Liquid-Jet Photoelectron Spectroscopy of Aqueous Solutions: Recent Breakthroughs and Current Challenges

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ABSTRACT

Liquid-jet photoemission spectroscopy (LJ-PES) has a long track record as a direct probe of both the electronic- and molecular/solute structure as well as interfacial characteristics of aqueous solutions. Energies of both directly emitted photoelectrons and electrons generated through second-order processes can be accurately determined with respect to the vacuum level as well as the Fermi level. The latter capability enables detailed characterization of explicit solution surface properties, including structure and charge distributions, thereby establishing a direct link between surface science and electrochemical descriptors. In addition, non-local ionization/relaxation processes and ultrafast electron delocalization upon core-hole excitation provide access to rich bulk-solution dynamical information. This includes proton, electron, and charge transfer, and enables explicit insight into the first-solvation shell energetics and composition. LJ-PES has been applied to a broad range of systems, spanning from simple atomic solutes to complex biomolecules in aqueous environments, such as adenosine triphosphate in interaction with metal cations.

Despite these breakthroughs, several key aspects of solutions, such as chiral solute-solvent interaction or low-yield reaction intermediates and products, remain experimentally challenging to access via LJ-PES. Many of these challenges arise from strong electron scattering in solution at low kinetic energies and from the still insufficiently understood electron scattering lengths in liquids. I illustrate these limitations with few examples: (1) the difficulty of accurately determining solute concentration profiles from the solution surface into the bulk on an absolute length scale, unless independent length calibration is available; and (2) the challenge of achieving an efficient electron detection, simultaneously covering a wide electron angular emission range aiming at extraction of the associated structure information, e.g., chirality in aqueous solution. I highlight the continued development of liquid-jet technologies to address these challenges.