Advances in femtosecond multiphoton absorption spectroscopy of organic systems
Aleks Rebane
Physics Department, Montana State University, Bozeman, MT 59717, USA

Multiphoton absorption (MPA) is an instantaneous process where two or more photons induce a transition from a lower-energy state to a higher-energy state, such that the energy difference between the states equals the combined energy of the absorbed photons. Probability of such transitions is notoriously low under ambient illumination conditions, but the efficiency of higher-order excitations increases rapidly with increasing photon flux. Due to proliferation of femtosecond lasers delivering $> 10^{30}$ photon cm$^{-2}$ s$^{-1}$, the emerging applications of two-photon absorption (2PA) and three-photon absorption (3PA) are thriving, especially in life sciences and materials research. Furthermore, critical improvements achieved in the experimental determination of multi-photon absorption cross sections is facilitating quantitative analysis of underlying molecular parameters, which has been a long-standing goal of the MPA research.

In this talk will summarize some recent results and advances, where quantitative multiphoton techniques are applied to a broad range of systems, including fluorescent proteins, DNA nucleotides, organometallic charge transfer complexes, porphyrin oligomers and pyrollo-pyrroles, just to name a few. In many cases, the experimentally measured multiphoton spectra deliver answers to important fundamental questions that more traditional studies including quantum-chemical calculations cannot provide. For example, it is well known that many chromophores that possess nominal inversion symmetry, in practice have their symmetry spontaneously lowered. Because in the parity-preserving systems multiphoton transitions follow strict selection rules, quantifying the strength of (nominally) parity-forbidden multi-photon transitions helps pinpointing physical mechanisms responsible for the breaking of symmetry. Another unique feature of MPA experiments is that they offer quantitative data about electrostatic dipole moments of complex systems, which are other methods fail to achieve. With this unique capability at hand, one can study how electrons behaves in metal-to-ligand charge transfer processes and perhaps even probe elusive intramolecular electric fields responsible for much of the higher-order structure and functionality of biomolecules.