Electronic Phase Relaxation and Structural Equilibration in a Molecular Polymer as Studied by Femtosecond-Coherence Spectroscopy

H. F. Kauffmann
Institut für Physikalische Chemie, Universität Wien, Österreich

Ultrafast fs-coherences that control the electronic/nuclear precursor routes of both polaronic-and neutral excitations have been investigated in conjugated polymers and related oligomeric model-compounds. In part 1 of this talk, *fluorescence wavepacket interferometry* will be presented which enables to measure coherent responses and their phase-relaxation. The coherences have been interrogated by the energy-selective fluorescence correlation signal and follow the functional form of discrete superpositions of site optical Free-Induction-Decays (oFID). The experiments enable to look into the homogeneous site-dephasing process
In part 2, time-integrated *3-pulse photon echo peak-shift* experiments have been employed to study electronic and vibrational motion in both a soluble, conjugated polymer and a series of oligomer-type model-compounds by using 70 fs, 200 kHz and sub-20 fs, 1 kHz tunable pulses in non-polar sovents. The combination of experiments figures –out three typical, ultrafast correlations (i) segmental solute – solvent scattering, (ii) intra-molecular site relaxation in the solute-segments(dyes) , and (iii)excitonic inter-site communication in the polymer and related ensembles of the oligomers. The profiles generated by the sub-20fs pulses exhibit persistent oscillatory behavior up to several ps with initial peak-shifts on sub-30 fs bases indicative of separable time-scales for electronic and nuclear dephasing in this regime. The preliminary results imply strategies to be devised for the design of multi-dimensional, optical photon-echo spectroscopies They may have the potential to measure excitation inter-site cross peaks and thus to elucidate excitation-phonon coupling and site-to-site electronic scattering from homogeneous dephasing, without any preconceived bias. The complications connected with n-D optical spectroscopy set-ups will be addresse