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Uncovering the excited-state dynamics of radicals using photoelectron spectroscopy

Radicals are intermediates in combustion processes and major players in the formation of polycyclic aromatic hydrocarbons (PAHs) and soot. During combustion, however, the molecules are often excited by thermal energy into excited electronic states. Therefore knowledge of the excited-state dynamics of the involved species is indispensable to fully understand this process and to simulate it correctly.

We produce radicals using the flash pyrolysis method and examine them in the gas phase using time-resolved time-of-flight mass spectroscopy and time-resolved photoelectron spectroscopy (TRPES)[1]. TRPES especially allows to distinguish 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.

During this presentation the advantages of TRPES will be presented and illustrated with the excited-state dynamics of two radicals, the benzyl radical[3] and the 2-methylallyl[4] radical.

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2. Mitric, R., et al., *Theoretical Methods for Nonadiabatic Dynamics "on the fly" in Complex Systems and its Control by Laser Fields*. Advances of Quantum Systems in Chemistry and Physics. 2011, Springer.
3. Röder, A., et al., *Femtosecond Time-Resolved Photoelectron Spectroscopy of the Benzyl Radical*. Physical Chemistry Chemical Physics, 2017. **19**: p. 12365-12374.
4. Röder, A., et al., *Femtosecond Dynamics of the 2-Methylallyl Radical: A Computational and Experimental Study*. Journal of Chemical Physics, 2017. **147**(1): p. 013902.