Dominik Stemer, Florian Trinter

Probing liquid interfaces with photoelectron spectroscopy

Interfaces in aqueous systems are central to many processes in chemistry, biology, and energy conversion. They govern ion transport, solvation, chemical reactivity, and radiation response. Liquid-jet photoelectron spectroscopy (LJ-PES) is a powerful technique that enables the electronic-structure characterization of bulk solvents and diverse solvated species [1, 2]. Over the past 20 years, LJ-PES has regularly been applied to probe liquid-specific phenomena, including surface aggregation of ions and solvated electrons [3, 4], solvent-driven scattering of photoelectrons [5, 6], and ultrafast electronic-relaxation processes in solution [7]. Here, we highlight recent advances in LJ-PES and discuss how these developments enable new perspectives for the study of liquid—liquid and liquid—gas interfaces.

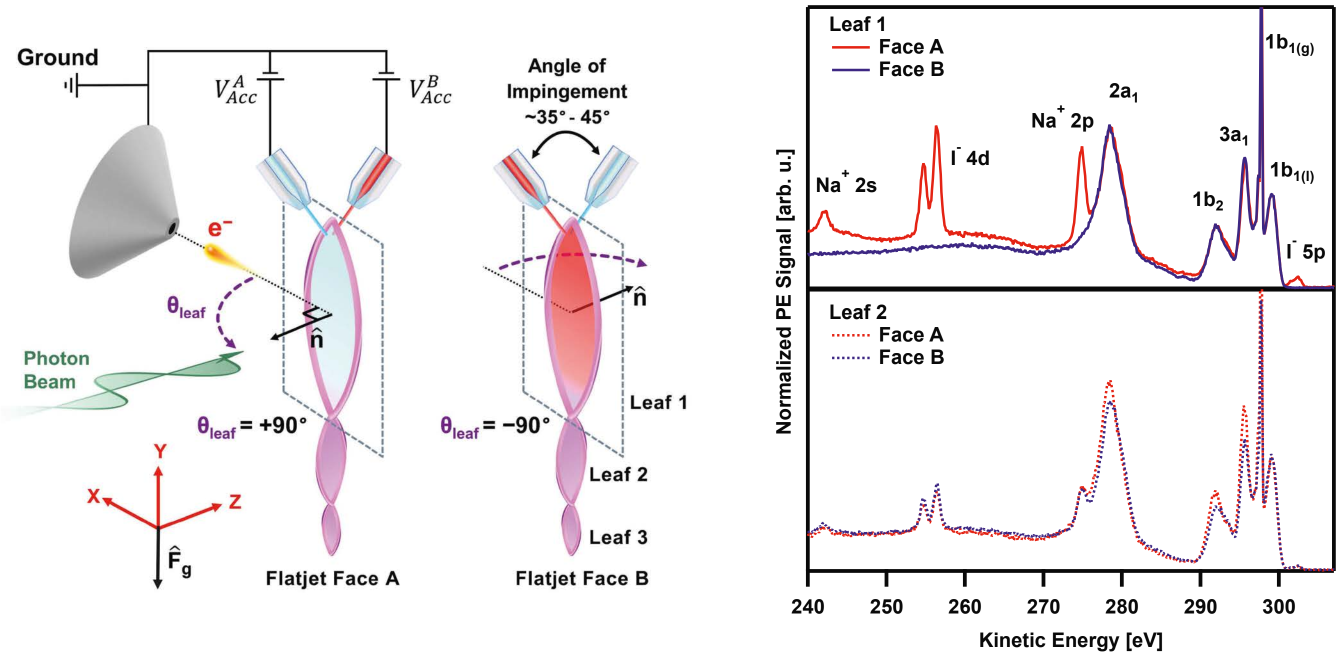

Fig. 1: Left: Experimental setup for photoelectron spectroscopy (PES) using a liquid flat jet (FJ). The FJ is created by the collision of two cylindrical jets, providing a large liquid surface for PES. It can be rotated around the downstream axis by an angle θ_{leaf} to probe both faces. We here define $\theta_{leaf} = 0°$ when the first leaf is perpendicular to the detector axis, illustrated by the electron skimmer orifice. Electrical connections for applying accelerating voltages $V_{Acc}{}^{A}$ and $V_{Acc}{}^{B}$ to the jets are shown at the top left. Right: Photoelectron spectra measured from each of the two faces of the first (top) and second (bottom) leaf of a mixed FJ formed by the impingement of aqueous sodium iodide (NaI) and water, with clear features corresponding to water ($2a_1$, $1b_2$, $3a_1$, and $1b_1$) and to NaI (Na^+ 2s, I^- 4d, Na^+ 2p, and I^- 5p). NaI features are only visible on one side of the first leaf, indicating that turbulent mixing there is minimal following initial impingement. Within the second leaf the two faces are indistinguishable. The figures are taken from Ref. [8] (Open Access).

Formation of stable liquid—liquid and liquid—gas interfaces using liquid flat jets

LJ-PES is primarily performed using cylindrical microjets injected into vacuum through suitable nozzles. However, more advanced liquid targets may be prepared through the impingement of two cylindrical jets, including free-flowing liquid sheets known as flat jets (FJs). These FJs consist of consecutive flat liquid “leaves”, oriented perpendicular to one another, with their dimensions determined through the balance of fluid flow and solution parameters (Fig. 1, left). For the case of a FJ formed by the impingement of aqueous sodium iodide (NaI) and water, we took advantage of the inherent surface sensitivity of LJ-PES to demonstrate that each face of the first liquid leaf retains the characteristics of the constituent solutions [8]. In other words, the first liquid leaf appears spectroscopically to be water when viewed from one side and aqueous NaI when viewed from the other (Fig. 1, right). These observations indicate that turbulent mixing within the first leaf is minimal, giving rise to a relatively well-defined liquid—liquid interface that becomes progressively

Dr. Florian Trinter
Molecular Physics
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, D-14195 Berlin
trinter@fhi-berlin.mpg.de
https://www.fhi.mpg.de/1400477/Trinter

DOI-Nr.: 10.26125/5950-fy64

blurred along the flow direction as interdiffusion occurs. These liquid structures are useful templates for the characterization and control of interfacial reaction dynamics, for example, through the application of a suitable electric field gradient. The flat surface of the FJs also provides ideal opportunities for the study of oriented molecules at the liquid—vapor interface with particular relevance for interfacial chemistry. We have also demonstrated that the impingement of liquid jets enables the formation of more complicated liquid structures, for example "sandwich" geometries [8], in which an aqueous solution is fully encapsulated by organic solvent layers, thereby providing experimental access to buried aqueous—organic interfaces.

Physics at liquid—gas interfaces

While tailored liquid targets provide a natural means to access interfacial chemistry, we are also able to leverage unique physical processes to distinguish signals arising from the liquid vs. the surrounding gas formed by evaporation, a key consideration for the study of interfaces. In our recent work [9], we identified and characterized radiationless electronic-relaxation decay following the creation of oxygen 1s double core holes (DCHs, Fig. 2, left) in liquid water. We found a significant shift of 12.5 eV to higher kinetic energies in our data for liquid water compared with published results for gaseous water [10] (Fig. 2, right). This clear distinction between gas-phase and liquid-phase water, which can be rationalized by the Born solvation model and induced polarization of the surrounding water molecules following secondary photoemission [9], establishes DCH spectroscopy as a powerful tool for exploring interfacial phenomena.

Additionally, by comparing H_2O and D_2O, we observed a strong isotope effect, demonstrating that DCH spectroscopy is sensitive to the delicate interplay between proton vs. deuteron motion and electronic decay. These highly excited DCH states (lifetime of ~1.5 fs) thus provide a unique opportunity to explore ultrafast nuclear dynamics on the few-femtosecond timescale without the need for femtosecond light pulses. This work establishes DCH spectroscopy as a sensitive and novel probe of nuclear dynamics at the liquid—gas interface, with particular application to systems where gas- and liquid-phase signals are not readily resolvable using standard observables such as binding energy (e.g., benzene [11]).

From liquid—gas to liquid—liquid interfaces: Expanding the frontier

Taken together, these developments expand the experimental frontier of PES from liquid interfaces. Liquid flat jets enable the preparation of stable and well-defined liquid—liquid and liquid—gas interfaces and are particularly relevant for studies of solvation, ion transport, and surface and interface chemical reactivity. They provide significant opportunities for both miscible and immiscible solutions, with the latter in particular offering a novel experimental approach to study phase-transfer-catalysed reactions. At liquid—gas interfaces, ultrafast electron and nuclear dynamics can now be tracked through hypersatellite Auger electron emission features, providing unique benchmarks for theory and insights into photon-impact-driven processes in water. The combination of these two developments could enable new insights into radiation chemistry at electrolyte—water or water—organic boundaries,

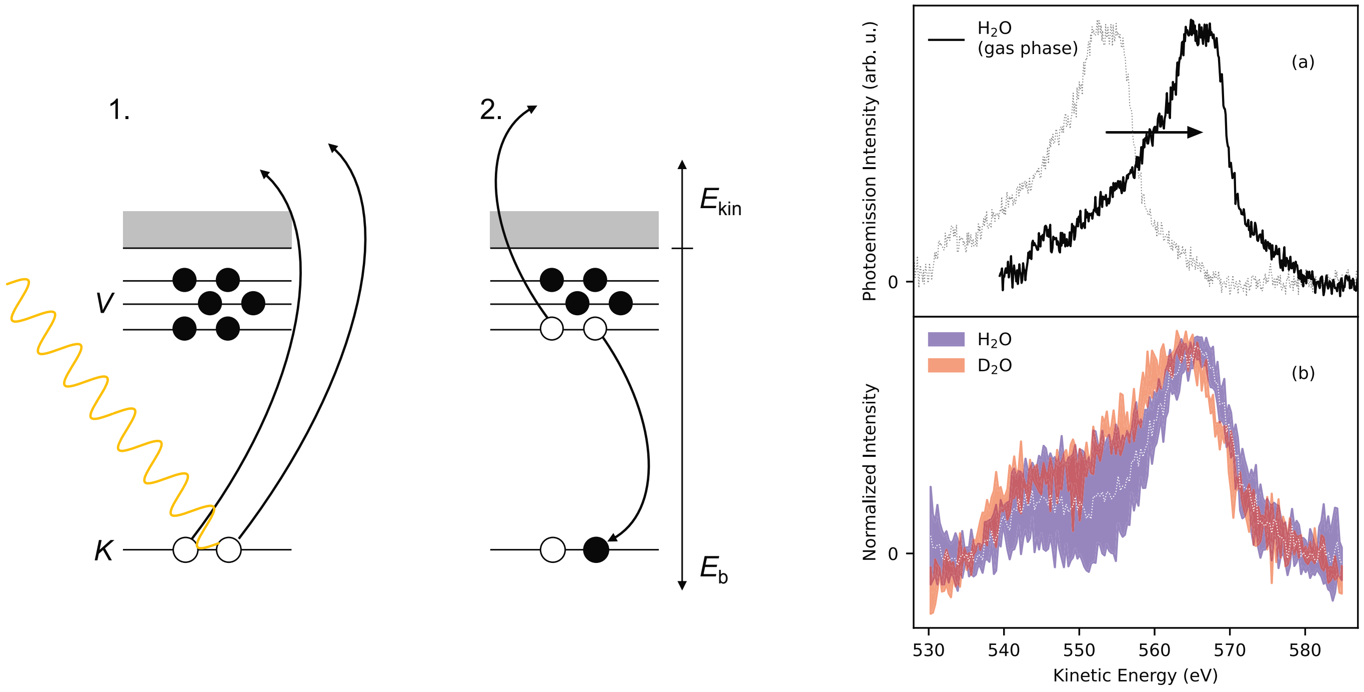

Fig. 2: Left: Schematic of the simultaneous ejection of two core (K) electrons (left) and the first radiationless electronic-relaxation decay step via valence-shell (V) rearrangement (right). E_{kin} denotes the resultant electron kinetic energy and E_b the corresponding binding energy. Right: Auger hypersatellite spectra of O 1s DCHs in (a) gaseous and (b) liquid water. The gas-phase data (dotted line, shifted by 12.5 eV [10]) are shown for comparison. Liquid spectra were measured for normal and deuterated water; the shaded band indicates experimental error across datasets, with the average for normal water shown as a thin dotted line. The figures are taken from Ref. [9] (Open Access).

advancing our understanding of interfacial chemistry relevant to biology, catalysis, and energy research.

References

[1] B. Winter, R. Weber, W. Widdra, M. Dittmar, M. Faubel, I. V. Hertel, Full Valence Band Photoemission from Liquid Water Using EUV Synchrotron Radiation, *J. Phys. Chem. A* 2004, **108**, 2625 – 2632.

[2] B. Winter, M. Faubel, Photoemission from Liquid Aqueous Solutions, *Chem. Rev.* 2006, **106**, 1176 – 1211.

[3] P. Jungwirth, B. Winter, Ions at Aqueous Interfaces: From Water Surface to Hydrated Proteins, *Annu. Rev. Phys. Chem.* 2008, **59**, 343 – 366.

[4] K. R. Siefermann, Y. Liu, E. Lugovoy, O. Link, M. Faubel, U. Buck, B. Winter, B. Abel, Binding energies, lifetimes and implications of bulk and interface solvated electrons in water. *Nat. Chem.* 2010, **2**, 274 – 279.

[5] S. Thürmer, R. Seidel, M. Faubel, W. Eberhardt, J. C. Hemminger, S. E. Bradforth, B. Winter, Photoelectron Angular Distributions from Liquid Water: Effects of Electron Scattering, *Phys. Rev. Lett.* 2013, **111**, 173005.

[6] S. Thürmer, D. Stemer, F. Trinter, I. Y. Kiyan, B. Winter, I. Wilkinson, Low-Energy Photoelectron Spectroscopy and Scattering from Aqueous Solutions and the Role of Solute Surface Activity, *J. Am. Chem. Soc.* 2025, **147**, 19868 – 19877.

[7] T. Jahnke, U. Hergenhahn, B. Winter, R. Dörner, U. Frühling, P. V. Demekhin, K. Gokhberg, L. S. Cederbaum, A. Ehresmann, A. Knie, A. Dreuw, Interatomic and Intermolecular Coulombic Decay, *Chem. Rev.* 2020, **120**, 11295 – 11369.

[8] D. Stemer, T. Buttersack, H. Haak, S. Malerz, H. C. Schewe, F. Trinter, K. Mudryk, M. Pugini, B. Credidio, R. Seidel, U. Hergenhahn, G. Meijer, S. Thürmer, B. Winter, Photoelectron spectroscopy from a liquid flatjet, *J. Chem. Phys.* 2023, **158**, 234202.

[9] F. Trinter, L. Inhester, R. Püttner, S. Malerz, S. Thürmer, T. Marchenko, M. N. Piancastelli, M. Simon, B. Winter, U. Hergenhahn, Radiationless decay spectrum of O 1s double core holes in liquid water, *J. Chem. Phys.* 2024, **160**, 194503.

[10] T. Marchenko, L. Inhester, G. Goldsztejn, O. Travnikova, L. Journel, R. Guillemin, I. Ismail, D. Koulentianos, D. Céolin, R. Püttner, M. N. Piancastelli, M. Simon, Ultrafast nuclear dynamics in the doubly-core-ionized water molecule observed via Auger spectroscopy, *Phys. Rev. A* 2018, **98**, 063403.

[11] H. C. Schewe, K. Brezina, V. Kostal, P. E. Mason, T. Buttersack, D. M. Stemer, R. Seidel, W. Quevedo, F. Trinter, B. Winter, P. Jungwirth, Photoelectron Spectroscopy of Benzene in the Liquid Phase and Dissolved in Liquid Ammonia, *J. Phys. Chem. B* 2022, **126**, 229 – 238.

Dr. Dominik Stemer


© Dominik Stemer

Dominik Stemer obtained his PhD in materials science and engineering from the University of California, Los Angeles, in 2020. In the group of Prof. Paul Weiss, he applied photoelectron spectroscopy to study self-assembled monolayers of biomolecules on metal surfaces. Since 2021, he has worked in Dr. Bernd Winter's group at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, where he has applied liquid-jet photoelectron spectroscopy to probe the electronic structure of chiral molecules in aqueous solutions. He will start an Emmy Noether research group in 2026.

Dr. Florian Trinter


© Marta Mayer, DESY

Florian Trinter studied physics at the Goethe-Universität in Frankfurt am Main and completed his PhD on interatomic Coulombic decay in 2017 in the group of Prof. Reinhard Dörner. He began his work on the electronic structure of water and aqueous solutions using liquid-microjet photoelectron spectroscopy in 2018 at the Fritz-Haber-Institut in Berlin. In 2024, he started an Emmy Noether research group on the dynamics of photoionization-induced processes in laser-prepared gas- and aqueous-phase samples at the Fritz-Haber-Institut and is a lecturer at Technische Universität Berlin.