Acetone Non-Adiabatic Rydberg State Dynamics: Relaxation and Fragmentation Studied by Femtosecond Photoelectron-Photoion Coincidence Spectroscopy

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For the investigation of photochemical processes with time-resolved photo-ionization spectroscopy, it is essential to obtain unequivocal experimental information about the fragmentation dynamics. Photoexcitation of acetone molecules to high-lying Rydberg states triggers complex relaxation dynamics which are governed by Rydberg-valence couplings. We apply time-resolved photoelectron-photoion coincidence (PEPICO) detection to disentangle parallel ionization channels and to follow the fragmentation and relaxation behavior of each channel separately [1]. Photoexcited population undergoes internal conversion to lower Rydberg states for which a sequential decay model reveals state-dependent decay time constants ranging from 100 to 300 fs following clear trends [3]. The corresponding non-adiabatic dynamics cause the conversion of electronic to vibrational energy leading to fragmentation after ionization to the cationic ground state (Fig. 1), for which the activation threshold can be accurately determined to be (0.79±0.04) eV [2]. Additionally, we observe a channel facilitating fragmentation of the neutral molecule (before ionization) via a Norrish-Type-I reaction [1]. These results demonstrate that in the complex situation of multiple, parallel relaxation pathways, less-differential probe techniques might not allow the unambiguous interpretation of transient signals.

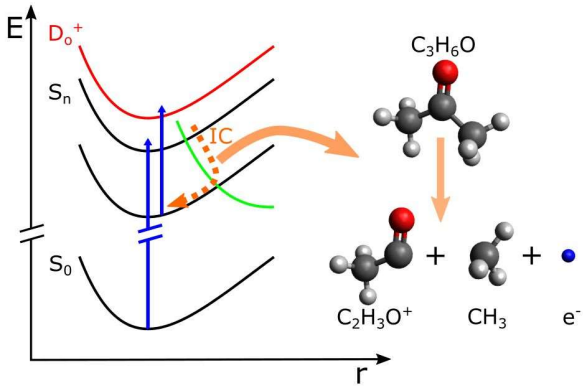

Fig. 1: Acetone photofragmentation triggered by Rydberg state (S_n) excitation.

References:

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[2] M. Koch, P. Heim, B. Thaler, M. Kitzler, and W. E. Ernst, J Phys B, accepted, https://doi.org/10.1088%2F1361-6455%2Faa6a71 (2017).

[3] M. Koch, B. Thaler, P. Heim, and W. E. Ernst, submitted (2017).