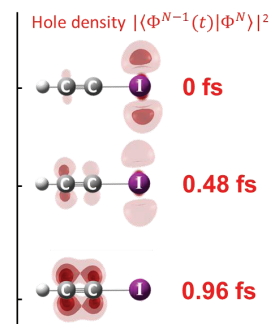


ATTOSECOND TIME-RESOLVED MOLECULAR SPECTROSCOPY

HANS JAKOB WÖRNER, *Laboratory of Physical Chemistry, ETH Zurich, Zürich, Switzerland.*

Attosecond time-resolved spectroscopy is beginning to provide experimental access to the most fundamental time scales of molecules, on which the electronic dynamics take place. A few recent experiments that access purely electronic dynamics, as well as coupled electronic and nuclear dynamics in molecules will be discussed. The theoretical developments that accompanied the experimental work will also be presented. The ionization of most molecules on the sub-femtosecond time scale prepares the molecular cation in a superposition of several electronic states that supports charge migration. Detailed measurements of the phase and amplitude of high-harmonic emission from spatially oriented iodoacetylene molecules have enabled the reconstruction of sub-femtosecond charge migration in the iodoacetylene cation (see figure)^a. The ionization of molecules by attosecond pulses and a synchronized infrared field was used to measure photoionization time delays between the two highest-lying occupied valence orbitals of H₂O and N₂O. These measurements revealed delays of up to ~160 as in the case of N₂O, which are characteristic of the transient trapping of the photoelectron by shape resonances^b. Finally, the extension of attosecond spectroscopy to the soft-X-ray domain (water window) will be discussed. The broad spectral bandwidth available in this domain has been exploited to synthesize one of the shortest attosecond pulses to date (43 as)^c. Transient absorption spectroscopy at the carbon K-edge has been used to study the photodissociation dynamics of CF₄⁺, revealing the rearrangement of the electronic structure during this ultrafast (~40 fs) process^d. An outlook on attosecond spectroscopy of both isolated and solvated molecules will be given.



^aP. M. Kraus *et al.*, *Science* **350**, 790 (2015)

^bM. Huppert *et al.*, *Phys. Rev. Lett.* **117**, 093001 (2016)

^cT. Gaumnitz *et al.*, *Opt. Exp.* **25**, 27506 (2017)

^dY. Pertot *et al.*, *Science* **355**, 264 (2017)