Advancing attosecond science to liquids and chiral molecules

Hans Jakob Wörner

Laboratory of Physical Chemistry, ETH Zürich, Zurich, Switzerland

Attosecond science is maturing into a transformative tool for measuring and understanding ultrafast electronic and structural dynamics, but its extension to complex systems is hampered by challenges of both technical and fundamental nature.

Our group has pioneered attosecond spectroscopy in liquids. Attosecond photoelectron spectroscopy with liquid microjets has been developed and applied to measure delays of 50-70 attoseconds between the photoemission from liquid vs. gas-phase water[1]. Detailed modelling has revealed that the delays are dominated by the influence of the first two solvation shells on the photoionization dynamics. This interpretation has been confirmed by attosecond photoelectron spectroscopy of size-resolved water clusters[2], which showed that the photoionization delays reflect the spatial delocalization of the electronic wavefunctions, which grows with the cluster size from monomers to tetramers but then saturates at a typical extension of 4-5 molecules[2].

In parallel, soft-X-ray absorption spectroscopy with attosecond pulses has been developed, first in gases[3] and then in liquids[4], enabling element-specific studies of solvated molecules in liquid water. This novel technique has been used to reveal the electronic and structural dynamics underlying ultrafast proton transfer in solvated urea[5] and the dephasing of conical-intersection-driven electronic dynamics in solvated pyrazine[6].

To date, spectroscopy with attosecond pulses has been missing the ability to distinguish chiral molecules, because of a lack of circularly polarized attosecond pulses. We have developed attosecond metrology in circular polarization[7] and applied it to the study of continuum–continuum transitions in electron vortices, establishing a general framework for attosecond circular-dichroism chronoscopy[8]. The first application of circularly polarized attosecond pulses to chiral-sensitive experiments enabled us to observe and control photoelectron circular dichroism (PECD) on the attosecond timescale and to directly measure chiral photoionization delays of up to ~240 attoseconds[9].

These advances chart a promising path for attosecond-resolved studies of molecular function in aqueous environments, opening exciting opportunities for understanding radiation damage, solvation dynamics, and chiral interactions at their fundamental electronic timescale.

References

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