Structure and dynamics of complex hydrogen-bonded systems
Bodis, P.

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Summary

The hydrogen bond is an essential structural feature that determines the physical and chemical properties of many substances. Hydrogen bonding keeps water in the liquid phase, and is one of the key elements that defines the structure of DNA. In this thesis, we investigate the structural dynamics of two types of complex hydrogen-bonded systems: rotaxanes and liquid water. Rotaxanes are a novel class of molecules that have become model compounds for molecular devices. They consist of a macrocyclic ring trapped onto a linear thread by two bulky stoppers. The thread may contain locations where the macrocycle preferably resides, so-called binding stations. The individual components of rotaxane-based devices are capable of performing mechanical motion with respect to each other when externally triggered by for example light. In the rotaxanes studied in this thesis, the thread and macrocycle are linked by means of hydrogen bonds. This allows for a large flexibility in the choice of the external stimulus, and accurate control over various co-conformations at ambient temperature. The second hydrogen-bonded system studied in this thesis, liquid water, has been the subject of many studies due to its exceptional role in biological and chemical processes. However, many questions regarding its structural dynamics and vibrational relaxation still remain unanswered.

To be able to follow the structural dynamics in these complex systems we need a tool that has both sufficient time resolution as well as sensitivity to structural changes in the proximity of hydrogen bonds. We find that 2D-IR and three-pulse photon echo spectroscopy are suitable techniques to observe the equilibrium structure and structural fluctuations of hydrogen-bonded rotaxanes. The mid-infrared spectral region provides us with the required structural sensitivity since the vibrations of hydrogen-bonded groups are sensitive probes of the hydrogen bonds. Initially, we focus on the equilibrium structure of a [2]rotaxane in solution using 2D-IR and 2-color vibrational spectroscopy. These techniques are applied to the CO-and NH-stretch modes of the system, both of which are sensitive to hydrogen-bonding. By plotting the pump-probe data as a 2D-graph with the frequencies of the probe and pump beam along the axes, one can observe so-called diagonal and
off-diagonal peaks. The diagonal peaks can be explained as a regular pump-probe signal, while the intensity of the cross-peak peaks is proportional to the coupling between different vibrational modes. Performing these experiments at parallel and perpendicular polarizations of the pump and probe beams with respect to each other, we can determine distances and angles between specific bonds in the two components of the rotaxane. While in the 2D-IR experiment we excite one CO-stretch and probe another CO-stretch mode, the two-color experiment zooms in on the coupling between the NH-stretch and CO-stretch modes. We show that 2D-IR spectroscopy can be used to determine the structure of rotaxanes with subpicosecond time resolution.

As a next step we focus on the structural fluctuations of rotaxanes. Using photon echo-peak shift spectroscopy we can study the flexibility of molecular machines on a nanoscopic level. Our findings suggest that structural flexibility or stiffness of the mechanically interlocked rotaxane is very similar to that of other hydrogen-bonded systems. Thus, when discussing molecular machines based on rotaxanes, we should consider them as constructed from pieces of rubber band rather than as molecular meccano.

Finally, we use UV-pump IR-probe spectroscopy to control and observe the shuttling of a molecular machine. This intermolecular motion can be triggered with UV photons, and mid-IR light is used subsequently to follow the structural changes within the device. We can thus investigate the elementary events of the shuttling mechanism. Our investigation of the shuttling rate in the succinamide-naphthalimide rotaxane as a function of temperature and length of the thread shows that the shuttling process involves two steps. It starts with the escape of the macrocycle from the succ station, followed by the macrocycle residing shortly on the thread. We find that the motion of the macrocycle during the latter step is a one-dimensional, biased, random walk, which makes it fundamentally different from motion in macroscopic devices. The final step is the rapid binding to either the initial succ or to the final ni station.

The last two chapters of this thesis are concerned with the vibrational relaxation of the water bending mode in isotopic mixtures of H$_2$O and D$_2$O. In spite of the vast amount of experimental and theoretical studies, the mechanism of the vibrational relaxation of the bending mode in water is as yet not well known. We investigate the concentration and temperature dependence of the H$_2$O bending-mode relaxation rate using IR pump-probe spectroscopy to elucidate this mechanism. We find that the relaxation rate increases at higher concentrations, and decreases with rising temperature. Using a simple semi-quantitative model, we find that we can describe the observed temperature dependence. Based on our experimental data and simulations we conclude that upon the excitation of the H$_2$O-bending mode the most probable channel of the energy dissipation is via the libration mode.