

Excited-State Dynamics in Open-Shell Molecules

Summary

In this thesis the excited-state dynamics of radicals and biradicals were characterized with femtosecond pump-probe spectroscopy.

These open-shell molecules play important roles as combustion intermediates, in the formation of soot and polycyclic aromatic hydrocarbons, in atmospheric chemistry and in the formation of complex molecules in the interstellar medium and galactic clouds. In these processes molecules frequently occur in some excited state, excited either by thermal energy or radiation. Knowledge of the reactivity and dynamics of these excited states completes our understanding of these complex processes.

These highly reactive molecules were produced via pyrolysis from suitable precursors and examined in a molecular beam under collision-free conditions. A first laser now excites the molecule, and a second laser ionizes it. Time-of-flight mass spectrometry allowed a first identification of the molecule, photoelectron spectroscopy a complete characterization of the molecule - under the condition that the mass spectrum was dominated by only one mass. The photoelectron spectrum was obtained via velocity-map imaging, providing an insight in the electronic states involved. Ion velocity map imaging allowed separation of signal from direct ionization of the radical in the molecular beam and dissociative photoionization of the precursor. During this thesis a modified pBasex algorithm was developed and implemented in *python*, providing an image inversion tool without interpolation of data points. Especially for noisy photoelectron images this new algorithm delivers better results.

Some highlighted results:

- **The 2-methylallyl radical** was excited in the $\pi\pi^*$ -state with different internal energies using three different pump wavelengths (240.6, 238.0 and 236.0 nm). Ionized with 800 nm multi-photon probe, the photoelectron spectra shows a s-Rydberg fingerprint spectrum, a highly positive photoelectron anisotropy of 1.5 and a bi-exponential decay ($\tau_1 = 141 \pm 43$ fs, $\tau_2 = 4.0$

± 0.2 ps for 240.6 nm pump), where the second time-constant shortens for lower wavelengths. Field-induced surface hopping dynamics calculations confirm that the initially excited $\pi\pi^*$ -state relaxes very fast to an s-Rydberg state (first experimentally observed time-constant), and then more slowly to the first excited state/ground state (second time-constant). With higher excitation energies the conical intersection between the s-Rydberg-state and the first excited state is reached faster, resulting in shorter life-times.

- **The benzyl radical** was excited with 265 nm and probed with two wavelengths, 798 nm and 398 nm. Probed with 798 nm it shows a bi-exponential decay ($\tau_1 = 84 \pm 5$ fs, $\tau_2 = 1.55 \pm 0.12$ ps), whereas with 398 nm probe only the first time-constant is observed ($\tau_1 = 89 \pm 5$ fs). The photoelectron spectrum with 798 nm probe is comparable to the spectrum with 398 nm probe during the first 60 fs, at longer times an additional band appears. This band is due to a [1+3']-process, whereas with 398 nm only signal from a [1+1']-process can be observed. Non-adiabatic dynamic on the fly calculations show that the initially excited, nearly degenerate $\pi\pi/p$ -Rydberg-states relax very fast (first time-constant) to an s-Rydberg state. This s-Rydberg state can no longer be ionized with 398 nm, but with 798 nm ionization via intermediate resonances is still possible. The s-Rydberg state then decays to the first excited state (second time-constant), which is long-lived.
- **Para-xylylene**, excited with 266 nm into the S_2 -state and probed with 800 nm, shows a bi-exponential decay ($\tau_1 = 38 \pm 7$ fs, $\tau_2 = 407 \pm 9$ fs). The initially excited S_2 -state decays quickly to S_1 -state, which shows dissociative photoionization. The population of the S_1 -state is directly visible in the masses of the dissociative photoionization products, benzene and the *para*-xylylene -H.
- **Ortho-benzyne**, produced via pyrolysis from benzocyclobutendione, was excited with 266 nm in the S_2 state and probed with 800 nm. In its time-resolved mass spectra the dynamic of the ortho-benzyne signal was superposed with the dynamics from dissociative photoionization of the precursor and of the *ortho*-benzyne-dimer. With time-resolved ion imaging gated on the *ortho*-benzyne these processes could be separated, showing that the S_2 -state of *ortho*-benzyne relaxes within 50 fs to the S_1 -state.