Project title: Transient absorption spectroscopy and coherences of molecules in the gas phase

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Current state of the art

Electronic and vibrational coherences are highly relevant for the ultrafast dynamics in molecular systems. They allow for novel ultrafast switching and transport processes [1]. As long as electronic coherences persist, coherent motion of an electronic excitation corresponding to the propagation of a wavepacket is feasible. At the same time coherent nuclear motions and vibrations can modulate electronic transition energies and induce electronic state changes via vibronic coupling [2]. In several systems indications for electronic coherences have been already found [1, 3, 4]. However, a clear assignment to electronic or nuclear coherences is not straight forward and currently subject of an intense research and debate [5, 6]. One issue is the fast dephasing of electronic coherences. The interaction with a thermal environment is a main source for dephasing processes. These interactions do not occur in molecules in the gas phase, which leads to longer lifetimes of the coherences, which can then be studied much more effectively.

Research goals and working program

The central goal of the present project is to implement an ultrafast transient absorption experiment for molecules in the gas phase. The increased lifetime of the coherences compared to the solution is expected to enable a detailed analysis of the wavepacket dynamics and the coupling between the involved degrees of freedom. A suitable pump-probe setup based on non-collinear optical parametric amplifiers is available. It provides tuneable ultrashort laser pulses with a duration of about 20 fs allowing for the necessary high time resolution. We applied this kind of setup already to investigate by femtosecond transient absorption spectroscopy vibrational coherences in ultrafast excited state proton transfer and were able to reconstructed from the analysis of the observed wavepacket motion the reaction path, see Fig.1[7].

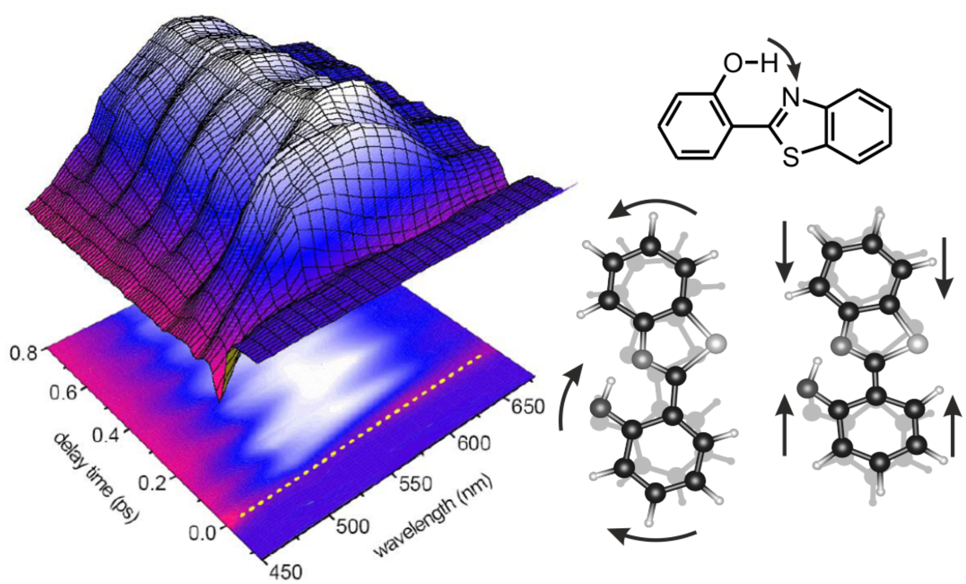

Figure 1: Coherences observed by femtosecond transient absorption spectroscopy in ultrafast proton transfer: The very fast transfer process induces vibrational coherences which are dominated by the vibrational modes shown on the right.

The planned experiments will be performed on small organic molecules such as thiophene, pyridine and pyrrole. They exhibit a high vapor pressure already at slightly elevated temperatures making them suitable for transient absorption measurements in the gas phase. The existing pump-probe setup will be extended by a heated, gas tight cell with thin windows as sample container. Since the considered molecules absorb in the UV the output of the NOPAs will be frequency doubled to obtain excitation and probe pulses in this spectral range. While thiophene and pyridine show slow dynamics pyrrole is known for a fast H-atom elimination [8]. The comparison will reveal the characteristic behaviour of the wavepacket dynamics in the different situations.

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