PhD summary (download PhD dissertation in Polish)

Femtosecond spectroscopy is nowadays one of the most progressive fields of science, in which many researchers from different disciplines (like physics, chemistry, biology, and medicine) are involved. Although the spectroscopy on this time scale is not older than 20 years, at present the laser systems which produce such ultrashort pulses are easily available and more and more laboratories are equipped with this experimental tool. The principles of the most popular spectroscopic techniques, in particular two-pulse (pump-probe) methods, are independent of the time scale on which they are used. However, when using femtosecond laser pulses, many physical side-effects have occurred which were not observed on longer time scales. Since a lot of researchers are not aware of their existence this may often cause the wrong interpretation of the experimental results. Thus, the basic aim of this PhD thesis is a detailed analysis of numerous linear and nonlinear physical phenomena which may be present in the femtosecond pump-probe spectroscopy.

In chapter 1 the mathematical treatment of ultrashort pulse propagation is shortly discussed. Chapter 2 is dedicated to linear effects related to the group velocity dispersion effect and polarization of the laser beams. When the femtosecond pulse passes through optical elements or sample cells, the transit times of different spectral components of the pulse (or transit times of different pulses at different wavelength) are comparable to the duration of the laser pulse. Therefore the group velocity dispersion becomes very important on the femtosecond time scale. Chapter 3 is dedicated to nonlinear physical processes. They are commonly observed when dealt with the femtosecond pulses since their short time duration results in high power densities in the media even for relatively weak pulse energy. The following effects belong to this category: white light continuum generation, multiphoton absorption, nonlinear Raman scattering, cross phase modulation, and optical Kerr effect. Both chapter 2 and 3 include many experimental results, as well as thorough literature review, a lot ofnumerical simulations, and some novel theoretical approaches.

The description of the experimental setup for transient absorption measurements is presented in chapter 4. A procedure of the elimination of all the possible aforementioned physical and photochemical distortions is also proposed. In chapter 5 the extension of this procedure to other widely used femtosecond pump-probe techniques (time-resolved Raman scattering, up-conversion and photon echo) is discussed. The example usage of the side-effects elimination scheme is presented in chapter 6. The analysis of femtosecond transient absorption measurements of one of the model photochromic Schiff bases compound (BSP) allows the determination of the time constant of excited state proton transfer process, which is one of the fastest reaction known in nature. The full deactivation path of the BSP molecule was also obtained, which is important for the applications of such photochromic systems.