Water Interacting with interfaces, ions and itself
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1 Introduction

1.1 Water and hydrogen bonds

One does not have to be a scientist to realize that without water the world would have looked much different. In fact, we would not be here to see it! All life relies on the presence of water. Water is an important and most of the time major component of cells, with its content ranging from 20% in plant seeds, ~80% in human cells, up to as much as 96% in jellyfish. Moreover water covers about 2/3 of the Earth’s surface and forms the habitat of many organisms. Water is barely ever encountered in a “pure” state, especially in biological systems where it acts as a transporter or medium in which biochemical reactions take place. Out of many, few major functions of water are:

- **solvent** - water often acts passively as the medium in which other molecules and/or ions are dissolved. As an example, mineral salts can only be obtained by plants in the form of solutes in water. Many crucial reactions of the metabolism take place in aqueous solution.
- **transporter** - many substances (blood cells, food, waste products) in our bodies are transported by water.
- **reactant** - water actively participates in chemical reactions like photosynthesis, e.g., by taking up or releasing photons.
- **lubricant** - water is a major constituent of joint membranes in between different bones. Another example is the pleural cavity that contains the lungs. A water film lubricates the two pleural walls, thus minimizing the friction of the lungs during respiration.
- **temperature controller** - water possesses high specific heat and can thus take up a lot of energy at a moderate increase in temperature. The vaporization of water at the surface of the organism (sweat) helps to maintain a constant temperature.

The above rather macroscopic functions of water can be traced back to its molecular scale interactions. With respect to biological systems we would like to underline a few examples of fundamental, molecular interactions of water and biomolecules. Many of these interactions, crucial for the proper functioning of cells, are still not well understood:

- **structure, stability and folding of proteins** - hydrophobic hydration and hydrogen-bond formation are crucial for protein structure and stability [93]. Moreover, water is thought to diminish repulsive phosphate-phosphate interactions (thanks to its high dielectric constant), and thus contributes significantly to the stability of nucleic acids [62, 103].
• molecular recognition involving bio-molecules - water can function as an extension of the protein structure, allowing various ligands to be accommodated at a given binding site [151].

• local energy dump - the interactions among water molecules and between water and biomolecules lead to a large number of vibrational modes that can be excited. As a result, the solvating water can accept a lot of energy.

It is intriguing that in spite of its simple chemical composition, water has such an impact on many biochemical processes. A water molecule consists of three atoms: two hydrogens and one oxygen. Out of the four pairs of valence electrons two are shared between the oxygen atom and the hydrogen atoms forming covalent O-H bonds and the other two are lone pairs. Due to its bend structure and an uneven distribution of partial charges water possesses a dipole moment. Water can act as both: as hydrogen-bond donor (the two hydroxyl groups) or hydrogen-bond acceptor (the two lone pairs on oxygen atom), and thus can form up to four hydrogen-bonds with its neighbors.

The high propensity of water molecules to form extensive hydrogen-bonded networks (see figure 1.1) is what makes water so special. Even though the whole hydrogen-bond network is a transient state (hydrogen bonds are ~20 times weaker than covalent bonds and are constantly broken and reformed), most water molecules are at all times at least 3 fold coordinated [2]. The polarity of water molecules makes water an excellent solvent for charged or polar particles. Inversely, uncharged particles dissolve in water rather poorly. The drive of water molecules to form hydrogen-bonded network has a strong biological impact. For instance, certain parts of a protein molecule can interact such to prevent water to access a specific binding site, in order to allow a ligand to bind there. The reason why such a small molecule like water would be expelled while other bigger ligand molecules are not [2] is due the drive of water molecules to stick together and to form hydrogen-bonded clusters. In other words, it is energetically highly
1.2 Introduction

Figure 1.2. Linear absorption spectrum of water in the mid-infrared region. The two water molecules depict the three intramolecular vibrational modes: the bend and the stretch vibrations, of which one is shown.

unfavorable for water molecules to break the hydrogen bonds to other water molecules.

We investigate the properties of water using its interactions with light. Water molecules absorb light at specific frequencies. As most substances, it strongly absorbs ultraviolet light as a result of electronic excitations. Water molecules do not absorb the visible spectrum, except for a very weak absorption in the red part of the spectrum (which make water look slightly bluish). Strong water-light interactions show up again in the mid-infrared region, due to the vibrational resonances of water (see figure 1.2).

1.2 VIBRATIONAL SPECTROSCOPY

The investigation of the vibrational properties of water molecules allows us to elucidate the local structure of the measured molecules, their dynamics and the role they play in energy redistribution pathways. The high sensitivity of the O-H stretch and bend modes to the strength of the hydrogen bonds allows us to probe the local environment via the frequencies of these modes. One can thus say that the intramolecular vibrations act as a window through which we can look outside, at the surroundings of the water molecule we probe.

For about a decade spectroscopists have addressed the structural and functional implications of the interactions between water and biomolecules [123, 124, 125]. One of the complications in understanding the role of water and its interactions with other molecules is the extreme diversity of systems in which it plays a role. Due to a strong interplay of interactions and the huge variety in structure and dynamics, the properties of water molecules in one system cannot be simply extrapolated to understand its behavior in another system.

In this thesis we use two spectroscopic techniques, one of them suitable for studying bulk systems, the other for investigating molecules at an interface. The first one is mid-infrared pump-probe spectroscopy [9, 47, 32, 49, 50, 86, 82, 171, 69, 96, 10], the second is surface sum frequency generation spectroscopy [23, 51, 52, 20, 24, 66, 145, 147, 148, 42, 142, 40, 41]. Both of these techniques probe
the vibrational properties of molecules. Using the dependence of the vibrational resonant frequency on the strength of the hydrogen-bonds, we can map the local structure of the probed molecules [10] and the distribution of vibrationally distinct molecular species. The time-resolved experiments provide information on the vibrational relaxation rates and, via polarization-resolved measurements, on the orientational mobility of molecules. In addition, both techniques can be extended to a two-dimensional scheme, in which one excites a specific molecular vibration and probes the response of a different vibration, either within the same molecule or in a neighboring molecule. The two-dimensional approach thus provides access to vibrational couplings, which contain information about the relative distances and orientations between molecular moieties.

Figure 1.3. A cartoon showing different molecular systems studied in this thesis. A - Water interacting with lipids and lipid membranes; B - NMA and NMA clusters in apolar environment; C - Bulk and interfacial water and D - Water molecules interacting with ions.
1.3 Outline

In this thesis we study the vibrational relaxation, the molecular-scale structure, and the vibrational energy transfer and reorientation of molecules in various bio-relevant systems. We study the properties of bulk water molecules, water molecules hydrating ions and lipids, and amide molecules. In the following chapter we describe the theoretical basis for understanding the molecular processes studied in this thesis. In Chapter 3 we describe the experimental setups used in the experiments. In Chapter 4 we study vibrational resonant energy transfer in bulk liquid water. Chapter 5 describes the vibrational dynamics and structure of water molecules interacting with ions. In Chapter 6 we discuss the effect of clustering on the vibrational energy relaxation of the N-methylacetamide (NMA) molecules. In chapter 7 we study the vibrational energy relaxation pathways of the amide vibrations of NMA molecules. The distribution of water molecules embedded in cell model membranes is discussed in Chapter 8. Chapters 9 and 10 describe the structure and energy transfer of interfacial water molecules.