

## Project title: Transient absorption spectroscopy of electronic coherences

Supervisors: Stefan Lochbrunner (German PI), Albert Stolow (Canadian PI)

### Current state of the art

Electronic coherences in molecular systems have become recognized as a "grand challenge" in Molecular Physics since they will allow for novel ultrafast switching and transport processes [1]. As long as electronic coherences persist, an electronic wavepacket can be formed and coherent motion of an electronic excitation corresponding to the propagation of the wavepacket is feasible. At the same time nuclear motions can modify electronic coherences and induce electronic 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, 7]. The present project will therefore deal with the challenge to find observables which are in an unique way sensitive to electronic coherences and allow to disentangle electronic from nuclear contributions. The understanding of this fundamental process will lead to new strategies for controlling electronic processes in complex molecular systems.

### Research goals and working program

The central goal of the present project is to implement ultrafast spectroscopic experiments which provide observables and signatures that can unambiguously be linked to electronic coherences in molecules. To this end, we will focus in the orientation of electronic transition dipole moments and the polarisation of the associated transient absorption signals. In this case, the coherent electronic dynamics can be disentangled from signatures due to nuclear motions and its characteristic features and temporal evolution can be analysed in depth. Understanding these dynamics is of crucial importance in designing future quantum technologies involving efficient switching processes and transport of charges and excitation energy.

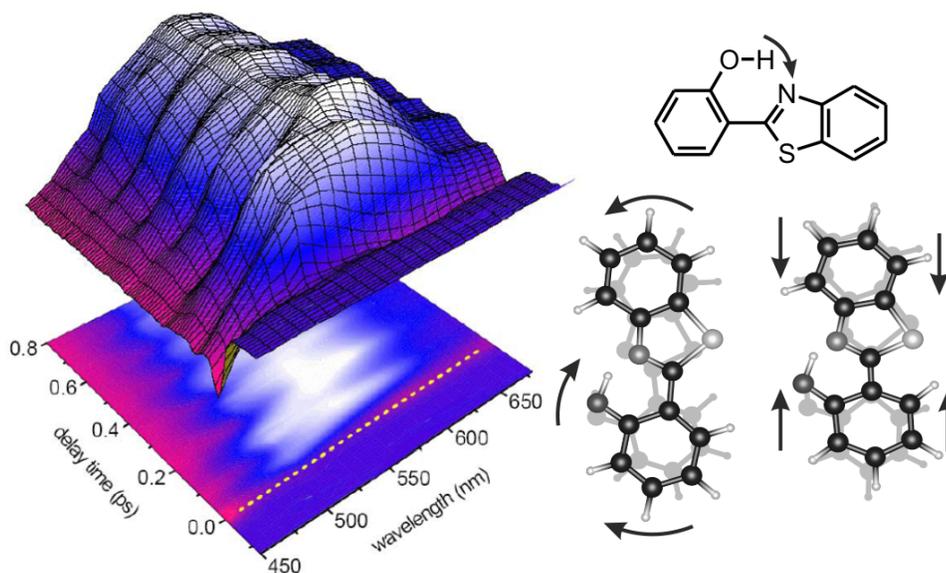


Figure 1: Coherences observed by femtosecond transient absorption spectroscopy in ultrafast proton transfer: The very fast transfer process induces vibrational coherences which are dominated by the vibrational modes shown on the right.

The experiments will be performed on molecular chromophores exhibiting a pair of optically addressable, electronically excited states. By means of an ultrashort pump pulse, a superposition of these states will be prepared. In polarisation sensitive ultrafast pump-probe experiments the orientation of the transition dipole to other electronic states will be monitored in time. As long as a coherence between the two excited electronic states exists, the transition dipole should change its direction periodically. In contrast to oscillations in the signal intensity or spectral position of absorption and emission bands, the orientation of the electronic transition dipole is a unique feature of the electronic part of the molecular wavefunction and not affected by vibrations. One challenge will be the vibronic coupling between the two excited states and the associated ultrafast non-Born-Oppenheimer dynamics calling for experiments with a very high time resolution. However, its understanding is crucial for the design of processes and applications based on electronic coherences in molecules.

The actual experiments are pump-probe measurements on porphyrines in solution using different polarisations for the excitation and the probe pulses. This polarisation sensitive transient absorption spectroscopy should reveal oscillatory signatures in the anisotropy reflecting the electronic coherences. The experimental setup is based on non-collinear optical parametric amplifiers providing tunable 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 reconstruct from the analysis of the observed wavepacket motion the reaction path, see Fig.1[8]. Furthermore, we have also experience in studying the time dependent anisotropy of the absorption signal in a similar way as proposed here. E.g., we uncovered by this approach an interligand electron transfer process in an iridium complex [9].

The design and analysis of the experiments will be guided by advanced quantum dynamics simulations which are conducted in close collaboration in a partner project of Oliver Kühn and in which the time-dependent observables are directly simulated. In addition, we combine our own expertise in femtosecond absorption spectroscopy of ultrafast molecular processes with that of Albert Stolow on time-resolved photoelectron spectroscopy to study related processes in the gas phase where dephasing processes are strongly reduced.

- [1] G. D. Scholes, G. R. Fleming, L. X. Chen, A. Aspuru-Guzik, A. Buchleitner, D. F. Coker, G. S. Engel, R. van Grondelle, A. Ishizaki, D. M. Jonas, J. S. Lundeen, J. K. McCusker, S. Mukamel, J. P. Ogilvie, A. Olaya-Castro, M. A. Ratner, F. C. Spano, K. B. Whaley, and X. Zhu, *Using coherence to enhance function in chemical and biophysical systems*, Nature **543**, 647 (2017).
- [2] H. Köppel, W. Domcke, and L. S. Cederbaum, *Multimode molecular dynamics beyond the Born-Oppenheimer approximation*, Adv. Chem. Phys. **57**, 59 (1984).
- [3] G. S. Engel, T. R. Calhoun, E. L. Read, T.-K. Ahn, Tomáš Mančal, Y.-C. Cheng, R. E. Blankenship, and G. R. Fleming, *Evidence for wavelike energy transfer through quantum coherence in photosynthetic systems*, Nature **226**, 782 (2007).
- [4] V. Butkus, J. Alster, E. Bašinskaitė, R. Augulis, P. Neuhaus, L. Valkunas, H. L. Anderson, D. Abramavicius, and D. Zigmantas, *Discrimination of diverse coherences allows identification of electronic transitions of a molecular nanoring*, J. Phys. Chem. Lett. **8**, 14732 (2017).
- [5] A. P. Spencer, W. O. Hutson, and E. Harel, *Quantum coherence selective 2D Raman-2D electronic spectroscopy*, Nat. Commun. **8**, 14732 (2017).
- [6] H.-G. Duan, V. I. Prokhorenko, R. J. Cogdell, K. Ashraf, A. L. Stevens, M. Thorwart, and R. J. D. Miller, *Nature does not rely on long-lived electronic quantum coherence for photosynthetic energy transfer*, Proc. Natl. Acad. Sci. U.S.A. **114**, 8493 (2017).
- [7] C. C. Jumper, S. Rafiq, S. Wang, G. D. Scholes, *From coherent to vibronic light harvesting in photosynthesis*, Curr. Opin. Chem. Biol. **47**, 39 (2018).
- [8] S. Lochbrunner, A. J. Wurzer, and E. Riedle, *The microscopic mechanism of ultrafast excited state proton transfer: a 30 fs study of 2-(2'-hydroxyphenyl)benzothiazole*, J. Phys. Chem. A **107**, 10580 (2003).

- [9] S. Tschierlei, A. Neubauer, N. Rockstroh, M. Karnahl, P. Schwarzbach, H. Junge, M. Beller, and S. Lochbrunner, *Ultrafast excited state dynamics of iridium (III) complexes and their changes upon immobilisation onto titanium dioxide layers*, Phys. Chem. Chem. Phys. **18**, 10682 (2016).