Summary

This Thesis deals with simulations of chiroptical spectra using a combination of molecular dynamics and quantum chemistry. Molecular dynamics was used to explore conformational behaviour of studied systems (proteins), quantum chemistry for calculation of spectral properties. The Quantum chemical methods are limited to relatively small systems. We overcome this problem mostly by a fragmentation of studied systems, when smaller, computationally feasible, fragments are created and used for the quantum chemical calculations. Calculated properties were then transferred to the big molecule.

Vibrational Optical Activity (VOA) spectra of poly-L-glutamic acid fibrils (PLGA), insulin prefibrillar form and native globular proteins were studied. The simulated spectra provided satisfactory agreement with the experiment and were used for its interpretation. Experimental Vibrational Circular Dichroism (VCD) spectra of poly-L-glutamic acid fibrils were only qualitatively reproduced by the simulation. We could reproduce the major amide I band and a smaller negative band associated with the side chain carboxyl group.

Our simulation procedure was then extended to a set of globular proteins and their Raman Optical Activity (ROA) spectra. Here we achieved an exceptional precision. For example, we were able to reproduce the main experimental differences between α-helical human serum albumin and concanavalin A containing mainly β-sheets, or between very similar human and hen egg-white lysozymes. In case of insulin fibrils, we found how the ROA technigue is sensitive to protein coformational changes. By using our simulation, we were able to extract the information of molecular structure and flexibility from the spectra.

Chiral systems were also studied by Electronic Circular Dichroism (ECD) and Circularly Polarized Luminiscence (CPL) spectroscopies. Using ECD we studied how the metal ion influence ECD spectra of respective metal-monensin complexes. The second project dealt with CPL of racemic europium complex induced by interaction with aminoacids.

The Thesis also contains methodical projects dealing with implementation of helical periodic boundary conditions in molecular dynamics and transfer of frequency-dependent polarizabilities for calculation of UV-vis and ECD spectra of larger systems.

Keywords: Molecular Dynamic, Spectra Simulations, Quantum Chemistry, Chirality, Optical Activity