How to unveil the excited-state dynamics of radicals using time-resolved photoelectron spectroscopy

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During my thesis I examined several open-shell species. Here I want to present one of my first projects, the benzyl radical, which is exemplary of my work.

The benzyl radical is an intermediate in combustion processes and a major player in the formation of polycyclic aromatic hydrocarbons (PAHs) and soot. During combustion, however, the molecule is often excited by thermal energy into excited electronic states or even formed in such an electronically excited state. Therefore knowledge of the excited-state dynamics of the involved species is indispensable to fully understand and to correctly simulate combustion processes.

We produce the benzyl radical using the flash pyrolysis method (see Figure 1) and examined it in gas phase using time-resolved time-of-flight mass spectroscopy and time-resolved photoelectron spectroscopy (TRPES)[1]. TRPES especially allows distinguishing between different electronic states and with that technique one can therefore follow directly the passage through conical intersections. In combination with non-adiabatic dynamic calculations (field induced surface hopping, FISH[2]), this approach allows a direct molecular-level insight into the nature and time scale of the relaxation processes induced by laser excitation in the benzyl radical[3].

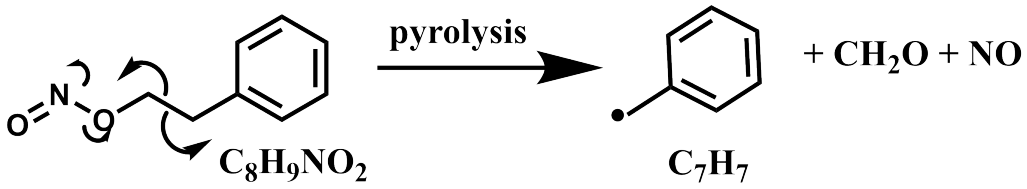

Figure 1: Production of the benzyl radical using flash pyrolysis

[1] Stolow, A., et al., *Chem. Rev.*, **2004**, *104*, 1719-1157

[2] Mitric, R., et al., *Advances of Quantum Systems in Chemistry and Physics,* **2011**

[3] Röder, A., et al., *PCCP*, **2017**, *19*, 12365-12374