TOWARDS THE RESOLUTION LIMIT OF PFI-ZEKE PHOTOELECTRON SPECTROSCOPY

HOLGER HERBURGER, VINCENT WIRTH, URS HOLLENSTEIN, FRÉDÉRIC MERKT, *Laboratorium für Physikalische Chemie, ETH Zurich, Zurich, Switzerland.*

The spectral resolution in Pulsed-Field Ionization Zero-Kinetic Energy (PFI-ZEKE) photoelectron spectroscopy is related to the state selectivity in the ionization process of the Rydberg states. The selectivity is determined by the applied electric field pulse sequence. Hollenstein *et al.*[a] used discrete electric field pulses with increasing field strength in combination with a preceding field pulse of opposite polarity. By using such field pulse sequences with the smallest possible field step size (i.e., approximately 9 mV/cm), a spectral resolution of $0.06\,\mathrm{cm}^{-1}$ could be achieved. To improve the resolution further Harper *et al.*[b] recently suggested replacing the sequence of field steps by a linearly increasing field, as used earlier by Reiser *et al.*[c], in combination with a prepulse of opposite polarity and obtained promising results on the PFI-ZEKE photoelectron spectrum of NO and CO_2. Using a home-built narrow-bandwidth long-pulse laser system (pulse lengths up to 50 ns) in combination with a field pulse ramp[b,c], we explore the resolution limit of this approach. To avoid overlap of spectral lines, we chose an atomic system, Ar, as test system and recorded PFI-ZEKE photoelectron spectra of transitions from the metastable states $(3p)^5(4s)[3/2]_2$ $\left({}^3P_2\right)$ and $(3p)^5(4s)'[1/2]_0$ $\left({}^3P_0\right)$ to the $(3p)^5\ {}^2P_{3/2,1/2}$ states of Ar^+. This system also offers the advantage of a precisely known ionization energy[d] with which the ionization energy determined with the new method can be compared.

[a] U. Hollenstein, R. Seiler, H. Schmutz, M. Andrist, and F. Merkt, *J. Chem. Phys.* **115**, 5461–5469 (2001).

[b] Oliver J. Harper, Ning L. Chen, Séverine Boyé-Péronne, and Bérenger Gans, *Phys. Chem. Chem. Phys.* **24**, 2777–2784 (2022).

[c] G. Reiser, W. Habenicht, K. Müller-Dethlefs, and E. W. Schlag, *Chem. Phys. Lett.* **152**, 119–123 (1988).

[d] V. L. Sukhorukov, I. D. Petrov, M. Schäfer, F. Merkt, M.-W. Ruf, and H. Hotop, *J. Phys. B: At. Mol. Opt. Phys.* **45**, 092001 (2012) and references therein.