Ion solvation in water: femtosecond spectroscopy of hydrogen-bond dynamics
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I Introduction

The importance of salt solutions may be best illustrated by the fact that two thirds of the earth's surface is covered by a salt solution of approximately $10^{15}$ litres. The salt content is an important parameter for the oceanic flow patterns, since it affects the density of water and its melting temperature. On a smaller scale, the physiological fluids that constitute a principal part of the human body consist mainly of water, and contain significant amounts of ionized solutes. Human blood can be (partly) replaced by 'physiological salt', which is nothing but a solution of salts and minerals in water, with a salt content similar to that of blood. The chemical reactions that take place in the human body are closely related to the behaviour of water molecules. The hydrolysis of adenosine triphosphate (ATP), forming adenosine diphosphate (ADP), a solvated phosphate group, and a solvated proton, is only one example of a chemical reaction in which solvation plays a crucial role.

A salt molecule consists of a cation and an anion, ions of positive and negative charges, respectively. The ions are held together by an ionic bond; the separate charges give rise to strong electrostatic attraction. When dissolved, the molecule falls apart in its constituent ions, that are separately solvated by the solvent molecules. These solvation interactions must overcome the rather strong ionic bond, in addition to the solvent–solvent interactions that may be distorted to accommodate the ions. It is surprising how well soluble many salts are in water. Potassium Fluoride, for example, is soluble up to 18 M: three water molecules for each pair of solvated $K^+$ and $F^-$ ions.

In this thesis, solutions of salt in water are studied. Water is the common solvent in nature, and may be considered the most important for that reason. However, solvation is in itself by no means limited to water. There are several practical applications for non-aqueous or mixed solvents. Since the reactivity of dissolved ions will depend on the solvation interactions, the solvent can be chosen so as to optimize the ions' reactivity, e.g. in batteries.

Connected to solvation, two notions are important in this thesis, that of hydrogen bonding and of solvation shells.

1.1 Solvation shells

The first theories that deal with electrolyte solutions, e.g. the Debye-Hückel theory at the beginning of the 20th century, did not take any molecular structure into account, but simply treated the solvent as a homogeneous medium with a dielectrical constant. The development of X-ray diffraction (1920s) and infrared spectroscopy (1930s) techniques revealed that liquid water does have a structure on the molecular scale, that is altered by the presence of solute molecules. Around many solutes, among which ions, the solvent molecules were found to reside preferably at specific distances from the solute molecule. These layers of solvent molecules around the solute are called solvation shells,
or hydration shells when the solvent is water. Because the solvation structure and its
dynamical behaviour are of great importance to the reactivity of the solute, there has been
an ever-growing interest in the study of these solvation shells.\textsuperscript{5,132,80}

A salt is said to be dissolved if its constituent ions reside separately within the solvent.
The solvent structure around the ion is characterized by the pair correlation function
$g(r)$, that gives the (time- and ensemble-averaged) probability of finding a water molecule
(usually either an oxygen or a hydrogen atom is measured) at a distance $r$ from the ion.
For small $r$, $g(r)$ will be zero because the Van der Waals repulsion prevents the molecules
to come too close to the ion. For greater $r$, $g(r)$ will go through a series of maxima and
minima, corresponding to subsequent solvation shells. In liquid water, only one or two
such maxima are pronounced.\textsuperscript{96} The number of molecules in the first solvation shell can
be calculated from $g(r)$, by integrating $g(r)$ from 0 to the first minimum, or by fitting
the first peak. Note that the existence of these shells does not provide much information
on the ion–solvent interaction: even a non-interacting hard sphere in a condensed-phase
solvent will give rise to their formation, since otherwise a cavity would exist within the
solvent. The distance between the shells, and the orientation of the solvent molecules
within the shells will be more strongly dependent on the interactions.

Experimentally, the pair correlation functions $g(r)$ can be obtained by X-ray, neutron
or electron diffraction, or with EXAFS (extended X-ray absorption fine structure). In the
latter technique, the modulation of monochromatic X-ray radiation is measured, result-
ing from the interference of low-energy electrons that scatter from different atoms in the
sample. The modulation depends on the distance between the atoms.\textsuperscript{96}

The solvent structure, and so the radial distribution function, are the result of four
structuring forces that act on the conformation of water molecules around ions.\textsuperscript{80} First, in
the case of anions, a hydrogen-bond interaction can exist between the ion and first-layer
solvent molecules that is directional. Second, both for anions and cations, the electric field
of the ion tends to align the dipole moment of the solvent molecules; this latter effect may
extend beyond the first shell, although decreasing outward due to the Coulomb potential.
Resulting from the hydrogen-bond interactions between water molecules, two other forces
can be identified. From the ion on outward, the first solvation shell tends to align the water
molecules in the second shell, and so on. Reversely, the bulk liquid will try to impose its
structure on the molecules closer to the ion.

Traditionally, the net structuring effect has been considered in terms of structure-
making and structure-breaking ions. Some ions are considered to promote a more rigid
hydrogen-bond structure around the ion, others would not change it or even weaken it
over relatively large distances. Of the four above-mentioned structurizing interactions,
the interactions that alter the hydrogen-bond structure are the ion–dipole interaction and
the anionic hydrogen bonds. In this thesis, experiments are presented that challenge this
view of structure-making and structure-breaking ions, by showing that there is no marked
change in structural rigidity even around the strongest structure-making ions.

Several new experimental and computational methods have been developed since the
first investigations of the solvation structure. One of the greatest obstacles in these studies
is that one has to separate the response from water molecules in the bulk solvent from
those that participate in the solvation structure.

Nuclear magnetic resonance (NMR) has been used since 1948.\textsuperscript{10,47} With NMR, the
‘chemical shift’, the change in magnetic resonance frequency of a nuclear spin, is measured.
The chemical shift depends very sensitively on the direct environment of the nucleus, and can be measured with great accuracy. Although NMR has been very valuable, e.g. in obtaining hydration numbers, with respect to hydration there are two disadvantages to this technique. First, the interpretation of the spectra is not straightforward: several effects contribute to the chemical shift, the separation of which is complicated, especially for protons. The second disadvantage is that the frequency of the magnetic field is at most 100 MHz, so that the time scale of the phenomena that can be measured with full accuracy is restricted to nanoseconds. A very precise measurement of the linewidth can partly compensate for the loss of accuracy, and extend the range to picoseconds. However, this linewidth must correspond to one specific type of nucleus; the molecules in the solvation shells that we study do exchange with the bulk solvent hundreds of times within the measurement of the linewidth, rendering NMR unsuitable for separating the responses from bulk and shell molecules.

The problem of distinguishing the solvating molecules can be solved by studying clusters existing of one ion and a fixed number of water molecules. In vibrational predissociation experiments, such clusters are prepared and selected using a mass spectrometer. The spectrum of frequencies at which one molecule is 'shattered' off the cluster is measured by shining laser light on the clusters and detecting the mass-selected fragments. Clusters have also been studied in molecular dynamics simulations. It must be realized that they are not real solutions. The hydrogen bonds and the vibrational spectra are different and furthermore, in real liquids, many more interactions are present due to the greater number of molecules.

Another experimental method that circumvents the problem of the strong inhomogeneity of an aqueous system, comprises the use of a probe molecule dissolved in water. In this type of experiment, information on the dynamics of the solvating water molecules is inferred from the time-dependent response of the molecule after excitation. For instance, it was observed that the fluorescence of a dye molecule dissolved in water shows a very rapid redshift with a time constant smaller than 100 femtoseconds, which indicates that solvating water molecules can show a very rapid reaction. A disadvantage of this technique is that it probes the dynamics and structure of the solvating water molecules rather indirectly.

In the past decade, computer power has increased enormously, and better modeling potentials for water molecules have been developed, resulting in a large number of molecular dynamics (MD) simulations of aqueous solutions. These simulations produce the position variables of all molecules at a discrete series of time steps, from which easily all relevant structural and dynamical parameters can be calculated. For example, statistics of configurational parameters in solvation structures were studied; ion-pairing was found to take place, even the pairing of ions with charges of equal sign. Also dynamics is easily accessed: the exchange of water molecules between the shell and the bulk solvent can be followed in detail; for monovalent ions these exchanges are found to take place on the order of one to a few hundreds of picoseconds. However, results from MD simulations should be regarded with some reservation, since they strongly depend on the potentials chosen: without experimental verification, their value is limited.
1.2 HYDROGEN BONDING

Hydrogen bonds play an important role in the solvation interactions. A hydrogen bond is an attractive directional interaction between a proton-donating D–H group and an acceptor A, denoted D-H⋯A. With directional it is meant that the bond has a preferred DHA angle, namely 180°. D and A are usually one of the following electronegative elements: F, O, Cl, N, Br or I.

The first reportings of interactions that are now called hydrogen bonds, date shortly after 1900. Weak interactions were identified, e.g. in ammonia salts, and given names like 'secondary valence' or 'weak union'. The term 'hydrogen bond' was first used by Pauling, who later gave it widespread attention by devoting a chapter to it in his book 'The nature of the chemical bond'.

Today, the role of the hydrogen bond in chemistry is widely acknowledged. Its importance lies in the association of molecules. Since the interaction is directional, it favors certain configurations and thus brings some order in liquids, and promotes the formation of certain crystal structures over others. The interaction energy is in the range of 0.1 to 20 kJ/mole. The thermal energy available for each vibrational coordinate at room temperature is 1.2 kJ/mole, so that most hydrogen bonds are easily formed or broken. Recent research identifies electrostatic and covalent interactions as the main physical interactions that constitute the hydrogen bond.

Hydrogen bonds are particularly important in liquid water, which would be a gas at room temperature when hydrogen bonds would not hold the molecules together. Each water molecule can participate in up to four hydrogen bonds, with an average of 3.4 at room temperature. The hydrogen bonds form an extensive network throughout the liquid, that is responsible for many remarkable macroscopic properties of water. For example, water reaches its maximal density at 4 °C, instead of at its melting point.

Dissolution of salt in water may lead to several changes with respect to the hydrogen-bond interactions. First, the hydrogen-bond structure that exists in liquid water may be 'mechanically' changed by the fact that the ions occupy a certain space in the solvent. The structure may either be enhanced, by promoting the local formation of ice-like structures, or weakened when the hydrogen bonds are bended or even broken if the size of the solute does not match the undisturbed hydrogen-bond structure. Second, the interaction of the ion's charge with the dipole moment of the water molecules can lead to a restructuring of the network; the electric field may polarize the hydrogen bonds, especially around cations. Finally, new hydrogen bonds can be formed between water molecules and anions.

1.3 THE O–H STRETCH VIBRATION

We have already remarked that in the study of aqueous solvation, hydrogen bonds are extremely important. The ideal probe of hydrogen-bond interactions is the O–H stretch vibration, since its frequency is directly correlated with the hydrogen-bond length, i.e. the intermolecular distance.

In figure 1.1, the absorption spectrum of the O–H stretch vibration in liquid water is shown. The symmetric and antisymmetric stretching vibrations in liquid H₂O are spectroscopically nearly indistinguishable. To avoid this latter effect, experimental work has mainly been devoted to dilute solutions of HDO in D₂O, where the O–H
and O–D stretching bands are well separated, being centered at 3400 and 2505 cm$^{-1}$, respectively, while the chemical (hydrogen-bonded) structure remains nearly unchanged.

Experimentally and theoretically, it has been shown that the frequency of the O–H stretch vibration and the hydrogen-bond length are linearly correlated within a large regime for water–water and ion–water hydrogen bonds. It appears that a stronger hydrogen bond weakens the covalent O–H bond, and reduces its vibrational frequency.

Due to the variation of hydrogen-bond lengths in liquid water, the spectrum is strongly inhomogeneously broadened (the term 'inhomogeneous' refers to the fact that the broadening results from the different environments that the molecules have in the liquid). The spectrum can be thought of as the sum of individual absorption bands. The width of one individual band is called the homogeneous linewidth. Experimentally, inhomogeneous broadening with an exchange between subbands that is faster than the time resolution of the experiment, cannot be distinguished from homogeneous broadening. Recent photon-echo experiments estimate the homogeneous linewidth between 60 and 120 cm$^{-1}$. Lifetime-broadening alone leads to a homogeneous linewidth of 7 cm$^{-1}$.

Infrared and Raman spectroscopic studies show that the most significant change of the O–H stretch spectrum is due to the anions. For most halogenic anions, notably Cl$^-$, Br$^-$ and I$^-$, a new component appears on the blue side of the spec-

\[\text{Figure 1.1. Spectrum of the O–H stretch vibration in liquid water.}\]
trum, depending on the nature of the anion and its concentration. Only for the strongest electronegative ion, $F^-$, an increased absorption at the red side of the spectrum is observed. It was concluded that in aqueous salt solutions, a new hydrogen bond is formed between the anion and the water molecule, which we will denote $O\cdot\cdot\cdot H$\textsuperscript{X}, where X represents the anion, the solid line connecting O and H a covalent interaction, and the dotted line denotes the hydrogen bond. For $X^\sim = Cl^\sim$, $Br^\sim$ or $I^\sim$, this hydrogen bond is weaker than the $O\cdot\cdot\cdot H$ hydrogen bond between two water molecules, and its strength decreases within the halogenic series. The decreasing redshift can be understood from the increasing diameter (decreasing field strength) in the series $F^\sim$, $Cl^\sim$, $Br^\sim$, $I^\sim$. For the even bigger perchlorate ion ($ClO_4^\sim$), the redshift is so small that the anion-bonded $O\cdot\cdot\cdot H$ absorption is well separated from the bulk absorption. The spectrum of a solution containing $ClO_4^\sim$ is shown in figure 8.1.

The spectral changes are too small to allow for an accurate study of the individual components. $ClO_4^\sim$ forms one of the few exceptions. Still, an approximate spectrum of the individual components can be extracted by subtracting known components from the full spectrum. To isolate the anion contribution, e.g. $I^\sim$ of a solution of NaI in water (HDO:D$_2$O), one can subtract the other components in two steps: first, the background absorption of pure D$_2$O with NaI must be subtracted. Second, a similarly prepared difference spectrum of a Na$^+$-containing salt with a large anion, that does not change the spectrum, must be subtracted. The absorption component thus obtained contains the absorption by the $O\cdot\cdot\cdot H$ stretch vibration in $O\cdot\cdot\cdot H$\textsuperscript{$I^\sim$} hydrogen-bonds, but may not be free from (inseparable) disturbances of the bulk-water structure by the $I^\sim$ ion. In addition, the absorption likely is still inhomogeneously broadened, as in pure water, as a result of which no information on the dynamical behaviour of these hydrogen bonds can be obtained from the spectrum.

The effect of cations on the absorption spectrum is smaller than that of anions. For the single-charged, moderately large cations Na$^+$ and K$^+$, almost no effect is observed. In a solution containing Li$^+$ or small double-charged ions such as Be$^{2+}$ or Mg$^{2+}$, the absorption at the red side of the spectrum increases. In contrast to the anion, cations cannot participate in hydrogen bond formation; their influence is limited to polarizing existing hydrogen bonds. The presence of anions and cations makes the absorption band of the $O\cdot\cdot\cdot H$ stretch vibration even more inhomogeneous than it already was for pure liquid water, which makes it even more difficult to obtain sensible information out of the absorption spectra.

It will be shown in this thesis that non-linear spectroscopy on the $O\cdot\cdot\cdot H$ stretch vibration of $O\cdot\cdot\cdot H$\textsuperscript{X} groups is an ideal tool to study the dynamical behaviour of the molecules in the solvation shells of anions. In real solutions, the dynamics of the solvating molecules is probed directly and exclusively.

1.4 Outline

In this thesis, the dynamical behaviour of solvation shells is studied using femtosecond mid-infrared pump–probe spectroscopy. In chapter 2, this experiment is described that has significant advantages over linear spectroscopy, as well as over the techniques discussed in 1.1. In chapter 3 and chapter 4, the vibrational relaxation of the $O\cdot\cdot\cdot H$ stretch mode
is described, focusing on its dependence on temperature, and on the nature and concentration of the ions, respectively. A critical discussion of recently published related work of Laenen and Thaller is presented in chapter 5. Experiments on the dynamics of the anionic hydrogen bond are discussed in chapter 6. The reorientational motions of solvation shells are studied in chapter 7. The final chapter is devoted to the study of the changes induced by ions in the bulk-water structure, i.e. the hydrogen-bond structure of water outside the first solvation shell.