HIGH-RESOLUTION PHOTOELECTRON SPECTROSCOPY OF 2-BUTYNE

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Using a coherent narrow-band vacuum-ultraviolet (VUV) laser source (bandwitdh of 0.008 cm^{-1})[a] coupled to a photoionization and pulse-field-ionization zero-kinetic-energy photoelectron (PFI-ZEKE) spectrometer, the threshold photoionization of polyatomic molecules can be studied at high resolution.
We present a new measurement of the PFI-ZEKE photoelectron spectrum of the origin band of the $X^+\ ^2E_{2(d)} \leftarrow X\ ^1A_{1(s)}$ ionizing transition of 2-butyne at a resolution of 0.15 cm^{-1}. Despite this high resolution, the spectral congestion originating from the combined effects of the internal rotation, the spin-orbit coupling and the Jahn-Teller effect prevented the full resolution of the rotational structure of the photoelectron spectrum. Combined with the known structure of the $X\ ^1A_{1(s)}$ ground state of 2-butyne, including the free internal rotation[bcd], the spectrum was used to derive information on the $X^+\ ^2E_{2(d)}$ ground state of the 2-butyne radical cation. The rotational branch structure of the spectrum points at a complex energy-level structure of the cation and at the importance of a shape resonance enhancing g photoelectron partial waves[e].

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