Disentangling complex relaxation dynamics in small organic molecules

The dynamics unfolding on the first few femtoseconds after optical excitation eventually define the photochemistry of many molecular systems. Following them in real time constitutes a formidable task both experimentally and theoretically. As such, most of them remain unexplored despite their importance. This is the case also for small organic molecules like ethylene, where the exact relaxation dynamics of its cation C_2H_4^+ (the simplest π radical) are not completely understood.

We used few-femtosecond vacuum-ultraviolet (VUV) pulses produced by high-order harmonic generation (HHG) in combination with a time-delay compensated monochromator (TDCM) to selectively excite the first four states of ethylene cation. The relaxation dynamics is subsequently interviewed in a pump-probe fashion by a 15-fs infrared (IR) pulse, which induces molecular fragmentation. Therefore, the delay-dependent ion yields contain a fingerprint of the ultrafast molecular dynamics followed by ethylene after ionization, which is normally hidden by the multitude of different possible mechanisms leading to the same final effect. We overcome the problem by using different VUV harmonics to selectively excite the first cationic states. Further comparison with the results obtained with the deuterated molecule, C_2D_4, and quantum-mechanical calculations allowed us to disentangle the complex dynamics that follow photoexcitation in ethylene and shed new light onto the internal relaxation process of small organic molecules.