopy. We have recently demonstrated the potential of table-top X-ray absorption spectroscopy with a water-window high-harmonic source, observing the temporal evolution of unoccupied molecular orbitals, as well as molecular shape resonances during chemical reactions [1]. Compressing the mid-infrared driving pulses to less than 2 optical cycles, we have demonstrated the extension of this table-top source to fully cover the oxygen K-edge with fluxes sufficient for time-resolved measurements [2]. Using the same technique, we have also demonstrated the generation of isolated attosecond pulses, which have established a new record of the shortest light pulses ever measured (43 attoseconds) [3]. We have used attosecond spectroscopy at the carbon K-edge to measure the $D_1 \rightarrow D_0$ relaxation of the ethylene cation, which occurs in 6.8 ± 0.2 fs, representing the fastest conical-intersection dynamics measured to date. Using attosecond spectroscopy at the silicon $L_{2,3}$-edge, we have observed the decay and revival of a 1.32-1.38-fs electronic wave packet in neutral silane, driven by both nuclear and non-adiabatic dynamics.

The second gap is the extension from the gas phase to the liquid phase, which is relevant to the vast majority of chemical and biophysical processes. I will discuss the first realization of time-resolved X-ray absorption spectroscopy in the liquid phase using a high-harmonic source [4]. Electronic and structural dynamics in liquid alcohols initiated by strong-field ionization have been studied by X-ray absorption spectroscopy at the carbon and oxygen K-edges. The appearance of ionization-induced absorption bands was observed to take place on a time scale significantly slower than the experimental cross correlation, revealing the occurrence of proton-transfer dynamics in the ionized alcohols. Finally, I will present the first extension of attosecond time-resolved photoelectron spectroscopy from molecules [5] to liquids [6], reporting on photoemission delays of liquid compared to gaseous water. The measured time delays range from 50-70 attoseconds and are shown to mainly originate from the solvation of water molecules, with liquid-phase electron scattering playing a minor role. This conclusion is quantitatively supported by complementary measurements of photoionization time delays of size-resolved water clusters. These combined developments set the stage for attosecond time-resolved studies of molecular systems of chemical complexity.

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

"High-order harmonic source spanning up to the oxygen K-edge based on filamentation pulse compression", Opt. Exp. 26, 11834 (2018)
[3] T. Gaumnitz, A. Jain, Y. Pertot, M. Huppert, I. Jordan, F. Ardana-Lamas, H. J. Wörner, "Streaking of 43-attosecond soft-X-ray pulses generated by a passively CEP-stable mid-infrared driver", Opt. Exp. 25, 27506 (2017)
[4] A. D. Smith, T. Balciunas, Y.-P. Chang, C. Schmidt, K. Zinchenko, F. B. Nunes, E. Rossi,V. Svoboda, Z. Yin, J.-P. Wolf and H. J. Wörner, "Femtosecond soft-X-ray absorption spectroscopy of liquids with a water-window high-harmonic source", J. Phys. Chem. Lett. 11, 1981 (2020)
[5] M. Huppert, I. Jordan, D. Baykusheva, A. von Conta, H. J. Wörner, "Attosecond delays in molecular photoionization", Phys. Rev. Lett. 117, 093001 (2016)
[6] Inga Jordan, Martin Huppert, Dominik Rattenbacher, Michael Peper, Denis Jelovina, Conaill Perry, Aaron von Conta, Axel Schild, Hans Jakob Wörner, "Attosecond spectroscopy of liquid water", Science 369, 974 (2020)