Chemical shifts in photoelectron spectroscopy of liquids

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Chemical shifts in X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), provide crucial insights into the electronic environment of atoms in different chemical states. While well-established in gas-phase and solid-state studies, ESCA chemical shifts in the liquid phase remain less explored. Recent advances in liquid-jet photoelectron spectroscopy (LJ-PES),[1] particularly absolute binding energy calibration methods,[2] now allow for unprecedented precision in aqueous-phase measurements. We present the first systematic study of chemical shifts in aqueous ESCA, focusing on carbon 1s binding energy variations across key organic functional groups. We analyze trends in oxidation states, correlate measured shifts with computed partial charges, and compare liquid-phase ESCA data with gas-phase and solid-state counterparts. Additionally, we explore secondary chemical shifts propagating through adjacent bonds and discuss the complementarity of ESCA and NMR in structural analysis. Our findings establish fundamental principles for interpreting chemical shifts in solution and pave the way for broader applications of LJ-PES in molecular chemistry and materials science.

Keywords: Chemical shifts, liquid jets, ESCA, XPS, Liquid-Jet Photoelectron Spectroscopy, chemical analysis, NMR.

Acknowledgement: Work supported by the Czech Science Foundation, grant number 24-12267O.

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