

Doctoral thesis abstract

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Ultrafast transient absorption in infrared; experimental setup development and measurement of proton transfer dynamics in 7-hydroxyquinolin-8-carbaldehyde derivatives

The main topic of the dissertation is design and development of an optical setup for time-resolved transient absorption spectroscopy in infrared. The setup is based on a 100 kHz repetition rate source consisting of a Ti:sapphire femtosecond oscillator and a regenerative amplifier. The source produces 75 fs long pulses with 6 μJ energy per pulse. Following are two nonlinear stages: optical parametric amplifier (OPA) and difference frequency generation (DFG). These stages produce infrared probe pulses tunable in the range of 2.4 – 10.5 μm . The pump pulse is a second harmonic (400nm) of the source infrared.

In the setup a new home-built compact infrared camera with two dimensional focal plane array based on a HgCdTe semiconductor alloy was introduced. The camera is sensitive in the range of 1.7 – 10.5 μm . It allows to measure 3 different infrared spectra derived from the same infrared source simultaneously thus extending measurement capabilities and decreasing detection noise.

Operating parameters of the optical setup were characterized. Spectra and energies of ultrashort actinic and probing pulses were measured. Temporal instrumental response function was determined using transient absorption in silica and cross-correlation frequency-resolved optical gating (XFROG). Noise analysis proving superior short-term stability of the infrared pulse train was performed. The typical RMS noise achieved in real sample measurements was estimated around 20 μOD .

Spectroscopic measurements were performed on two chemical systems. Solutions of coumarin 337 in acetonitrile and electron-donating N-methylaniline served as a reference for setup tuning. The obtained results showing an intermolecular electron transfer process were compared to earlier published in literature and discussed.

The original measurements were performed on acetonitrile solutions of two methyl derivatives of 7-hydroxyquinolin-8-carbaldehyde. An excited-state prototropic tautomerisation mechanism called „molecular crane” was postulated for these molecules in literature. The available actinic pulse wavelength allowed to selectively excite one of the ground-state tautomeric forms and monitor the following vibrational dynamics in order to verify the mechanism. As a result of a series of ultrafast transient absorption measurements accompanied by ultrafast fluorescence measurements, a hypothesis covering the excited state kinetics of the compounds was proposed. The observed fluorescence decay was assigned to intersystem crossing, while ultrafast vibrational dynamics was explained with possible excited state intramolecular proton transfer (ESIPT).

Several other chosen measurement results were published in the appendix.