HIGH-RESOLUTION PHOTOELECTRON AND PHOTOIONIZATION SPECTROSCOPY

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Since its development in the late 1950s and early 1960s [a] [b], photoelectron spectroscopy has established itself as an important method to study the electronic structure of molecules, their photoionization dynamics, and the structure and dynamics of molecular cations. In recent years, and particularly since the development of pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy [c], considerable progress has been made in the resolution that can be achieved by photoelectron spectroscopy. This progress relies on the systematic exploitation of the unusual physical properties of high Rydberg states and enables one today to resolve the rotational structure in the photoelectron spectra of even large molecules and the hyperfine structure in the photoelectron spectra of small molecules.

This talk will begin with a brief historical review of photoelectron spectroscopy. Then, the relationship between photoelectron spectroscopy, photoionization spectroscopy and the spectroscopy of high Rydberg states will be discussed. It will be explained how this relationship is currently exploited to improve the resolution achievable by PFI-ZEKE photoelectron spectroscopy. Then, the physical principles that are at the heart of the latest methods related to high-resolution photoelectron spectroscopy will be described together with their fundamental limitations. Depending on the resolution and the spectral range needed to address a specific scientific problem, a choice can be made between several different methods with spectral resolutions ranging from 30 GHz to better than 1 MHz [d].

The talk will summarize the current state of the art in gas-phase photoelectron spectroscopy and be illustrated by several examples, primarily taken from the research in my group, in which photoelectron spectroscopy has contributed to answer questions concerning the structure and dynamics of small-sized molecular cations.

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