Time-resolved dissociation dynamics studied by inner-shell photoelectron spectroscopy

Being able to observe, in real-time, a chemical reaction such as the bond cleavage of a molecule has been an intensive subject of research in various scientific domains such as molecular physics, chemical physics, and biology. With the birth of femtosecond light sources [1], ultrafast nuclear dynamics can be routinely studied with a time resolution below 10 fs. Over the past 20 years, Time-Resolved PhotoElectron Spectroscopy (TRPES) [2],[3] has been a very popular technique to investigate the evolution of the valence electronic structure of a molecule following photoexcitation [4], [5], [6]. While this technique relies on the photoionization of a valence electron, we present here the first experiments where the UV-induced photodissociation dynamics of methyl-iodine molecule is directly imaged in the I 4d inner-shell photoelectrons that result from ionization of the molecule by an intense soft X-ray pulse from the Free Electron Laser in Hamburg (FLASH) [7]. Thanks to the high localization of the inner-shell orbitals which ensure its site-selectivity, we show that inner-shell TRPES is a more sensitive probe of the nuclear dynamics.

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