Symmetry breaking in core-valence double ionization of allene

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Conventional electron spectroscopy is an established one-electron-at-the-time method for revealing the electronic structure and dynamics of photoionized systems. By combining an electron-electron coincidence technique with the use of soft X-radiation we have measured a double ionization spectrum of the allene molecule in which one electron is removed from a C1s core orbital and one from a valence orbital, obtaining much more detailed information on doubly ionized systems compared to Siegbahn's Electron-Spectroscopy-for-Chemical-Analysis method. This core-valence double ionization spectrum shows the effect of symmetry breaking in an extraordinary way[1], when the core electron is ejected from one of the two outer carbon atoms. To explain the spectrum, we utilized a new theoretical approach combining the benefits of a full self-consistent field approach with those of perturbation methods and multi-configurational techniques, thus establishing a powerful tool to reveal molecular orbital symmetry breaking on such an organic molecule, going beyond Löwdin's standard definition of electron correlation. In view of the broken symmetry and the attosecond timescale on which the core-valence process must take place, we note the relevance of this work to pure electron-correlation-driven charge migration in ionized molecules as currently hunted for in experimental investigations.

Keywords: Electron-electron correlation, core-valence double ionization, symmetry breaking.

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