

Perspectives for Time Resolved Structural Studies Derived from Pump-Probe Spectroscopy

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Advances in the structure resolving techniques will enable to follow the time evolution of nuclear coordinates during reactions of chromophores in the condensed phase. Evidence for coherent contributions in a crystalline environment, even for large bond elongation comparable to a transition state, is derived in this report from pump-probe spectra of vibrational wave packets. We discuss three examples demonstrating intramolecular vibrational and electronic coherence as well as long-lasting coherences induced in the surroundings. The different types of coherence can provide interesting topics for future structural investigations. They form the basis for coherent control in the multidimensional solid phase with strong interactions.

On a dissociative electronic state, recombination imposed by the environment is accompanied by an energy loss of several thousand wavenumbers in the first hard collision. Nevertheless, vibrational coherence is transferred to the lower energetic vibrational manifold indicated by a high modulation contrast in the subsequent wave packet dynamics¹. This contrast is maintained even for a nonadiabatic transition to another electronic state.

Coherence among a well-defined subgroup of vibrational levels can be displayed via the evolution of fractional revivals. Dispersion on the anharmonic molecular potential is a prerequisite for the revivals and they occur after some ten ps, beyond typical times for an irreversible loss of phase. We demonstrate that an appropriate linear chirp advances the fractional revivals. For Br₂:Ar a 1/6 revival is shifted from 3.5 ps to 1.2 ps, and the dephasing time for four coherently coupled vibrational levels of 1 ps is derived in this way. The chirp extends the pulse duration beyond the vibrational period of 270 fs. The fidelity in the imprint of the phase information during the electronic excitation with the pump pulse clarifies that the electronic dephasing time in the crystalline environment exceeds several hundred fs². The revivals are a consequence of spatial interference patterns of the wave packets and to follow them in time with structural methods can provide deep insight in the propagation properties.

The change in the electronic wave function during the pump process provides an initial kick to the surroundings with a subsequent oscillation around the new equilibrium position. We show that it is possible to single out for a diatomic chromophore those surrounding atoms which respond to the kick and are, however, decoupled from the chromophore vibration. A pronounced oscillation with the zone boundary phonon frequency of the solvent, lasting more than 40 intramolecular periods, can be monitored in this case. It originates from the modulation of the terminal state energy of the probe process³.

¹ M. Bargheer, M. Gühr, N. Schwentner, "Collisions transfer coherence." *Israel J. Chem.* **2004**, 44, 9-17

² M. Gühr, H. Ibrahim and N. Schwentner, "Controlling vibrational wave packet revivals in condensed phase: Dispersion and coherence for Br₂ in solid Ar.", *Phys. Chem. Chem. Phys.*, **2004**, 6, 5353 – 5361

³ M. Gühr, M. Bargheer, N. Schwentner, "Generation of coherent zone boundary phonons by impulsive excitation of molecules", *Phys. Rev. Lett.*, **2003**, 91, 085504

