Water Interacting with interfaces, ions and itself

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Summary

In this thesis I present a series of experiments which elucidate the structure and dynamics of molecules involved in various biologically relevant systems. The understanding of these molecular-scale properties is crucial for understanding the behavior of biological systems as a whole. Most of our work is dedicated to water, which plays a crucial role in mediating and actively participating in biochemical reactions.

Many biochemical processes occur on very short timescales - sometimes even on a millionth of a millionth of a second (picosecond). In order to capture molecules as they take part in a molecular process (in analogy to taking a picture of a fast moving object in a macroscopic world), we use ultrashort (femtosecond) laser pulses as ‘flashes’ for our experimental ‘camera’. The molecules are ‘seen’ via their molecular vibrations, which, due to the sensitivity of the vibrational frequency to the structure, conformation and direct environment of the molecule, form an excellent probe to study a large range of biomolecular systems.

In many of these experiments we use two laser pulses. The first of the two pulses excites a molecule (in this thesis water or N-methylacetamide) to the first excited vibrational state. With the second, weaker pulse we monitor the dynamics of the excited molecule. These dynamics comprise the orientational motion, the hydrogen-bond dynamics, the resonant energy transfer to other molecules, and the relaxation of the excitation by which the molecule returns to the vibrational ground state. Hence, this experiment provide useful information about the molecular motions and the interactions of the molecule with its surroundings.

For some of the experiments we have expanded the experimental setup to a two-dimensional pump-probe scheme, where the two dimensions are the frequencies of the pump and probe pulses. The excitation of one of the vibrational resonance, while probing the other provides information on the coupling between the different vibrational modes, and thereby on the relative orientation and position of the molecular groups on which these modes are located.

The molecules of interest are not always forming a bulk medium. In many cases water molecules are located at various interfaces like a cellular water-membrane interface. In order to obtain information about those molecules we used time-resolved two-dimensional sum frequency generation (SFG) spectroscopy. This technique allows us to probe vibrational properties of only the molecules located at the interface. It thus provides highly surface-specific information on interfacial energy flow patterns which is essential for the understanding of chemical processes at aqueous interfaces.
Resonant energy transfer in bulk water
In chapter 4 I report on the study of the vibrational energy relaxation and resonant vibrational (Förster) energy transfer of the OD stretch vibrations of pure D$_2$O and mixtures of D$_2$O and H$_2$O. We monitored the occurrence of vibrational resonant energy transfer (VRET) of the OD vibrations by measuring the dynamics of the anisotropy of the vibrational excitation of the OD vibration for different concentrations of HDO in H$_2$O. With increasing HDO concentration, the distances between the OD oscillators decrease and the anisotropy decay becomes faster, showing the increased contribution of resonant energy transfer between the OD oscillators. For pure D$_2$O the anisotropy decays with a time constant of $\sim 150$ fs, showing that the transfer of vibrational energy between different D$_2$O molecules is extremely efficient. We find the ratio of Förster resonant energy transfer rates of the OH vibrations of H$_2$O and the OD vibrations of D$_2$O to be $\sim 2.3$. This ratio can be well explained from the difference in cross-section and spectral distribution of the OD and the OH stretch vibrations in water and heavy water.

Water interacting with ions
In chapter 5, I report results of our studies on the vibrational relaxation dynamics of the bending mode of the H$_2$O water molecules in the presence of different salts (LiCl, LiBr, LiI, NaI, CsI, NaClO$_4$ and NaBF$_4$). We find that the bending mode of water molecules that are hydrogen-bonded to an anion exhibit much slower relaxation rates ($T_1 \sim 1$ ps) than water molecules that are hydrogen-bonded to other water molecules ($T_1 = 400$ fs). The effect of the anion on the absorption spectrum and relaxation time constant of the water bending mode is not only determined by the strength of the hydrogen-bond interaction but also by the shape of the anion. For ClO$_4^-$ and BF$_4^-$ the water forms its hydrogen bond towards the narrow O–O and F–F ridges of the ions, and we find that this special geometry affects the linear and nonlinear spectral response of the bending mode of the water molecule.

Vibrational relaxation in NMA molecules
In chapters 6 and 7 I report the results of 2-dimensional polarization-resolved pump-probe experiments on a model system for small peptide model molecules - N-methylacetamide (NMA). We studied the pathways of vibrational energy relaxation of the amide I and amide II vibrational modes of hydrogen-bonded NMA aggregates and single NMA molecules.

The results for the hydrogen-bonded NMA aggregates show that there is no energy transfer between the amide I and amide II modes. Instead we find that irrespectively of which mode is excited, the vibration relaxes via rapid energy transfer to a non-thermal intermediate state. This relaxation is followed by a second process that leads to full thermal equilibration of the excitation energy. The spectral dynamics associated with the latter relaxation step shows that the thermalization involves the dissociation of larger NMA aggregates like trimers and higher order structures, into dimers and monomers.

In chapter 7 I report on our study of the vibrational energy relaxation mechanisms of the amide I and amide II modes of NMA monomers. In contrary to
the results for the hydrogen-bonded NMA clusters, we find that for part of the NMA molecules (∼20%) the excited amide I vibration transfers its excitation energy to the amide II vibration with a time constant of 8.3±1 ps (with a back transfer time constant of 16.6±2 ps). In addition to this energy exchange process, we observe that the excited amide I and amide II vibrations both relax to a final thermal state. For the amide I mode this latter process has a time constant of ∼1.5 ps, which dominates the vibrational relaxation of this mode.

Using polarization-resolved measurements, we find that the average reorientation time of the amide I vibration within the NMA aggregates is ∼6 ps, whereas for a single NMA molecules this reorientation time is longer and amounts to ∼9 ps. This difference in reorientation time can be well explained from the difference in viscosity of the solvents used in the experiments. The relative angle between the transition dipole moments of the amide I and amide II modes is \( \theta(AI,AII) = 56^\circ \pm 3^\circ \), and is unaffected by the presence of inter-NMA hydrogen bonds.

**Distribution of water molecules in lipid membranes**

In chapter 8 we study water molecules embedded in 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) model membranes. We investigate the effect of the local environment of the membrane on the vibrational relaxation properties of water, at various hydration levels (∼2-12 water molecules per lipid). We find that water molecules at the membrane’s interface experience very different local environments, depending on which site of the lipid they are hydrogen-bonded to. Water molecules forming strong hydrogen-bonds with phosphate and carbonyl groups relax faster than water molecules that are hydrogen-bonded to other water molecules. We investigate the anisotropy decays of water molecules for different isotopic compositions (D\(_2\)O/H\(_2\)O) of the hydrating water. We find that for isotope ratios D\(_2\)O/H\(_2\)O >0.1 the main contribution to the anisotropy decay comes from vibrational resonant energy transfer (VRET). The rate of VRET gives information on the distribution of water molecules at the membrane surface. Our findings demonstrate that the distribution of water molecules is highly inhomogeneous in tightly packed membranes. Throughout the membrane interface there are regions poor in water and regions with nearly bulk-like water nanopools.

**Dynamics and structure of interfacial water molecules**

The last two chapters of the thesis are dedicated to studies of the structure and dynamics of water molecules at water-air and water-lipid interfaces using two-dimensional surface sum-frequency generation (2D-SFG) spectroscopy. In chapter 9 I report on the investigation of the structure of heavy water at the two interfaces. We found that the similarity between the static SFG spectra of water at the water-air and water-lipid interfaces breaks down in the 2-dimensional sum frequency generation measurements. This shows that the structure of the water-air interface strongly differs from that at the water-lipid interface. The technique of 2D-SFG is thus shown to provide a new way of investigating the structure of aqueous interfaces.

In chapter 10 I report on the study of the energy transfer dynamics of wa-
ter molecules at water-air interface using 2D-SFG spectroscopy. Our measurements reveal the presence of surprisingly rapid energy transfer, both between hydrogen-bonded interfacial water molecules (intermolecular), and between the OD group sticking out from the water surface (free OD) and the OD located on the same water molecule and pointing towards the water bulk (intramolecular). The results show that the energy transfer between the stretching vibrations of surface water and bulk water is extremely rapid and efficient, which is an important property for chemical reactions taking place at the water surface.