

## **Exploring and Exploiting Molecular Coherences**

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Many concepts for controlling molecular processes rely on coherences persisting for a sufficient amount of time. E. g. vibronic wavepackets with a controllable initial momentum or interferences between wavepackets can be exploited to steer the dynamics in a molecule. However, such schemes can only work if the coherent wavepacket motion is related to the reaction path and dephasing processes are slower than the control process. We present investigations of vibrational and electronic coherences in molecules, that clarify their relation to the reactive dynamics and characterize the usable time window.

We establish for proton transfer compounds the connection between the wavepacket motion and the reaction path by femtosecond spectroscopy of [2,2'-bipyridyl]-3,3'-diol which contains two reactive H-chelate rings. The two protons of the two rings can be transferred in a concerted or in a sequential way. Decreasing the excitation wavelength leads to an increase of the sequential transfer yield and simultaneously to a stronger coherent excitation of an antisymmetric bending vibration. Thus, changes of the wavepacket motion are associated with changes in the reaction path. In addition, the excitation of an antisymmetric mode must be due to the symmetry breaking sequential reaction path since selection rules do not allow for a direct optical excitation.

To drive vibrational coherences in medium sized molecules via electronic transitions, a setup for the generation of shaped pulses or pulse trains in the UV was developed. The visible output of a NOPA is shaped by a liquid crystal mask in a 4-f-arrangement. The resulting pulse is converted to the UV by sum frequency mixing with a strongly stretched NIR pulse. This leads to a direct transfer of the visible phase and amplitude allowing for highly structured UV pulses with almost arbitrary phase and amplitude properties. Thereby complex pulse shapes with substructures down to 20 fs are generated [1].

Vibrational and electronic dephasing are characterized in a perylene bisimide dye in solution. The vibrational dephasing time in the electronically excited state is deduced from the damping of vibrational coherences generated by 10 fs pump pulses. To separate the contribution of population redistribution from pure dephasing, the population kinetics are measured separately via the time dependent intensity of specific vibronic transitions in the emission. The analysis shows that dephasing occurs on a time scale of 1 ps and that population redistribution and pure dephasing contribute with similar strength. Using double pulses and varying the relative phase of the carrier waves, the electronic decoherence time was determined from the population rise in the  $S_1$  state to about 70 fs.

[1] C. Schrieffer, S. Lochbrunner, M. Opitz, and E. Riedle, *Opt. Lett.* **31** (2006), 543.