EXPLORING THE RESOLUTION LIMIT OF PFI-ZEKE PHOTOELECTRON SPECTROSCOPY

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The spectral resolution in pulsed-field-ionisation zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy is related to the state selectivity in the diabatic ionisation of the Rydberg states by time-dependent electric fields. The selectivity is determined by the applied electric-field pulse sequence. Hollenstein *et al.*[1] used discrete electric-field pulses with increasing field strength in combination with a preceding field pulse of opposite polarity and achieved a spectral resolution of $0.06\,\mathrm{cm}^{-1}$. To improve the resolution further, Harper *et al.*[2] recently replaced the sequence of field steps by a linearly increasing field, as used earlier by Reiser *et al.*[3], in combination with a prepulse of opposite polarity and obtained promising results on the PFI-ZEKE photoelectron spectrum of NO and CO_2. They called this new method pulsed-ramped field-ionisation (PRFI)-ZEKE photoelectron spectroscopy.

Using a home-built narrow-bandwidth long-pulse laser system (pulse lengths up to $50\,\mathrm{ns}$, bandwidth$< 50\,\mathrm{MHz}$) in combination with a pulsed field ramp,[2,3] we explore the resolution limit of this approach. To avoid overlap of spectral lines, we chose the atoms Ar, Kr, and Xe as test systems and recorded PRFI-ZEKE photoelectron spectra of transitions from the metastable state $(n\mathrm{p})^5((n+1)\mathrm{s})[3/2]_2\ (^3\mathrm{P}_2)$ of the neutral rare-gas atom to the $(n\mathrm{p})^5\ ^2\mathrm{P}_{3/2}$ state of the corresponding ion, with $n = 3$, 4, 5 for Ar, Kr, and Xe, respectively. We present PRFI-ZEKE photoelectron spectra that exhibit both adiabatic and diabatic ionisation dynamics. The resolution of these spectra is improved to $0.05\,\mathrm{cm}^{-1}$ which constitutes the resolution record in photoelectron spectroscopy.[1] The determined ionisation energies are compared with precisely known literature values[4]. The current resolution is limited by adiabatic field ionisation below $n = 190$ and by electric stray fields, which affect the field-ionisation dynamics above $n = 190$.

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