
Chapter 1

Introduction

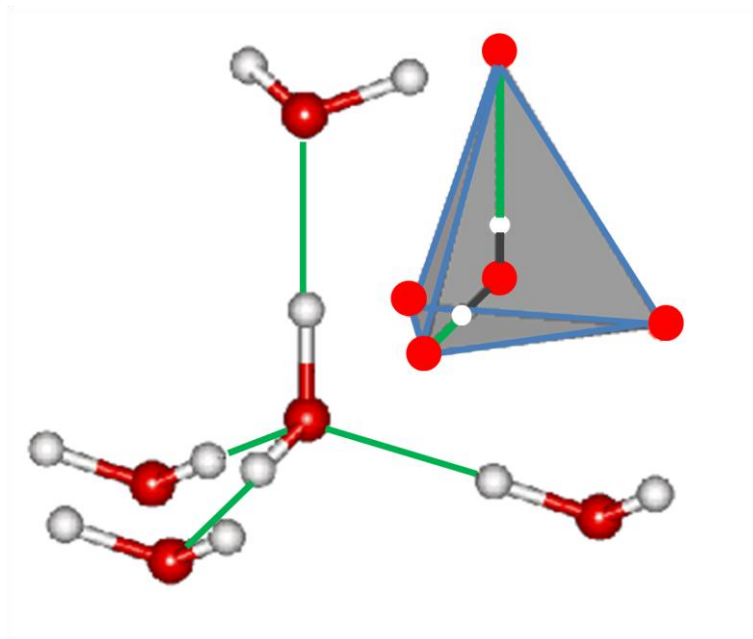


Figure 1.1 Tetrahedral structure of water

Water is the most ubiquitous liquid on Earth. It covers more than 70 % of the Earth's surface. A significant fraction of the human body (>60%) is water. It can exist in three states of matter: ice, liquid and vapour, and ice can adapt many crystalline forms. Due to its ability to form H-bonds water has a number of anomalous properties: decrease of viscosity with pressure, large heat capacity, melting with pressure among many others.^{1, 2} One of the most interesting properties is the density maximum at 4 °C. This maximum can be thought of as resulting from the competition of an ordered ice like

structure with a disordered liquid structure. Below 4 °C the ice like structure starts to dominate and above the liquid structure is dominant.³

Water molecules form an extended three dimensional hydrogen bond network. This network is highly dynamic as H-bonds break, form and stretch on the picosecond timescale.⁴ It is known that in the ice like I_h (hexagonal form) a water molecule is H-bonded to four other water molecules in a tetrahedral arrangement (Figure 1.1), with each central water molecule acting as a double acceptor (oxygen having two lone pairs) and double donor (hydrogen). In the liquid phase the tetrahedral structure is largely preserved. However it acquires some degree of disorder as revealed by neutron diffraction and X-ray data.⁵⁻⁷ Thermodynamic studies showed that approximately 13 % of hydrogen bonds are broken upon transition from ice to a liquid structure.⁸ However, in the last decade some new studies appeared which challenged the existence of a tetrahedral structure of water.⁹⁻¹¹ Nilsson *et al.*⁹⁻¹¹ using X-ray absorption and Raman spectroscopy (XAS and XRS) together with studies modelling core electron excitations concluded that the water network is composed mainly from strongly hydrogen bonded chains or rings. This interpretation was strongly criticized by Soper¹² and Head-Gordon *et al.*¹³ Soper¹² argued that interpretation of the data supported by computer spectra presented by Nilsson *et al.*⁹ is not correct. Three other groups used XRS and X-ray emission spectroscopy (XES) to study liquid water¹⁴⁻¹⁶ and found no evidence for the water chain structure. The XES studies showed that the region that was associated with chain structure by Nilsson *et al.*⁹ is in fact dominated by three- hydrogen bonded species not two as in the chain structure.

Water has been a subject of extensive studies, but despite such large interest, the structural and dynamical properties of water, in particular in the presence of a solute, are still not fully understood.^{3, 17-31} It is now established that water actively engages

and interacts with biomolecules, e.g. membranes, proteins in a number of ways. Water molecules, by forming directional, weak bonding allow the reorientation and reconfiguration of the protein's three dimensional structure.³ Water not only governs the structure and dynamics of biomolecules, but also their function and stability.^{3, 28} Hydrophobic and hydrophilic interactions were especially widely studied. From these studies different interpretations and models emerged.^{32, 33} For example Bakker *et al.*³⁴ using midinfrared pump-probe spectroscopy suggested that water in the vicinity of hydrophobic groups is immobilized, whereas no immobilized water molecules were found in molecular dynamics simulations by the group of Laage *et al.*³⁵ This disagreement is significant as the structure and dynamics of water near hydrophobic and hydrophilic residues is critical in the mechanism of protein folding (details in Chapters 2 and 4).

In this work structural and dynamical properties of water are investigated in aqueous solutions of a broad range of solutes, from purely hydrophilic molecules through peptides and proteins to the almost entirely hydrophobic tert-butanol. The experimental technique used is ultrafast Optical Kerr Effect spectroscopy (OKE). OKE is a nonlinear four wave mixing spectroscopy which implements femtosecond pulses to study molecular dynamics through polarizability relaxation. It has been widely applied to study the liquid state for almost 30 years.³⁶⁻⁵⁶ It was successfully used to study water dynamics by Vohringer *et al.*^{50, 51} and Righini *et al.*⁵² and protein solutions by Wynne *et al.*^{36, 37} and Tokmakoff *et al.*⁵⁶ Different experimental geometries are used to access the anisotropic and isotropic response of the sample.^{41, 42, 55} In this work the conventional pump-probe geometry with optical heterodyne detection (OHD-OKE) is employed to study the anisotropic signal.^{53, 55} To access the

isotropic component of the signal, the diffractive optic element transient grating geometry was implemented (DOE-OKE).⁴²

1.1 Thesis Overview

Experimental and theoretical conditions required for the OKE spectroscopy are described in **Chapter 2**. The two experimental set ups used in this study are described: (1) OHD-OKE using the pump-probe geometry and (2) TG-OKE based on the diffractive optic element. These two experiments are used to measure the anisotropic and isotropic response, respectively. The data analysis procedures are explained using pure liquid water as an example. In **Chapter 3** both the anisotropic and isotropic responses of salt solutions are described. This chapter is based on the publication: *Heisler, I.A.; Mazur, K.; Meech, S.R.; 2011, Low-Frequency Modes of Aqueous Alkali Halide Solutions: An Ultrafast Optical Kerr Effect Study, Journal of Physical Chemistry B, 115, 1863-1873*. In **Chapter 4** the anisotropic response of five simple solutes is analysed. A two-state hydration model for dilute solutions is described. The different effect of hydrophobic and hydrophilic interactions on the response are described. This chapter is based on the publication: *Mazur, K.; Heisler, I.A.; Meech, S.R.; 2011, THz Spectra and Dynamics of Aqueous Solutions Studied by the Ultrafast Optical Kerr Effect, Journal of Physical Chemistry B, 115, 2563-2573*. In **Chapter 5** solutions of three model peptides are described. Particular attention was paid to water behaviour in the vicinity of hydrophilic and hydrophobic moieties. This chapter is based on the publication: *Mazur, K.; Heisler, I.A.; Meech, S.R.; 2010, Ultrafast Dynamics and Hydrogen-Bond Structure in Aqueous Solutions of Model Peptides, Journal of Physical Chemistry B, 114, 10684-10691*. The aqueous solutions of three globular proteins are analysed in **Chapter 6**. The water dynamics observed

are correlated with surface hydrophobicity of the protein. This chapter is based on the paper: Mazur, K.; Heisler, I.A.; Meech, S.R.; *Water dynamics at protein interfaces: Ultrafast Optical Kerr effect study*, which is accepted for publication in the Journal of Physical Chemistry A.

1.2 References

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