

ULTRAFAST MOLECULAR PHOTODISSOCIATION DYNAMICS STUDIED BY FEMTOSECOND PHOTOELECTRON-PHOTOION COINCIDENCE SPECTROSCOPY

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To completely characterize photodissociation mechanisms with time-resolved spectroscopy, it is essential to obtain unequivocal experimental information about the fragmentation dynamics induced by the laser pulse. We apply time-resolved photoelectron-photoion coincidence (PEPICO) detection in combination with different excitation schemes to obtain a mechanistic picture of the fragmentation process. For gas phase acetone molecules excited to high lying Rydberg states we are able to disentangle different ionization channels and investigate the fragmentation behavior of each channel separately. In particular, the high differentiability of PEPICO allows to distinguish channels where fragmentation proceeds after ionization from channels with fragmentation in the neutral.

We show that excited Rydberg state population undergoes internal conversion due to coupling to valence states, which takes place within (150 ± 30) fs. The corresponding non-adiabatic, ultrafast relaxation dynamics to lower lying states causes conversion of electronic to vibrational energy and is found to play a crucial role in the fragmentation process (see figure 1). By studying the influence of photon energy, pulse duration, chirp and intensity of the laser pulses, we are able to determine the energy-threshold that is required for fragmentation, as well as corresponding fragmentation ratios. Surprisingly, for excitation with pulses possessing a strong negative chirp we observe significantly reduced fragmentation, indicating different internal conversion pathways and the associated intramolecular vibrational redistribution.

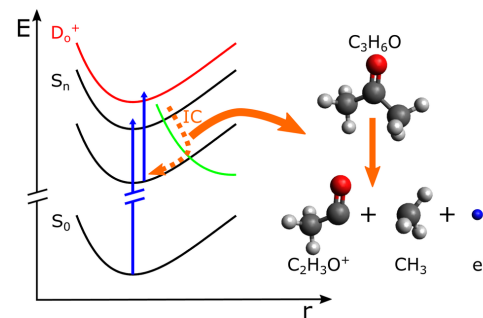


Figure 1: Schematic conversion process of electronic to vibrational energy leading to fragmentation in the ion.