X-RAY STUDY OF ICE AND WATER ON SURFACES AND IN AQUEOUS SOLUTIONS

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Abstract

Since antiquity, water has been considered as the most important substance on Earth. In fact, the abundance of liquid water on this planet allowed for the emergence and evolution of life. At the molecular level, the structure of an individual water molecule may seem simple; however, the intermolecular interaction between water molecules in the form of hydrogen bonding gives rise to water’s various properties that can be considered anomalous when compared to other liquids. The nature of the water hydrogen bond is so complex that there is still a debate in the scientific literature about the structure of liquid water. In this dissertation, several synchrotron x-ray techniques were used to investigate water in its liquid and solid phases in terms of its structure in and interaction with different model systems that mimic the environments in which water is usually found in nature.

First, the effect of ion solvation on the local structure of water was explored using x-ray absorption spectroscopy (XAS) and small angle x-ray scattering (SAXS). There is a charge density dependence of the ability of cations in the restructuring of the water molecules in their vicinity. The monovalent Na\(^{+}\) tends to weaken H-bonds between water molecules, while the divalent Mg\(^{2+}\) and trivalent Al\(^{3+}\) form stable, highly ordered, high-density hydration shells. Furthermore, solvated Mg\(^{2+}\) and Al\(^{3+}\) form ordered quasi-lattice structures in the solution. Fluoride (F\(^{-}\)) anion was found to act as a nucleation site for the formation of tetrahedral, low-density structures in liquid water due to its ability to form H-bonds with water, similar to the effect of temperature decrease. XAS spectra of alkali halide solutions confirm that all alkali cations break water-water H-bonds to a varying degree, while Cl\(^{-}\) and Br\(^{-}\) have no distinguishable effect on water, and I\(^{-}\) tends to break H-bonds.
Next, the structure of water confined in AOT reverse micelles was studied using x-ray Raman scattering spectroscopy (XRS), which is an alternative method for measuring x-ray absorption spectra. According to the literature, water in AOT reverse micelles exhibits slower dynamics, especially as the size of the reverse micelles is decreased. However, XRS spectra show spectral changes that are indicative of an increasing fraction of weakened/distorted H-bonds, possibly due to the immobilization of the water molecules by the hydrophilic headgroups in the interior surface of the reverse micelles.

The effect of ice adsorption on the electronic structure of hydrophobic methyl-terminated Si(111) surface was studied by C 1s XAS. Despite macroscopic observations of hydrophobicity (i.e. the formation of three-dimensional ice clusters on the surface to maximize water-water H-bonding and minimize surface-water interaction), the water molecules perturb the electronic structure of the surface methyl groups. The transition to the LUMO orbital of the methyl group is symmetry-forbidden according to the dipole selection rule, which governs the x-ray absorption process. A small intensity can be observed only due to the asymmetrical vibrations of the C-H bonds. Upon ice adsorption, the LUMO peak intensity is enhanced dramatically, indicating that water molecules directly interact with and increase the asymmetric character of the excited state orbitals of the methyl groups.

Finally, x-ray photoelectron spectroscopy (XPS) and XAS were used to study the growth and structure of ice on Pt(111). Pt 4f and O 1s XPS spectra show that the crystalline ice prepared by isothermally heating amorphous ice on Pt(111) is not homogeneous. Instead, the ice multilayer forms three-dimensional crystallites, and a significant area of the first monolayer on Pt(111) is exposed to vacuum even at relatively high total coverages. In addition, experimental data from XAS and infrared reflection absorption spectroscopy (IRAS) confirm that the free OH groups on the surface of ice give rise to the XAS pre-edge feature, which is shifted as the ice surface is terminated with NH$_3$. However, the pre-edge also contains contributions from disordered H-bonding in bulk ice, likely due to the presence of various phases of amorphous ice.
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Chapter 1

Introduction

1.1 Water and the Hydrogen Bond

The structure of the free water molecule is simple and very well known; it is comprised of two hydrogen atoms covalently bonded to an oxygen atom that has two lone electron pairs. The molecular geometry is bent with $C_{2v}$ symmetry, with an H-O-H angle of $\sim 104.5^\circ$ and an O-H bond length of $\sim 0.957$ Å [Fig. 1.1(left)] [1]. The dissociation energy of the intramolecular O-H bonds is 117.8 kcal/mol ($\sim 5.1$ eV) for the first O-H bond (H-OH) and 101.5 kcal/mol ($\sim 4.4$ eV) for the remaining O-H bond [1]. The molecular orbital diagram of a water molecule is depicted in Fig. 1.1(right) where the $1a_1$ orbital is the O 1s core orbital, $2a_1$ is an inner valence orbital with a predominantly O 2s character, $1b_2$ is a strongly bonding valence orbital, $3a_1$ is a valence orbital with both bonding and lone pair characters, and $1b_1$ is a nonbonding lone pair orbital. The unoccupied orbitals $4a_1$ and $2b_2$ are antibonding orbitals.

The high electronegativity of the O atom in a water molecule results in a highly polarized molecule where the O atom has a partial negative charge and the H atoms have
The intermolecular interaction between water molecules occurs as a hydrogen bond (H-bond), which is energetically weaker than a covalent bond but stronger than a van der Waals interaction. H-bonds are known to be formed between a polar X-H group (hydrogen donor) of a molecule (where X is an electronegative atom, e.g. F, O, or N) with the F, O, or N atom (hydrogen acceptor) of another molecule, which has at least one nonbonding orbital filled with a lone electron pair [2]. Water H-bonds are formed with an almost linear O-H—O angle and an O-O distance of \( \sim 2.75 \) Å for ice and \( \sim 2.8 \) Å for liquid water [1, 2]. The strength of the H-bond in a water dimer is about 5 kcal/mol or only \( \sim 5\% \) of the intramolecular O-H bond energy [1].

The traditional view of the H-bond as an electrostatic attraction was first proposed by Pauling in 1939 [3]. Later, a model of H-bond involving charge transfer and even covalent interaction was introduced [4–8]. Now, H-bonds are assumed to be a combination of different interactions, namely electrostatic attraction (the dominant
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effect), charge transfer, dispersion, and Pauli repulsion [9]. Indeed, the complexity of the nature of H-bonds gives rise to some interesting properties, such as the cooperativity effect [10]. In water, the O-O distance is shown to decrease from \(\sim 2.95 \, \text{Å} \) for a water dimer [11] to \(\sim 2.85 \, \text{Å} \) for a trimer [12], \(\sim 2.79 \, \text{Å} \) for a tetramer [13], and finally \(\sim 2.75 \, \text{Å} \) in a pentamer [14]. The cooperativity effect of H-bonding in water is also manifested in an observed increase in the dipole moment from 1.86 D for a gas-phase water molecule to 2.6-3.1 D for liquid water and ice [15]. Another evidence comes from \textit{ab initio} theoretical study, which shows that the total interaction energy of different water chains is not additive and that the non-additive contribution accounts for \(\sim 16\% \) of the total energy [16]. The cooperativity effect of H-bonds is not observed exclusively in water, but also in other molecules such as methanol and polyamides [2].

The mechanism for the H-bonding formation in water has been elucidated through a combination of the theoretical constrained space orbital variations (CSOV) analysis with experimental data from photoelectron spectroscopy (PES) and x-ray emission spectroscopy (XES) [17]. It was proposed that since a purely electrostatic model failed to account for the relatively strong attractive interaction between water molecules, electrostatic interaction must be enhanced by minimizing Pauli repulsion, which can be achieved through charge transfer between the oxygen lone pair and the antibonding OH orbital of a neighboring water molecule accompanied by internal \(s-p\) rehybridization of the \(3a_1\) orbital [17]. Therefore, the molecular orbitals of H-bonded water molecules should be described as new hybrid orbitals instead of the molecular orbitals of discrete water molecules. However, this picture of H-bonding involving charge transfer is different from covalent bonding in which electrons are equally shared.
1.1.1 Ice

Despite the apparent simplicity of the structure of the free water molecule, the complexity of its H-bonding capability gives rise to the formation of the various phases of ice depicted in the phase diagram in Fig. 1.2(left). The most common form of ice that exists in nature, such as in snow crystals, glaciers, etc., is hexagonal ice (ice $I_h$) where one water molecule is H-bonded to four of its neighbors in an almost perfectly tetrahedral geometry with $\sim 109.5^\circ$ O-O-O bond angle and $\sim 2.75$ Å O-O distance [Fig. 1.2(middle)] [1, 2]. The oxygen atoms in the hexagonal lattice are arranged in the chair conformation, forming stackings of $\sim 0.95$ Å thick bilayers separated by $\sim 3.7$ Å [Fig. 1.2(right)]. The position of the hydrogen atoms, on the other hand, is not as ordered, but it follows the Bernal-Fowler ice rule [18, 19]. According to this rule, two H atoms must be close to an O atom, thereby keeping the individual water molecules intact, the two H atoms in a water molecule must point towards two adjacent O atoms of neighboring water molecules, and only one H atom can be located along the axis between two neighboring O atoms. There are many equally possible configurations.
of the H atoms that satisfy these conditions, and the resulting random arrangement is called proton disorder. Ice $I_h$ is often considered as a model system for H-bonding tetrahedrality, which is especially important in the interpretation of the x-ray absorption spectra of liquid water. Cubic ice (ice $I_c$), which is a metastable phase, also has a tetrahedral configuration of the water molecules with an O-O distance of 2.75 Å; however, it forms bilayers with a different stacking arrangement, forming a cubic structure identical to that of diamond [1, 2].

As of 2009, fourteen other phases of crystalline ice have been characterized [20], labeled ice II to ice XV on the phase diagram. These can be prepared by increasing pressure, lowering temperature, adding dopant molecules, or any combination of the three. In all of these crystalline ices, water molecules still form a tetrahedral arrangement and the hydrogen atoms follow the ice rule. In addition to the various crystalline phases, ice can also be prepared in its amorphous form. Amorphous ice (also called amorphous solid water) is metastable and is usually prepared by rapidly cooling water droplets, dosing water vapor on metal surfaces at low temperatures, or applying pressure to crystalline ice at low temperatures [2]. The structure and properties of amorphous ice are still poorly understood; however, it was recently suggested that high-density amorphous ice is important in understanding the structure of liquid water [21].

1.1.2 Liquid Water

The ability to form H-bonds is the defining characteristic of water that accounts for the properties of liquid water that can be considered anomalous when compared to other liquids. Some of these properties include higher density of the liquid phase
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Figure 1.3: Illustration of (left) continuum model of water where water molecules form a continuous tetrahedral H-bonding network with a wide distribution of bond lengths and angles, and (right) the new density fluctuation model of water where the grey patches represent high tetrahedrality and red patches represent high density.

compared to the solid, density maximum of the liquid at 4°C, a heat capacity minimum at 56°C, high surface tension, unusually high melting and boiling points for a molecule of its size and mass, and an isothermal compressibility minimum at 46°C. However, unlike ice, the structure of liquid water is not as well understood and is under debate in literature. Part of this difficulty is due to the dynamical nature of the water H-bonds, which constantly break and reform on the picosecond time scale.

Currently, the widely accepted “textbook” model for the structure of liquid water is called the continuum model. According to this model [Fig. 1.3(left)] (often also called tetrahedral model), each water molecule is directly H-bonded to four other water molecules, as in ice, forming a continuous tetrahedral H-bonding network only with some distortions in the H-bond angles and distances. This model originated from the work of Bernal and Fowler in 1933 [18] based on their interpretation of x-ray diffraction (XD) pattern. More than three decades later, Narten et al. derived the radial distribution functions (RDF) from XD measurements and determined that water
molecules have an average of 4.4 nearest neighbors [22], supporting the tetrahedral coordination model. However, the lack of angular information from the RDFs means that they are insensitive to whether the neighboring water molecules are located at an O-H—O angles that can be defined as H-bond. Aside from XD, the continuum model is also supported by neutron diffraction (ND) [23–25], infrared (IR) and Raman spectroscopy [26–28], ultrafast pump-probe vibrational spectroscopy [29], and molecular dynamics (MD) simulations [30–36]. However, a reverse Monte Carlo study demonstrated that a wide range of structures with different local H-bonding environments can fit XD and ND data equally well [37, 38]. Also, it was shown that IR and Raman data cannot be simply described with a specific structure such as the tetrahedral water structure [37, 39]. MD, in particular, has been the most dominant and popular technique for studying the structure and properties of water since the work of Barker and Watts [30] and Rahman and Stillinger [40] in the late 1960s. Although results from MD simulation overwhelmingly support the distorted tetrahedral H-bonding network of liquid water [30–36], both classical MD and the more sophisticated \textit{ab initio} MD based on density functional theory (DFT) have failed to fully reproduce the properties of liquid water due to the exclusion of van der Waals interaction in the simulations. In addition, although MD often uses experimental data such as from XD and ND to validate a potential, a recent study shows that even the most popular potentials such as SPC/E and TIP4P-POL2 cannot reproduce x-ray diffraction data and they tend to yield overstructured pair correlation functions (PCFs) [37].

In recent years, a new model of liquid water emerged based on the density fluctuations of the liquid at ambient conditions. X-ray absorption spectroscopy data demonstrated that liquid water is dominated by asymmetrically H-bonded species
with an average of $\sim 2.2$ H-bonds per water molecule [41, 42], and the complementary x-ray emission spectroscopy showed evidence for the presence of two different components in liquid water, one with distorted H-bonds and the other with ice-like tetrahedral H-bonds [43]. This is further supported by recent small angle x-ray scattering data, suggesting that the two components have different densities and that they fluctuate constantly [44]. A more detailed description of this model can be found in Section 1.3 of this chapter.

1.2 X-ray Absorption Spectroscopy

This section details x-ray absorption spectroscopy (XAS), the main spectroscopic technique featured prominently in all chapters of this dissertation. In general, XAS encompasses two broad energy regions: near edge x-ray absorption fine structure (NEXAFS), also called x-ray absorption near edge structure (XANES), and extended x-ray absorption fine structure (EXAFS). NEXAFS generally covers the energy region from the absorption edge to about 30 eV above the edge and the fine structure arises from electronic excitations to unoccupied orbitals, and shape resonances appear due to the multiple scattering of low energy photoelectrons. The EXAFS energy region starts about 30 eV above the edge and the spectrum is dominated by the scattering of high energy photoelectrons from one atom by neighboring atoms. In this dissertation, the term XAS refers only to the near edge region. For a more general description of the XAS technique and applications, see Ref. [45] and for its application to water, see Ref. [21].
1.2.1 Basic Theoretical Concept

XAS is a process in which a core electron of an atom is excited to an unoccupied orbital, thereby creating a core hole. Since the energies of the core levels are unique to each element, XAS can be used to selectively probe a specific atom in a molecule or a heterogeneous system. Excitation to an unoccupied orbital gives XAS sensitivity to the chemical environment of the atom. XAS is often used in surface science and it is a powerful tool to selectively excite and probe the chemical environment of adsorbate atoms.

The absorption cross-section $\sigma_x$ is proportional to the transition probability $P_{if}$, which can be calculated from Fermi’s Golden Rule,

$$\sigma_x \propto P_{if} = \frac{2\pi}{\hbar} | \langle f | \tilde{V} | i \rangle |^2 \rho_f(E),$$  \hspace{1cm} (1.1)

where $\langle f |$ and $| i \rangle$ are the final and initial states, respectively. $\tilde{V}$ is related to the harmonic time-dependent perturbation $V(t)$ through $V(t) = \tilde{V}e^{-i\omega t}$ and $\rho_f(E)$ is the energy density of final states. Simplifications of equation 1.1 by substituting $V(t) = \frac{e}{mc} \vec{A} \cdot \vec{p}$ for the perturbation of an electron in an electromagnetic field with vector potential $\vec{A} = eA_0 \cos(\vec{k} \cdot \vec{x} - \omega t)$ yield

$$\sigma_x \propto P_{if} = \frac{\pi e^2}{2\hbar m c^2} A_0^2 | \langle f | e^{i\vec{k} \cdot \vec{x}} \vec{e} \cdot \vec{p} | i \rangle |^2 \rho_f(E),$$  \hspace{1cm} (1.2)

where $\vec{e}$ is the polarization vector and $\vec{p}$ is the sum of the linear momentum operators. Assuming that the wavelength of the electromagnetic radiation is larger than the size of the atom (i.e. $k \cdot x \ll 1$), which is valid for small Z elements, dipole approximation
can be used to further simplify equation 1.2 into

\[ \sigma_x \propto P_{if} \propto | \langle f | \vec{e} \cdot \vec{p} | i \rangle |^2. \]  

(1.3)

Substituting \( \vec{p} = \frac{im}{\hbar} [\hat{H}, \vec{r}] \) yields a final simplified expression for the absorption cross-section that is proportional to the dipole transition matrix element

\[ \sigma_x \propto | \langle f | \vec{r} | i \rangle |^2, \]  

(1.4)

which is non-zero if the transition obeys the dipole selection rule, i.e. \( \Delta \ell = \pm 1 \) and \( \Delta m = 0, \pm 1 \). Therefore, for an electron from the K-shell, e.g. O 1s electron, only excitations to \( p \) orbitals are allowed. In a molecule, for example in \( \text{H}_2\text{O} \) described in Section 1.1, where the valence orbitals are the result of combinations between atomic orbitals, the transition probability depends on the amount of \( p \) character.

A simplified MO diagram of a free water molecule and the depiction of the XAS process as well as the electron density plots of the occupied and unoccupied valence orbitals are shown in Fig. 1.4. Due to the high electronegativity of the O atom, the electron density of the occupied orbitals is polarized towards the O atom. Therefore, according to the orthogonality principles, the unoccupied antibonding orbitals are polarized towards the H atoms. In other words, the antibonding character pushes the electron density away from the O-H bonds. As a result, the unoccupied orbitals are spatially extended outside the water molecule on the H atom sides. The formation of a H-bond with a neighbor on the donor side (H atom side), therefore, will perturb the unoccupied orbitals and these changes can be detected through XAS. This also demonstrates that O 1s XAS of water is only sensitive to donating H-bonds but not
Figure 1.4: Electron density plots of the valence, LUMO, and LUMO+1 orbitals of water.

to accepting H-bonds.

Another aspect of XAS that must be taken into consideration is the fast time scale of the electronic excitation process compared to that of nuclear motions, which is the basis for the Franck-Condon principle [45]. For example, the excitation time scale of O 1s electron in water is \(~8\) attoseconds [46] while the H-bond breaking and reforming occurs at the picosecond time scale. Therefore, the nuclei can be regarded as frozen during the electronic excitation process, which occurs as a vertical transition with respect to the nuclear coordinates. Fig. 1.5 shows two cases of electronic excitations where the lower potential energy curves correspond to the ground state and the upper curves represent the excited state. If the nuclear coordinates of the ground and excited states are similar (Fig. 1.5a) and the initial state is in the \(v = 0\) vibrational state, a
vertical transition leads to a maximum overlap only with $v' = 0$. Overlaps with higher vibrational states are negligible, resulting in a sharp, narrow peak. On the other hand, if the excited state potential energy minimum is located at a different internuclear distance compared to the ground state (Fig. 1.5b), the initial state at $v = 0$ vertically overlaps with a number of excited vibrational states, resulting in a vibronic transition with a broad peak. The Franck-Condon principle offers a distinct advantage to XAS in its application to liquid water compared to conventional vibrational spectroscopy where the excitation process occurs at the same time scale as nuclear motions. In XAS, since all water molecules are considered frozen during the spectroscopic time scale, the spectrum represents an average snapshot of the molecular configurations during the measurement.

One limiting feature of XAS in its application to aqueous solutions is that all O atoms within the probing depth in the sample contribute equally to the absorption
intensity; therefore, if the solute molecule contains oxygen atoms, it is difficult to distinguish the spectral contribution from water and from the solute. One way to circumvent this problem is by subtracting the pure solute spectrum from the total spectrum, as demonstrated in Chapter 4.

1.2.2 XAS of Gas-Phase H<sub>2</sub>O and Changes due to Condensation

Figure 1.6: XAS spectra of the gas and condensed phases of (a) H<sub>2</sub>O [41, 47] and (b) CH<sub>4</sub> [21, 48]. Note that the different photon energy scales on the top and bottom axes correspond to the C and O K-edges, respectively. For the spectrum of H<sub>2</sub>O ice, the intensity above the dotted line is from disorder in the bulk related to the presence of various phases of amorphous ice.
The O 1s XAS spectrum of gas-phase H₂O is shown in Fig. 1.6a [41]. The two prominent peaks located at \( \sim 534.2 \) eV and \( \sim 536 \) eV correspond to the excitation of a 1s electron to the 4a₁ and 2b₂ orbitals, respectively. The intensities of these peaks reflect the amount of the 2p character in these orbitals, according to the dipole selection rule. At higher energies, starting from the peak at \( \sim 537.25 \) eV, transitions to Rydberg orbitals (i.e. higher shell orbitals such as 3p, 4p, etc) are observed, eventually converging towards the ionization potential (IP) at 539.6 eV. The broader peak widths of the 4a₁ and 2b₂ peaks compared to the first Rydberg peak is a consequence of excitations into different vibrational final states due to the Franck-Condon principle described in Section 1.2.1. The continuum region above the IP is devoid of any structures since the excited electron at these energies becomes a free electron wave.

When water vapor is condensed into ice, the XAS spectrum changes dramatically. The discrete transitions into the 4a₁ and 2b₂ orbitals disappear and the spectrum is, instead, dominated by a broad peak at \( \sim 540-541 \) eV denoted post-edge (Fig. 1.6a [47]). For comparison, the spectra of gas-phase [48] and condensed [21] CH₄ are displayed in Fig. 1.6b. Similar to gas-phase H₂O, the spectrum of gas-phase CH₄ contains discrete peaks from transitions into the LUMO and LUMO+1 orbitals. However, condensed CH₄, which does not form H-bonding, shows very little changes from the gas-phase spectrum although the peaks are slightly broadened. Therefore, the formation of the post-edge feature in ice is a consequence of H-bonding, which, as described in Section 1.1, involves electronic structure perturbations that lead to intermolecular charge transfer, resulting in the formation of new hybrid molecular orbitals [17].
1.2.3 XAS of Liquid Water and Its Interpretation

Theoretical simulations have shown that the post-edge peak in tetrahedrally bonded ice has a dominant $p$ character, while the dipole-forbidden orbitals with mainly $s$ character are located at lower energies [49]. When one $H_2O$ is removed from the donor side, the tetrahedral symmetry is broken, and the lower energy LUMO states, which previously have a pure $s$ character, gain a significant amount of $p$ character through hybridization and become available for excitation [49]. This is what we can observe from the O 1s XAS spectrum of liquid water.

The experimental O 1s XAS spectrum of liquid water compared to gas-phase water and ice is shown in Fig. 1.7 [41, 42, 47]. While the spectrum of liquid water is similarly broadened as that of ice, the shape is significantly different. The post-edge peak (540-541 eV) has a decreased intensity, while the LUMO states, which are quenched in ice, become more prominent in the liquid phase due to the asymmetrical distortions of H-bonds. The important spectral features in liquid water in addition to the post-edge are the pre-edge ($\sim 535$ eV) and the main edge ($\sim 537.5$ eV). The orbitals that give rise to the pre- and post-edge features can be understood by examining the excited state orbitals of a water molecule that forms a donating H-bond with another water molecule forming a water dimer, as shown in Fig. 1.8. At the pre-edge excitation [Fig. 1.8(left)], the excited orbital of the donor water molecule is localized along the free (non-H-bonded) OH group because the two internal OH bonds are inequivalent due to the asymmetrical H-bonding. It was determined previously through DFT simulations that the localized orbital on the free OH group appears due to the mixing between the gas-phase $4a_1$ and $2b_2$ orbitals, generating a pre-edge peak whose energy position is located between the two gas-phase orbitals [49]. Due
Figure 1.7: XAS spectra of water in the (a) gas [41], (b) liquid [42], and (c) solid [47] phases.

to this, the pre-edge is considered as a signature for distorted or weak H-bonds in water [21, 41, 42, 49]. Although it is still highly debated, various experimental as well as theoretical simulations results have supported this. For example, the experimental spectrum of ice surface, which contains many free OH groups, shows a significant pre-edge intensity, which is quenched upon NH$_3$ adsorption as the OH groups on the surface form H-bonds with NH$_3$ [21, 42, 47]. This will be explored in more detail in Chapter 6. In addition, XAS study of adsorbed water on Ru(0001) clearly shows that
Figure 1.8: Two-dimensional electron density plots of the excited state orbitals of a donating water molecule in a water dimer (pictured as the water molecule with the red oxygen atom) at the (left) pre-edge and (right) post-edge excitations.

The pre-edge is observed at low coverages when the water monolayer is incomplete and there are many uncoordinated OH groups, and it disappears when the monolayer is complete and all OH groups are H-bonded [50]. The interpretation for the localization of the pre-edge excited orbital on the free OH group is also supported by a resonant Auger spectroscopy study, which found that after a pre-edge excitation, the excited electron stays localized on the water molecule for longer than 20 femtoseconds [21, 46]. On the other hand, the post-edge peak is a signature for intact/strong H-bonds, as observed in the spectrum of ice. The orbital corresponding to the post-edge excitation,
shown in Fig. 1.8(right) is localized along the coordinated (H-bonded) OH group. This is supported by resonant Auger spectroscopy, which determined that after a post-edge excitation, the electron delocalizes on a time scale of $\sim 500$ attoseconds [21, 46]. As indicated by the phase changes in Fig. 1.8(right), the post-edge excited orbital is also an antibonding orbital, not only along the internal OH bond but also along the donating H-bond; therefore, the post-edge peak is located at a higher energy position. The main edge is also mainly derived from broken H-bonds although there are also small contributions from intact H-bonds, and it has been experimentally and theoretically shown to be related to increasing density in ice [51]. However, at this point there is still no clear molecular orbital picture that can explain the fundamental nature of the main edge.

Therefore, from the appearance of the pre-edge and main edge and the quenching of the post-edge, we can conclude that in liquid water there is a large fraction of asymmetrically H-bonded water molecules called single donor (SD) species as well as a smaller amount of ice-like tetrahedrally H-bonded water molecules called double donor (DD) species [21, 42]. In fact, the spectrum of liquid water more closely resembles that of the ice surface with its many uncoordinated OH groups than that of bulk ice [42].

The $\text{O} 1s$ XAS spectra of water at $25^\circ\text{C}$ and $90^\circ\text{C}$ are displayed in Fig. 1.9 [21, 42]. With increased temperature, there is an intensity redistribution from the post-edge to the pre- and main edge as the DD species are converted into SD. The difference spectrum between $90^\circ\text{C}$ water and $25^\circ\text{C}$ water follows the same trend as that between $25^\circ\text{C}$ water and bulk ice, but eight times lower in magnitude, indicating that the local structures in room temperature and hot water are very similar. A combination
Figure 1.9: XAS spectra of water at 25°C (black solid line) and 90°C (red dashed line), normalized to the same area [21, 42]. At the top, the difference spectra are displayed: 25°C water minus bulk ice from Fig. 1.7 (thick black line) and 90°C water minus 25°C water (red circles with error bars, multiplied by a factor of 8).

of experimental and theoretical results concluded that liquid water contains 65-85% SD species and 15-35% DD species with an average of ~2.2 H-bonds [42], in direct contrast to the tetrahedral model. This interpretation is supported by theoretical XAS calculations [52] but it has been disputed by a number of other experimental and theoretical studies [53–58]. Nevertheless, XAS has been proven as a sensitive technique for detecting changes in the H-bonding environment in water [21, 59–63].
CHAPTER 1. INTRODUCTION

1.2.4 Bond-Length-With-a-Ruler

The “bond-length-with-a-ruler” principle in the interpretation of XAS spectra was developed by Stöhr et al. [45, 64–66]. The $\sigma^*$ shape resonance above or near the ionization potential (IP) appears when the excited core electron is briefly trapped in a molecular potential barrier before leaving the system. A molecular orbital picture of this phenomenon describes a process in which the electron is excited into an unoccupied antibonding molecular orbital above the ionization potential before it is ejected as a photoelectron. The energy position of the $\sigma^*$ resonance is, therefore, dependent on the splitting between bonding and antibonding orbitals, as illustrated in Fig. 1.10, which, in turn, is correlated with the bond length, since the $\sigma^*$ orbital is located along the intermolecular axis. A smaller splitting, which results from a longer bond length, positions the $\sigma^*$ orbital at a lower energy relative to the IP, while a larger splitting (shorter bond length) results in the $\sigma^*$ position at a higher energy. Sette et al. empirically found a linear correlation between $\sigma^*$ resonance position relative to the IP and the bond length that can be predict unknown bond lengths with a high precision [64].

Figure 1.10: Illustration of the relationship between the bonding-antibonding splitting and the energy position of a $\sigma^*$ peak relative to the ionization potential (IP). The left figure depicts a shorter bond length (larger splitting) compared to the right figure, which places the $\sigma^*$ orbital higher in energy relative to the IP.
The bond-length-with-a-ruler model has been used to characterize the different species of many molecular adsorbates on surfaces [45]. For example, for the case of adsorbed O\textsubscript{2} on Pt(111), it was demonstrated that as the substrate temperature is increased, the $\sigma^*$ resonance peak of the O 1s XAS spectra is shifted to lower energy, indicating that the O-O bond is progressively lengthened and the O\textsubscript{2} molecule exists as different structures [67, 68].

Figure 1.11: Simulated XAS spectra for an ice cluster with 17 water molecules as a function of the intermolecular O-O distance (from Ref. [69] and [21]).

In the case of water, the post-edge can be assigned to a shape resonance analogous to adsorbed O\textsubscript{2} on Pt(111). It has been discussed in previous sections that the post-edge peak of water and ice arises from strong hydrogen-bonding between two water
molecules, which is described as a result of orbital mixing in addition to strong dipole-dipole interaction [17]. Therefore, the energy position of this peak is dependent on the H-bond distance as a core electron is excited into this high-lying, unoccupied mixed orbital. Fig. 1.11 shows simulated XAS spectra of ice clusters as a function of donating H-bond (oxygen-oxygen) distance [69]. The energy position of the post-edge peak is shown to be dependent on the O-O distance in a roughly linear correlation with a factor of 8 eV/Å [69].

Experimental evidence for the bond-length-with-a-ruler concept in liquid water is presented in a study by Cavalleri et al. where the XAS spectra of HCl aqueous solutions at various concentrations were measured [70]. It was shown that at higher concentrations of HCl, the post-edge peak is noticeably shifted to higher energy accompanied by a decrease in the pre- and main edge peaks [70]. This was explained in terms of the two different structures of protonated water that have different H-bond lengths. Eigen species (H$_3$O$^+$) with 1.55 Å intermolecular O-H distance dominates at higher HCl concentrations while the Zundel species (H$_2$O$_5^+$) with a longer intermolecular O-H distance (1.7 Å) is present at lower concentrations.

Therefore, the sensitivity of the post-edge position to H-bond distance can be used as a powerful tool to investigate certain effects that modify the H-bonding network of water, such as ion hydration.

### 1.2.5 XAS Detection Methods

Although XAS is a very common tool in surface studies, its application to water was only developed recently and it has been plagued by many experimental difficulties. This section offers a brief overview of the various detection methods of XAS. More
Transmission mode (T-mode) is the most straightforward method to measure XAS in bulk liquid samples, where the intensity of the photons through a sample cell with a thickness \( x \) is measured with and without the sample inside \( (I\text{ and } I_0, \text{ respectively}) \) while the photon energy is scanned over the O 1s near-edge region (usually 525 to 570 eV) \[71\]. The absorption coefficient \( \mu \) can be determined through the Beer-Lambert Law

\[
I = I_0 e^{-\mu x}.
\] (1.5)

This method is inherently bulk sensitive since the x-ray penetrates through the entire water sample.

Fluorescence yield (FY) is an indirect XAS detection mode in which the decay of the core-hole via a radiative process is used to determine absorption \[45\]. After a core hole is created from an x-ray absorption process, an electron from the higher lying orbitals decays to fill the hole while releasing photons. The intensity of the emitted photons is proportional to the absorption coefficient at certain incident photon energy. This technique is also often used for bulk liquid samples. However, when the sample depth is larger than the x-ray penetration length (i.e. when the sample is not sufficiently dilute), non-linear effects due to self-absorption are observed as saturation of the strongest spectral features \[72, 73\]. Mathematical corrections must, therefore, be applied to compensate for the saturation effects \[60, 74\].

Electron yield detection methods involve the non-radiative decay processes of core holes. In Auger electron yield (AEY), the energy that is released when a higher energy electron fills the core hole is used to remove another electron (Auger decay
process) [45]. AEY signal is obtained by setting the electron analyzer energy window to the kinetic energy of the Auger electron and measuring the emitted Auger electrons. Due to the relatively high kinetic energy of Auger electrons, this method is surface sensitive.

A second commonly used electron yield detection method is total electron yield (TEY) XAS, which collects emitted electrons of all energies, including low energy electrons that result from the inelastic scattering of Auger electrons [45]. As a result, this method is more bulk sensitive compared to AEY. In general, although electron yield detection methods are very commonly utilized in surface science, its ultra-high vacuum requirement is incompatible with liquid samples that must be kept in ambient conditions. However, this problem has been solved by recent experimental advances such as liquid microjets and differential pumping systems.

1.2.6 X-ray Raman Scattering

Another method to indirectly measure x-ray absorption intensity is through x-ray Raman scattering (XRS). Unlike conventional XAS techniques mentioned previously, which use soft x-ray ($h\nu = 100$-1000 eV), XRS uses hard x-ray ($h\nu = 2$-10 keV), which does not require vacuum environments. In this technique, high energy photons are inelastically scattered and a small fraction of the energy loss is used to excite a core-level electron in an x-ray absorption process.

The connection between XRS and XAS has been theoretically and experimentally established [75–77]. The transition probability for photon scattering $\omega$ for XRS is described as

$$\omega \propto (1 + \cos^2 \theta) \mid \langle f \mid e^{i\vec{q} \cdot \vec{r}} \mid i \rangle \mid^2,$$

(1.6)
where $\theta$ is the scattering angle and $\vec{q}$ is the momentum transfer defined as $q = (4\pi/\lambda)\sin(\theta/2)$. When $qr < 1$, which can be satisfied by collecting scattered photons at certain scattering angles, the exponential term can be reduced to the first two terms of the Taylor expansion, and the equation becomes

$$\omega \propto (1 + \cos^2 \theta) \sin^2 \theta | \langle f | r | i \rangle |^2,$$

(1.7)

which contains the dipole transition matrix element as in XAS.

The dependence on scattering angle is an important aspect in XRS measurements because at large scattering angles, momentum transfer $\vec{q}$ becomes larger and the $qr < 1$ condition is not satisfied. Therefore, the expansion of the exponential term in equation 1.6 would include non-dipole contributions. Experimentally, this appears as non-dipole excitations in the spectrum, e.g. $s \rightarrow s$ transition, which in the case for water appears in the pre-edge [21], and consequently the spectrum does not reflect the true x-ray absorption process. However, by measuring scattering at the proper angle, XRS has proven itself as a reliable and highly reproducible method for measuring x-ray absorption spectra.

1.3 New Model of Liquid Water

1.3.1 Two Components in Liquid Water

It has been described in Section 1.2.3 that XAS shows that liquid water contains a large number of weak or distorted H-bonds. Experimental results from x-ray emission spectroscopy (XES), a complementary technique to XAS that probes occupied valence
orbitals through a radiative decay of the core hole, offers direct evidence that there are two components in liquid water, which can be observed through the energy splitting of the lone pair 1b$_1$ orbital, resulting in the appearance of two peaks [43].

Since the initial state of XES corresponds to the final state of XAS, each spectral feature of the water O 1s XAS spectrum can be selectively probed using XES. It was determined that the higher energy lone pair peak (1b$_1''$) is linked to the XAS pre-edge and, therefore, it corresponds to the distorted H-bonded water species, while the lower energy peak (1b$_1'$) is linked to the post-edge and is attributed to tetrahedral-like water molecules [43]. The energy position of the 1b$_1''$ peak is close to that of gas-phase water 1b$_1$ peak while the energy of 1b$_1'$ is close to the corresponding peak in ice. Quantitative analysis through a curve-fitting procedure yields 2:1 ratio of distorted species to the tetrahedral species [43], confirming XAS findings. It was also shown that an intensity redistribution from the post-edge to the pre- and main edge in XAS as the water temperature is increased corresponds to an increased intensity of the XES 1b$_1''$ peak relative to 1b$_1'$, which can be explained as a conversion of one species to the other, i.e. from tetrahedral to distorted species [43, 44].

1.3.2 Small Angle X-ray Scattering

Small angle x-ray scattering (SAXS) is a technique in which x-ray photons are elastically scattered by particles in an inhomogeneous sample, and the scattering intensity is recorded as a function of momentum transfer $Q$, which is related to the scattering angle $2\theta$ through $Q = 4\pi \sin(\theta)/\lambda$ where $\lambda$ is the x-ray wavelength. By definition, in a SAXS measurement, scattering at small angles is measured and, therefore, correlations from large distances can be extracted from the data. It is a sensitive probe
for density variations in solution samples and it is a common technique for studying
the structure and interactions of biomolecules [78]. The scattering intensity $I(Q)$ is
defined as $I(Q) = F(Q) \times S(Q)$ where $F(Q)$ is the form factor or scattering from one
individual particle and $S(Q)$ is the structure factor or correlation between particles.
From SAXS data, information such as the size of the scattering units, the distance
between scattering units, and the electron density difference between the scattering
units and the surrounding medium can be extracted. For a more detailed description
of SAXS and its applications, the readers are directed to Ref. [79].

Recently, the observation of a low-$Q$ intensity enhancement in the SAXS data
of liquid water [44], which is especially strong at supercooled temperatures [80], was
proposed as evidence for the presence of density heterogeneities in liquid water. This
enhancement is not observed for simple liquids such as CCl$_4$ [44]. Molecular dynamics
simulations using the SPC/E potential also failed to reproduce the low-$Q$ scattering
intensity enhancement observed in the experimental data of liquid water [44]. This
indicates that the enhancement is not caused by normal thermal fluctuations, but
rather by density heterogeneities in the liquid. Through the extrapolation of struc-
ture factor at $Q = 0$, the isothermal compressibility at each temperature can be
obtained from the water experimental SAXS data, and the resulting plot of isother-
mal compressibility as a function of temperature agrees very well with the existing
literature, which shows an anomalous behavior with a minimum at $\sim 46^\circ$C [44]. The
temperature-dependent isothermal compressibility curve obtained from the SPC/E
model, however, indicates a normal liquid behavior [44].
1.3.3 Density Fluctuations in Liquid Water

In combination with XAS [42] and XES [43] results, it was concluded that the density heterogeneities in the SAXS data arise from the different components in water that have different densities [44]. The tetrahedrally H-bonded water molecules, which predominantly contribute to the post-edge in XAS and the $1b_1$ peak in XES, form low-energy/low-entropy structures that have a lower density than the average of the liquid. The distorted H-bonded water molecules, which are observed as the pre-edge in XAS and the $1b_1$ peak in XES, form high-entropy, high-density structures with a larger number of distorted H-bonds that compensate for the loss of enthalpy. However, these two species do not persist over long time scales and they interconvert continuously within the H-bond breaking and reforming time scale [44].

The effect of temperature increase, which is observed in XAS as an intensity redistribution from the post-edge to the pre- and main edge, can, therefore, be interpreted as a conversion from the tetrahedral species to the distorted species as H-bonds are broken. However, a secondary effect also occurs as the existing distorted species undergoes thermal excitation and becomes more disordered until it structurally resembles gas-phase water. This is observed from the lower energy shift of the XAS pre-edge and higher energy shift of the $1b_1$ XES peak as temperature is increased (i.e. closer to the $4a_1$ and $1b_1$ peak positions of gas-phase water in XAS and XES, respectively) [44].

The presence of two distinct structures in liquid water at ambient conditions is hypothesized as an extension of the low and high-density structures in amorphous ice and supercooled water. It is known that when water is rapidly cooled to below its
crystallization temperature, it forms low-density amorphous ice (LDA) at low pressures (below 0.2 GPa) [81] and high-density amorphous ice (HDA) at high pressures (above 0.2 GPa) [81]. Further increase in pressure can convert HDA into very high-density amorphous ice (VDHA) [82, 83]. There is a hypothesis of a second critical point [84, 85] where this phase separation ends, although there is no agreement on the location. Stanley et al. proposed that there is a liquid-liquid phase transition between high and low-density liquid in the supercooled region and the extension of the phase separation beyond the second critical point is called the Widom line [84–87]. It is hypothesized that this transition extends to the ambient region, leading to the observation of high and low-density liquid water (HDL and LDL, respectively) that exist as two constantly fluctuating structures instead of clearly separated phases as in the glassy water region [21, 44]. The dominance of the H-bond distorted HDL over the tetrahedral LDL species at ambient temperatures is because high-density water exists on the high temperature side of the Widom line, while low-density water exists on the low temperature side.

1.4 X-ray Photoelectron Spectroscopy

Based on the photoelectric effect, modern XPS was developed in the 1950’s by Kai Siegbahn as Electron Spectroscopy for Chemical Analysis (ESCA) [88]. Similar to XAS, XPS is also a process that involves core-hole creation. However, unlike XAS where the core electron is excited to an unoccupied orbital, in XPS the core electron is ejected from the system in an ionization process. Experimentally, the photon energy determines whether XPS or XAS occurs as a result of photon absorption. While in a normal XAS measurement the photon energy is scanned over an energy range
corresponding to the near edge region, in a typical XPS measurement, the photon energy is fixed at a value higher than the binding energy of the core electron while the kinetic energy of the ejected electron is measured.

Since the total energy before and after the photon absorption event must be conserved, the electron binding energy can be determined from the relationship:

$$E_b = \hbar \nu - E_k + \phi,$$

where $E_b$ is the exact binding energy, $\hbar \nu$ is the photon energy, $E_k$ is the kinetic energy of the photoelectron, and $\phi$ is the work function for metals (zero for nonmetals).

Since the binding energies of core electrons are unique for each element, XPS is a sensitive tool for probing a specific atom to distinguish it from the other atoms in the sample, such as in an adsorbate/substrate system. In addition, since the core electron binding energy is influenced by the valence electrons, changes in the local environments of an atom (e.g. chemical bonding, adsorption to a substrate, changes in molecular orientation) can be detected from XPS through the observation of binding energy shifts and/or changes in peak widths.

The intensity of an XPS peak depends on various factors such as the intensity of the incident x-ray photons, the concentration of the atoms of interest in the sample, the photoemission cross-section, the analyzer acceptance angle, the inelastic mean-free path of the photoelectrons, the transmission function of the analyzer, and detector efficiency. The core-hole lifetime causes a Lorentzian broadening to the line shape of an XPS peak according to Heisenberg’s uncertainty principle, where short lifetimes lead to a broader peak and vice versa.
Due to the short mean free path and escape depth of electrons (in the order of several Å), only electrons ejected from the top few layers of the sample can be detected. XPS is, thus, inherently surface sensitive and is an ideal technique for studying adsorbed ice on substrates. For example, in combination with XAS, XPS was used to determine that in a water monolayer adsorbed on Pt(111) and Ru(0001) single crystals, the water molecules coordinate to the metal atoms with H-down orientation [89, 90].

1.5 Thesis Outline

The main theme of this dissertation is the synchrotron x-ray study of water, both in solid and liquid phases, in terms of structure and interaction with solutes in aqueous solutions as well as with surfaces. The present chapter has described evidence for the new model of liquid water in its bulk state, and it is important to examine the implications of this model when water interacts with other systems such as solutes and interfaces, as a more realistic model system for water in nature.

Subsequent chapters in this dissertation are organized as follows. Chapter 2 provides a more thorough description of the experimental techniques (e.g. sample preparation, experimental setup and conditions, advantages and limitations) used in this dissertation, such as XAS, XPS, and SAXS. However, the specific details for each experiment may vary and will be noted in the experimental sections of Chapters 3 to 6.

Chapters 3 and 4 focus on the study of liquid water in aqueous solutions of ions and in reverse micelles, respectively. Specifically, in Chapter 3 O 1s x-ray absorption spectra from both soft and hard x-ray techniques as well as small angle x-ray scattering
were used to study the effect of different ions on the structure of the surrounding water molecules. In Chapter 4, O 1s XA spectra measured by XRS show that water confined in reverse micelles has a higher number of distorted H-bonds compared to pure water.

The focus is shifted from liquid water to ice in Chapters 5 and 6. In Chapter 5, the interaction between ice and hydrophobic methyl-terminated Si(111) is studied using XAS and it is revealed that there is a direct electronic interaction between water and the methyl groups on the surface. Finally, Chapter 6 describes the growth and structure of crystalline ice on Pt(111) using XPS and XAS.

1.6 References


CHAPTER 1. INTRODUCTION


Chapter 2

Experimental Details

2.1 Transmission-Mode XAS

2.1.1 Sample Preparation

In Chapter 1, it is mentioned that T-mode XAS is the simplest and most direct way to measure x-ray absorption. However, literature on T-mode XAS of water is scarce. In 1987, Yang and Kirz measured EXAFS of water placed between two Si$_3$N$_4$ windows with PMMA spacer [1]. In 2005, Näslund et al. measured T-mode XAS spectrum of liquid water using a similar sample cell consisting of two Si$_3$N$_4$ windows with polystyrene nanospheres as spacers [2]. More recently, Nagasaka et al. developed a flow cell for water T-mode XAS measurements [3]. For soft x-ray measurements of water in aqueous solutions, T-mode XAS is not as commonly used as fluorescence yield [4, 5] or total electron yield [6, 7]. Despite all of its advantages, the unpopularity of T-mode XAS is due to the restrictive sample requirements. Due to the short attenuation length of soft x-ray in water, the sample thickness should
ideally be between 200-500 nm to obtain a good spectrum. Samples that are too thin yield noisy spectra while those that are too thick have low transmission. Fig. 2.1 shows the O K-edge transmission intensity at 200 nm and 500 nm sample thickness*, yielding ∼30% and ∼60% absorption respectively. In addition, the sample thickness must be relatively uniform and the sample cell must be leak-tight because soft x-ray measurements are performed in either low vacuum or helium environment.

The sample cells for T-mode XAS were prepared at the Stanford Nanofabrication Facilities (SNF) from Si(100) wafers (Silicon Specialists Inc., Hayward, CA) coated on both sides with 200 nm Si₃N₄ (performed by International Wafer Services, Santa Clara, CA). 10 nm SiO₂ was deposited on the inside Si₃N₄ surface using plasma enhanced chemical vapor deposition (PECVD), and for the bottom half of the cell 300 nm thick Au (with 5 nm Cr prime layer) was sputtered to form the frame and spacers, using photoresist as the mask. The spacers were 10 × 10 μm² squares and

*Obtained from x-ray transmission of a solid calculator from Lawrence Berkeley National Laboratory Center for X-ray Optics website, http://www-cxro.lbl.gov/
the separation between the spacers was 40 µm. The silicon was wet-etched in 22.5% KOH solution to make 500 × 500 µm² x-ray transparent areas where the Si₃N₄ on the outside on the wafer was plasma-etched (unetched area remained protected by Si₃N₄, which is very slowly etched in KOH) and the wafers were cut into 5 × 5 mm² pieces. The wafers were cleaned with Piranha solution (4:1 H₂SO₄:H₂O₂) before they were used in measurement.

Figure 2.2: Depiction (not to scale) of the T-mode XAS sample cell and sample preparation method.

Fig. 2.2 depicts the finished sample cell and the sample preparation method. A
small droplet of the aqueous solution sample was placed on the bottom half of the cell (with the Au frame and spacers) and the top half was placed over it and pressed to squeeze out excess liquid. The sides of the cell were sealed with epoxy glue to prevent the evaporation of the liquid in the low vacuum or helium environment.

### 2.1.2 Experimental Setup

![Figure 2.3: Picture of the transmission endstation connected to SSRL BL 10-1.](image)

T-mode XAS measurements were performed at beamline (BL) 10-1 at the Stanford Synchrotron Radiation Lightsource (SSRL). The endstation (Fig. 2.3) consists of two parts separated by a 200 nm Si$_3$N$_4$ window: the ultra high vacuum (UHV) I$_0$ section with a base pressure of less than $5 \times 10^{-9}$ Torr and a sample chamber with low vacuum ($< 5$ mTorr). The I$_0$ section is used to detect and normalize the spectra to any instabilities or noise from the beamline. The sample chamber is equipped with
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Figure 2.4: The experimental setup inside the sample chamber. The beam goes through the 25 µm pinhole before hitting the sample and the transmitted beam is measured by the photodiode. The figure is not to scale.

a 25 µm diameter molybdenum pinhole mounted on a vertical linear transfer rod, a manipulator with a rod on which up to four sample cells can be mounted, and a silicon p-n junction photodiode (International Radiation Detectors, Inc.) (see Fig. 2.4 for the experimental setup).

2.1.3 Data Analysis

Data analysis of T-mode XAS is fairly simple; an example for the pure water spectrum is described in Fig. 2.5. The raw transmission spectra of an empty cell (dashed line) and water in cell (solid line) are shown in Fig. 2.5A; the structure in the empty cell originated from the oxide coating of the sample cell and from oxygen contamination
Figure 2.5: T-mode XAS analysis for liquid water. (A) Raw transmission spectra of the empty cell (dashed line) and water in cell (solid line), (B) the final XAS spectrum of water.
in the beamline optics. The absorption spectrum was then obtained by dividing the water spectrum by the empty cell spectrum and taking the negative logarithm. A linear background was then subtracted from 520-532 eV and finally the area of the spectrum between 532 and 550 eV was normalized to 1. The final spectrum is displayed in Fig. 2.5B.

2.1.4 Advantages and Limitations

Besides the simple data analysis, another advantage of T-mode XAS is that it does not suffer from saturation effects due to self absorption as in FY-XAS [4]. Compared to XRS, the direct absorption cross-section is much larger than the inelastic scattering cross-section, resulting in much a shorter measurement time (\(\sim 5\) minutes for one scan). Also, the presence of large atoms that can contribute to background scattering in XRS is not a problem in T-mode XAS, thereby allowing it to measure a greater variety of solutes.

The limitations of T-mode XAS are generally related to sample uniformity. Although the sample cell described in Section 2.1.1 can effectively limit the sample thickness to less than 500 nm, the liquid sample does not uniformly fill the cell. Instead, images from scanning transmission x-ray microscopy (STXM) have shown that water or aqueous solutions samples tend to form areas with different thicknesses throughout the cell (Fig. 2.6). To circumvent this problem, a pinhole with a 25 \(\mu\)m diameter was used to probe a region of the sample where the thickness is more uniform. There are still slight variations in the spectrum of water measured in T-mode compared to XRS or STXM (where the 50 nm beam spot size is smaller than the length scale of the thickness inhomogeneities) [8]. However, T-mode XAS is still
2.2 X-ray Raman Scattering

2.2.1 Sample Preparation

Unlike T-mode XAS, XRS sample preparation is very simple. Since the penetration depth of hard x-ray photons in water is much larger than soft x-ray (∼0.50 mm compared to 500 nm), no special sample cells are required. In addition, hard x-ray measurements do not require vacuum environments. Water or aqueous solution sample was placed in a 60 mL polyethylene bottle with a Si$_3$N$_4$ window (purchased...
Figure 2.7: The partial experimental setup for XRS: A - He ion chamber where the beam from the beamline is measured to detect any instability, B - sample bottle with Si$_3$N$_4$ window, and C - detector with slit.

from Silson Ltd. UK, with $5 \times 5$ mm$^2$ membrane size, 1 $\mu$m membrane thickness, $1 \times 1$ cm$^2$ frame size) glued over a cutout area through which the incident and scattered x-ray photons can pass. To avoid beam damage, the sample was circulated with a Teflon-coated magnetic stirring bar and the bottle was placed on a stirring plate.

2.2.2 Experimental Setup

This section describes the general experimental setup for XRS. Specific details that vary between different measurements (e.g. beam spot size, resolution, and photon flux) are described in the experimental sections of Chapters 3 and 4.

XRS measurements were performed at SSRL BL 6-2, equipped with Si(111) and Si(311) double crystal monochromators for low resolution and high resolution measurements, respectively. Raman scattering at $\sim 45^\circ$ scattering angle was analyzed
using a high-energy-resolution multicrystal spectrometer consisting of 14 Si (440) analyzer crystals with a diameter of 100 mm in a Rowland geometry (1 m radius) and a fixed Bragg angle of 88°. This setup selects 6.46 keV photons with momentum transfers of \( Q = 2.6 \pm 0.5 \, \text{Å}^{-1} \), which is well within the dipole limit (see the supplementary information of Ref. [9]). The monochromator energy was scanned from 6980 to 7032 eV corresponding to an energy transfer of 520 to 572 eV, which is the O K-edge region. The x-ray path from the beampipe to the detector (including the sample) was kept in 1 atm He to avoid background scattering from air. A single element Si drift detector was used in photon counting mode with an electronic window set to reduce the background signal from unwanted background scattering. Pictures of the XRS experimental setup are displayed in Figs. 2.7-2.9.
2.2.3 Data Analysis

Analysis of XRS data is generally quite straightforward as shown in Fig. 2.10 for pure water. The energy position between each individual scan (e.g. Fig. 2.10A, lower curve) was examined and corrected if a drift was observed, then the scans were summed to obtain the upper curve in Fig. 2.10A. The energy scale of the spectrum was then shifted by the elastic peak position (∼6460 eV), a linear background below the pre-edge was subtracted to eliminate the background from Compton scattering, and the spectrum was normalized by area to 1 between 532 and 550 eV. The Poisson error bars were obtained by taking the square root of the summed spectrum (i.e. the total count) and treating them with the same energy shift and normalization as
CHAPTER 2. EXPERIMENTAL DETAILS

2.2.4 Advantages and Limitations

As mentioned in Section 2.2.1, the greatest advantage of XRS over soft x-ray XAS is its flexibility in sample handling and experimental conditions. In addition, XRS...
spectra display no saturation effects and the intensity scale is highly reliable. XRS spectra are also highly reproducible as evidenced by the water spectra measured during different experiments separated by many years, even at different synchrotron facilities (i.e. Advanced Photon Source (APS) and SSRL), which are identical within statistical error bars [10].

The inherent limitations of XRS are related to the low scattering cross-section; so for one sample, many scans measured over a period of several hours must be summed to obtain good statistics of the spectrum. The signal count from O 1s absorption is proportional to the number of O atoms in the probed sample depth; therefore, samples containing high solute concentrations are more difficult to measure. In addition, scattering from large atoms contributes to the background and reduces the signal to noise ratio. In some cases, a combination of these factors can result in a measurement time of up to three days for one sample.

Improvements in signal count often require a trade-off with resolution, which is another limitation of XRS. Older XRS studies used low resolution Si(111) monochromator that produced higher photon flux, but limited the energy resolution to $\sim$1 eV [9–12] (compared to soft x-ray resolution of $\sim$0.1 eV), which is often insufficient for observing small changes in the spectra. Recently, higher resolution spectra ($\sim$0.5 eV) were measured using Si(311) monochromator [8, 13]; the lower photon flux was compensated by the recent upgrades in the SSRL ring current. Other ways to improve signal intensity require deviations from the dipole approximation. Although the photons are scattered in all directions, only a small fraction is collected by the analyzer. This is related to the dependence on scattering angle to satisfy the dipole approximation described in Section 1.2.6. Although collecting more photons at larger
scattering angles would definitely improve the signal count since the transition probability is proportional to \( q^2 \), unwanted contributions from non-dipole transitions would also increase. One possible way to collect a higher fraction of scattered photons is by adding more analyzer crystals in the vertical direction, which will be implemented in the near future at SSRL BL 6-2.

2.3 Other Experimental Techniques

2.3.1 Surface Science XPS and XAS

Surface science measurements were performed at elliptically polarized undulator (EPU) beamlines 5-1 and 13-2 at SSRL. Experiments must be carried out under UHV conditions to ensure the cleanliness of the sample, and detectors must also be kept under vacuum due to the short mean free path of electrons. The UHV endstation consists of two chambers: preparation chamber where substrates are cleaned, adsorbates are prepared \textit{in-situ} in UHV, and samples can be characterized; and the main experimental chamber where XPS, XAS, and/or XES measurements are performed. The main chamber is kept at a base pressure of lower than \( 1 \times 10^{-10} \) Torr during experiments while the preparation chamber pressure can go up to \( 1 \times 10^{-8} \) Torr during sample loading, gas dosing, and/or ion sputtering.

The preparation chamber is equipped with a load-lock sample loading system, ion gun, gas doser, low energy electron diffraction (LEED) optics, Hiden HAL-201-RC quadrupole mass spectrometer, and (formerly) a Bruker Vector 33 FT-IR with a narrow band HgCdTe detector system. The main chamber is equipped with a Scienta SES-200 hemispherical electron analyzer for XPS measurements, a partial electron
yield XAS detector, and a grating spectrometer for XES. Samples can be transferred from the preparation chamber to the main chamber using a horizontally mounted manipulator connected to a liquid nitrogen cooling system that can cool samples down to $\sim 90$ K. With EPU beamlines, the E-vector polarization of the incoming beam can be rotated so that the x-ray can probe orbitals of different symmetries. A grazing incidence angle of less than 6° relative to the incoming beam was used to minimize beam damage and increase surface sensitivity. To further minimize beam damage, samples were scanned during XPS and XAS measurements and ice films were prepared with D$_2$O was used instead of H$_2$O. The total energy resolutions were 0.3 eV and 0.1 eV for XPS and XAS, respectively.

Figure 2.11: Picture of the UHV surface science endstation at SSRL BL 13-2
A picture of the endstation is shown in Fig. 2.11. Specific details of sample preparation and measurement conditions are described in the experimental sections of Chapters 5 and 6.

### 2.3.2 Small Angle X-ray Scattering

SAXS measurements were performed at BL 4-2 at SSRL using a beam energy of 11 keV and an optical fiber coupled CCD detector. The sample holder consisted of a quartz capillary with a diameter of 1.5 mm. The sample holder, detector and the path in between were placed in a vacuum of $1 \times 10^{-3}$ Torr in order to reduce the background scattering. The sample holder was connected to a constant temperature bath in order to maintain and control the sample temperature. The scattering vector is defined as $Q = \frac{4\pi \sin \theta}{\lambda}$, where $\lambda$ is the wavelength and $\theta$ is one half of the scattering angle. In order to reduce beam damage, the data were continuously collected for 10 frames for 1 minute each, and all scattering images were averaged afterward. Since the scattering of the empty capillary contribute $\sim 20\%$ of the total scattering at $Q > 0.05 \, \text{Å}^{-1}$, it had to be measured separately and subtracted from the total scattering signal to obtain the scattering only from the sample.
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2.4 References


Chapter 3

The Structure of Water in Ion Solutions

This chapter is adapted from three separate manuscripts:


My contributions as the first author in these manuscripts include performing the experiments, analyzing the data, and writing most of the manuscript.

3.1 Introduction

The interaction between solvated ions and water has been a subject of great interest due to its importance in various chemical and biological processes. In the 19th century, Franz Hofmeister observed that different salts influence protein precipitation in different ways [1]. It is now believed that this so-called “Hofmeister effect” is due to the ability of ions to either increase or decrease the ordering of the surrounding water molecules [2]. Ion size has been shown to be correlated to the ability to bind water tightly; smaller ions with high charge densities tend to be structure makers while larger ions with lower charge densities are generally structure breakers [3, 4]. This classification has been derived from measurements of macroscopic properties such as viscosity [5, 6] and hydration entropy [7]. The relative strength of ion-water interaction has been quantified through size-exclusion chromatography to determine the apparent dynamic hydration numbers (ADHN), i.e. the number of water molecules bound to an ion as it elutes through the chromatographic column [8]. The results generally agree that ions with higher charge density have higher numbers of tightly bound water molecules. This has also been proposed as the mechanism behind cellular ion channels being closed to strongly hydrated Na\(^+\) ions while allowing formally larger, but more easily dehydrated, K\(^+\) ions to pass through [9–12].

While the relative strengths of the direct interaction between different ions and water molecules in the first hydration shell are well understood, the effect of ions
on the hydrogen (H-) bonding of water beyond the first hydration shell is still debated despite extensive research. The classification of ions as structure-breakers or structure-makers can even be misleading in this regard. A Monte-Carlo study by Hribar et al., for example, proposed that small ions interact with water molecules through strong electrostatic interaction accompanied by H-bond breaking while large ions that interact weakly with water facilitate the formation of H-bonds [4], contrary to the conventional definition. Neutron diffraction studies suggested that monovalent ions have pressure-like effect on water that extends beyond the first hydration shell [13]. However, it is unclear whether the effect on the second shell can be directly observed from the experimental data or whether it arises from the empirical potential structure refinement (EPSR) simulation model [14]. The pressure-like effect has been confirmed for NaCl solutions in a molecular dynamics study of the self-diffusion coefficient of water, which reflects the mobility of water molecules in NaCl solutions [15]. Ultrafast vibrational pump-probe spectroscopy [16, 17], on the other hand, proposed that ions only influence water molecules in the first hydration shell (i.e. in direct contact with the ion). More recently, a combined experimental study using dielectric spectroscopy and femtosecond infrared spectroscopy revealed that there is a cooperativity effect between cations and anions in the structuring of the water molecules in the solution and that in some solutions the effect of the ions extends beyond the first hydration shell [18].

Multivalent cations such as Mg$^{2+}$ and Al$^{3+}$, in particular, are considered as strongly interacting with water molecules in their hydration shells due to their high charge density. The structure of the first hydration shell of Mg$^{2+}$, Al$^{3+}$, and a variety of other cations has been extensively characterized experimentally using neutron
CHAPTER 3. THE STRUCTURE OF WATER IN ION SOLUTIONS

diffraction, x-ray diffraction, and extended x-ray absorption fine structure (EXAFS) spectroscopy as well as computationally using molecular dynamics simulation (for a comprehensive review, see Ref. [19]). Infrared spectroscopy analyzed using a double difference method shows that Mg$^{2+}$ and Al$^{3+}$ form at least one and two well-defined hydration shells, respectively [20, 21]. However, the observation of distinct O-D stretch bands corresponding to H-bonds between first and second hydration shells for Mg$^{2+}$ as well as between second and third hydration shells for Al$^{3+}$ [20, 21] indicates that at least one more hydration shell is present for each cation.

The dependence on size of the effect of ions in water can clearly be seen in alkali and halide ions. From viscosity and hydration entropy data, only the smallest alkali cations (i.e. Li$^+$ and Na$^+$) are considered as structure-makers while the rest (i.e. K$^+$, Rb$^+$, and Cs$^+$) are structure-breakers [3, 7, 22]. However, the exact role of Na$^+$ in this classification from other measurements is somewhat unclear as it is also often categorized as a structure breaker. For instance, in a neutron diffraction study analyzed through the EPSR method [23], it was suggested that although Na$^+$ binds water more tightly than K$^+$ does (i.e. Na$^+$ is a local structure maker), both cations disrupt water-water H-bonding beyond the first hydration shell. Similar to the alkali cations, the relative strengths of the halide ions as structure makers or structure breakers are dependent on their sizes. This is corroborated by various experimental studies such as nuclear magnetic resonance (NMR) and dielectric relaxation spectroscopy [2] as well as molecular dynamics simulations [24–26].

Among halides, fluoride (F$^-$) is certainly regarded as a unique in terms of its effect on the structure of the surrounding water. For example, F$^-$ was found to have the highest ADHN among all singly charged ions, including small monovalent cations
such as Li$^+$ and Na$^+$; in fact, only di- and trivalent cations (e.g. Mg$^{2+}$, Al$^{3+}$, Cr$^{3+}$) have higher ADHNs than F$^-$ [8]. It is the only halide with a negative hydration entropy [3, 7] and a positive Jones-Dole viscosity B coefficient [2, 7]; therefore, F$^-$ is traditionally classified as a structure-making ion, while other halides are considered as structure-breakers.

Various experimental studies have demonstrated the strength of the interaction between water and fluoride. For instance, infrared [22, 27] and Raman [28] spectroscopies show a red-shift in the O-D/O-H stretching band of F$^-$ containing solutions and blue-shift for other alkali halide solutions. The red-shift in the O-H (or O-D) stretching band is commonly associated with the strengthening of H-bonds and blue-shift with the weakening of H-bonds. Results from Raman $\xi$-function dispersion study also suggest that F$^-$ form strong H-bonds with water [29], and neutron diffraction data interpreted using the EPSR method indicates that F$^-$ increases the structure of the water molecules in its first hydration shell [30]. Other experimental studies [21, 31] and a number of molecular dynamics simulations [24, 32–34] have supported this; therefore, it is generally undisputed in literature that F$^-$ forms a strong interaction with water.

The structure-making effect of F$^-$ is generally attributed to its small size and, consequently, high charge density relative to other halides. Indeed, other ions that strongly interact with water, such as Mg$^{2+}$ and Al$^{3+}$, tend to have high charge densities. According to literature, the residence time of water molecules in the first hydration shell of F$^-$ (20 - 30 ps [24, 35, 36]) is longer than that of Cl$^-$ (5 - 9 ps [24, 35, 36]); however, it is still many orders of magnitude shorter than those of Mg$^{2+}$ ($\sim$10$^{-6}$ s) and Al$^{3+}$ ($\sim$1-6 s) [19, 37]. In addition, while various studies suggest the presence
of strongly bound second and third hydration shells for Mg$^{2+}$ and Al$^{3+}$ [20, 21], respectively, there is no such evidence for F$^-$.

Therefore, water is bound more weakly to F$^-$ than to Mg$^{2+}$ or Al$^{3+}$, which can be explained by the higher charge densities of Mg$^{2+}$ and Al$^{3+}$ due to their smaller sizes (ionic radii of 72 pm and 54 pm, respectively) and the multiple charges compared to the singly charged F$^-$ (ionic radius of 133 pm). In addition, F$^-$ is unique among other monatomic ions because it is capable of forming strong H-bonds with water molecules. The lone pairs of electrons can act as H acceptors, and, therefore, the water molecules in the first hydration shell only have one available H donor. On the other hand, the water molecules in a cation’s first hydration shell point their O atoms towards the cation, leaving two available H donors. Thus, the nature of the hydration shell formed by F$^-$ differs from those formed by cations such as Mg$^{2+}$ and Al$^{3+}$.

Results from XAS measurements of aqueous solutions of ions have so far yielded conflicting interpretations. Total electron yield (TEY) XAS studies by Cappa et al. proposed that XAS spectral changes are caused by a direct electronic perturbation by the anions to the surrounding water molecules while monovalent cations have no significant effect on the structure of water and divalent cations affect water structures through charge transfer [38, 39]. The fluorescence yield (FY) XAS study by Näslund et al., on the other hand, concluded that anions do not affect the electronic structure of the water molecules and that changes in the XAS spectra are instead caused by the reorganization of H-bonding among the water molecules near the cations [40]. Although soft x-ray XAS is a commonly used technique for surface studies, its application to liquid samples such as water and aqueous solutions has been plagued by
saturation effects exhibited in both FY and TEY detection modes [40, 41]. TEY-XAS spectra, in particular, have been demonstrated to suffer from saturation effects, which can seriously complicate data interpretation by affecting relative intensities in different spectral regions [41, 42].

In this chapter, XAS (measured through both soft x-ray and XRS) and SAXS were used to investigate the effect of various ions on the local structure of water in the solution. First, we studied the effect of increasing cation charge (Na$^+$, Mg$^{2+}$, Al$^{3+}$) on the structure of the hydration shells and found that while Na$^+$ weakens the H-bonding among the water molecules in the vicinity of the ions, both Mg$^{2+}$ and Al$^{3+}$ form stable, highly ordered, high-density hydration shells. Next, we used XAS and SAXS to explore the effect of fluoride anion, which increases the fraction of low-density structures in the solution due to the strong fluoride-water H-bonds. Lastly, we measured the O 1s XAS spectra of various alkali halide solutions using T-mode XAS and found that all alkali cations weaken water H-bonds although the magnitude of the effect varies between different ions; for halides, chloride and bromide ions do not significantly affect the structure of water, while iodide weakens water H-bonds.

3.2 Water in the Hydration Shell of Cations

3.2.1 Experimental Details

NaCl (1 and 4 M), MgCl$_2$ (1 and 2.8 M), and AlCl$_3$ (1 and 2.8 M) solutions were prepared using commercially obtained salts without further purifications (NaCl and MgCl$_2$·6H$_2$O >99% from Fisher Chemical and AlCl$_3$·6H$_2$O 99% from Acros Organics) dissolved in Millipore-purified H$_2$O ($\sim$18 MΩ cm). XRS measurements were
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performed at the Stanford Synchrotron Radiation Lightsource (SSRL) at the hard x-ray beamline (BL) 6-2 equipped with a Si(311) double crystal monochromator. The experiments were done in two separate runs (NaCl and AlCl$_3$ in one run and MgCl$_2$ in a separate run). The spectra of pure water measured in both runs were identical within statistical error bars, confirming the reliability and reproducibility of XRS demonstrated in a previous study [43]. The experimental setup (which is described in more detail in Chapter 2) was identical for both runs; the only difference was the synchrotron ring current (100 mA for MgCl$_2$ and 200 mA for NaCl and AlCl$_3$), which only influenced the photon flux (∼2.5 × 10$^{12}$ photons/sec for the NaCl and AlCl$_3$ run and ∼0.8 × 10$^{12}$ photons/sec for the MgCl$_2$ run) and, consequently, count rate and measurement time. The beam spot was focused down to ∼0.1 × 1 mm$^2$ and the overall energy resolution amounted to 0.55 ± 0.02 eV full width at half maximum (FWHM). The energy scale was calibrated by recording elastic peak every five scans.

<table>
<thead>
<tr>
<th>Sample</th>
<th># Scans</th>
<th>Total Count</th>
<th>Background</th>
<th>Signal and % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>5</td>
<td>9477</td>
<td>1028</td>
<td>8449 ± 1.2%</td>
</tr>
<tr>
<td>1 M NaCl</td>
<td>8</td>
<td>9764</td>
<td>1116</td>
<td>8648 ± 1.1%</td>
</tr>
<tr>
<td>4 M NaCl</td>
<td>23</td>
<td>14060</td>
<td>2310</td>
<td>11750 ± 1.0%</td>
</tr>
<tr>
<td>1 M AlCl$_3$</td>
<td>13</td>
<td>9652</td>
<td>1315</td>
<td>8337 ± 1.2%</td>
</tr>
<tr>
<td>2.8 M AlCl$_3$</td>
<td>28</td>
<td>11990</td>
<td>3335</td>
<td>8655 ± 1.3%</td>
</tr>
<tr>
<td>1 M MgCl$_2$</td>
<td>26</td>
<td>6280</td>
<td>1207</td>
<td>5073 ± 1.6%</td>
</tr>
<tr>
<td>2.8 M MgCl$_2$</td>
<td>98</td>
<td>10756</td>
<td>4206</td>
<td>6550 ± 1.6%</td>
</tr>
</tbody>
</table>

Total count and background were measured at ∼7000 eV and ∼6995 eV photon energies (energy transfer of ∼538 eV and ∼533 eV), respectively. Signal is total count subtracted by background and % Poisson error is estimated by dividing the square root of total count by the signal.

The number of scans and total count rate were dependent on the type of the salt, concentration, and photon flux for different runs, as summarized in table 3.1.
SAXS measurements were performed at SSRL BL 4-2 and the description of the experimental setup can be found in Chapter 2.

3.2.2 Results and Discussion

X-ray Raman Scattering Spectroscopy

Fig. 3.1a displays the O 1s XRS spectra of water in NaCl solutions at 1 M (red) and 4 M (blue) concentrations compared with the spectrum of pure bulk water (black). The O 1s XRS spectrum of water is generally divided into three regions: pre-edge (535 eV), which is sensitive to weak/distorted H-bonds; main-edge (537-538 eV), which is also mostly sensitive to weak H-bonds but it also contains contributions from strong H-bonds; and post-edge (540-541eV), which corresponds to strong/intact H-bonds [42, 44, 45]. The presence of NaCl results in an increase of the pre- and main-edge and decrease of the post-edge, and the effect is enhanced with increased concentration, suggesting that more weakly H-bonded water molecules (i.e. HDL species [46]) are present. This observation agrees with the previously published fluorescence yield (FY) XAS spectra of NaCl [40]. At first glance, the general trend of the spectral changes, shown in the difference spectra (top of Fig. 3.1a), i.e. the spectra of aqueous solutions minus the spectrum of pure water, seems similar to the changes caused by temperature increase (i.e. intensity redistribution from the post-edge to the pre-edge and main edge) [46]. However, upon a closer inspection, a significant difference can be observed between the effect of temperature increase and NaCl solvation.

Fig. 3.2 shows the spectra of pure liquid water (black) and 4 M NaCl (blue) at 25°C compared with the spectrum of liquid water at 90°C (from Ref. [46]), with the difference spectra (90°C H2O - 25°C H2O in red and 4 M NaCl - 25°C H2O in blue)
Figure 3.1: O 1s XRS spectra of (a) NaCl (red: 1 M, blue: 4 M), (b) MgCl$_2$ (red: 1 M, blue: 2.8 M), and (c) AlCl$_3$ (red: 1 M, blue: 2.8 M) solutions compared with pure water (black). The difference spectra, obtained by subtracting the spectrum of pure water from the solutions are displayed above of each set of spectra.
Figure 3.2: O 1s XRS spectra of pure water at 25°C (black) compared with pure water at 90°C (red, from Ref. [42]) and 4 M NaCl solution (blue). The difference spectra between 90°C water and 25°C water (red) and between 4 M NaCl and 25°C water (blue) are displayed at the top. The inset shows the enlarged pre-edge region.

An enlarged view of the pre-edge peak (inset of Fig. 3.2) clearly displays that although the intensity of the pre-edge peaks of 90°C H₂O and 4 M NaCl both increase relative to 25°C H₂O, the peak position of 90°C H₂O also shifts to lower energy while that of 4 M NaCl is unshifted compared to 25°C H₂O. In hot water, the pre-edge shift towards lower energy (i.e. closer to the gas-phase position) has been interpreted as due to the increased disorder in the H-bond distorted (HDL) species of water through thermal excitation as the temperature of the system is increased, while the intensity redistribution from the post-edge to the pre- and main-edge is a signature
of H-bond weakening (i.e. conversion from LDL to HDL) [46]. However, in the case of NaCl solvation, H-bonds are weakened or distorted without introducing additional thermal energy to the system, consistent with the increased pre-edge located at the same energy position as 25°C H$_2$O. The conversion from LDL to HDL species is also consistent with the expected effects of pressure increase, in agreement with the conclusions of Mancinelli et al. [13].

The XRS spectra of 1 M and 2.8 M MgCl$_2$ and AlCl$_3$ are compared with the spectrum of pure water (black) in Figs. 3.1b and 3.1c, respectively. By replacing the Na$^+$ cation with Mg$^{2+}$ and Al$^{3+}$, we can investigate the effect of increasing charge density of the cation. In Fig. 3.1b, the difference between 1 M MgCl$_2$ and H$_2$O is very small. However, at higher concentration, the spectral changes become more apparent, namely the pre-edge becomes less well defined and the entire spectrum is shifted by 0.14 eV although the intensity ratio between pre- and post-edge only changes slightly from pure water. For AlCl$_3$ solutions, shown in Fig. 3.1c, the changes are already visible at 1 M concentration and strongly enhanced at 2.8 M. In addition to the shift to higher energy (∼0.1 eV for 1 M AlCl$_3$ and ∼0.3 eV for 2.8 M AlCl$_3$), a decrease in the pre-edge intensity is observed along with an increase in the post-edge region. The XRS spectra of AlCl$_3$ solutions, and the absence of any features due to the presence of OH$^-$ species as a result of hydrolysis, are consistent with the published FY-XAS spectra of the same sample [40].

According to the “bond-length-with-a-ruler” concept [47–49], the energy position of the post-edge is correlated to the H-bond distance in water [50]. Theoretical simulations have shown that as the H-bond distance of ice is elongated, the post-edge peak is shifted to lower energy and the same effect can be expected also for
water [51]. In addition, experimental FY-XAS data of HCl solutions have shown that at high concentrations, in which the protonated water predominantly exists in the Eigen form (H$_3$O$^+$) with a shorter H-bond distance compared to pure water, a shift of the post-edge to higher energy is observed accompanied by a decreased pre-edge and increased post-edge [50]. The spectrum of 2.8 M AlCl$_3$ solution, in fact, resembles the spectrum of 6 M HCl solution, although a direct comparison is difficult since the spectra were measured using different methods. AlCl$_3$ solutions can undergo hydrolysis, producing an acidic solution. However, relatively high concentrations (i.e. 4 and 6 M) of HCl are required to obtain spectral changes related to short H-bonds due to the presence of the Eigen species of protonated water [50], while the spectral changes in AlCl$_3$ solutions are already observable at relatively low concentrations (i.e. 0.5 M, not shown). In addition, for strongly hydrolyzed solutions such as FeCl$_3$, a peak at 530-532 eV (below the pre-edge) appears due to the presence of hydroxyl groups [52], which is not observed for the spectra of AlCl$_3$ solutions. Therefore, the presence of protonated water in AlCl$_3$ solutions cannot account for these spectral changes. The addition of AlCl$_3$, and to a lesser extent MgCl$_2$, to water, thus, causes the formation of shorter (and, therefore, stronger) H-bonds in water.

The observation that MgCl$_2$ and AlCl$_3$ solvation induces changes to the XRS spectra in the opposite way from NaCl is already an indication that the multivalent cations Mg$^{2+}$ and Al$^{3+}$ affect water structure differently from the monovalent Na$^+$ cation. Since all O atoms in the sample contribute equally to the absorption intensity, XAS (and, by extension, XRS) cannot distinguish water in the hydration shells of the ions and water molecules outside the hydration shells. As relatively high concentrations are required to clearly see the spectral changes, we can assume that only
water molecules in close proximity of the ions are affected. However, since H-bonding is probed, our data concern water-water interactions, likely between the first and second hydration shells, and not simply ion-water interaction.

In earlier work by Cappa et al. [38, 39], the XAS spectral changes were assigned as due to distortions of the unoccupied states in the field of the cation and the role of charge transfer from water to the cation was emphasized. However, charge transfer from, or orbital mixing involving, occupied valence levels should lead to absorption at lower energy corresponding to valence transitions rather than transitions into higher excited states. Such transitions are indeed observed in the hydration sphere of open-3d-shell transition metals [52] and in dative bonding involving the oxygen lone-pair in water binding through the oxygen to a Pt(111) surface [53], but not in the case of closed-shell ions even as highly charged as Al$^{3+}$ [52]. There is thus no experimental indication for the proposed mechanism as actually noted by Cappa et al. [39].

Before discussing in depth the effect of the cations, we must also first consider the role of the Cl$^-$ anion. X-ray and neutron diffraction studies as well as molecular dynamics simulations have determined that, on average, six water molecules comprise the first hydration shell of Cl$^-$ with a Cl-O distance of $\sim$3.15 Å and Cl-O-H angle of less than 12° [19]. With an almost linear Cl-O-H angle, Cl$^-$ is located at roughly the same position as an acceptor O atom in bulk water, only at a longer distance [23]. Therefore Cl$^-$ ions can fit into the H-bonding network of water without any significant restructuring of the surrounding water molecules. However, the longer Cl-O distance ($\sim$3.15 Å) compared to the O-O distance in bulk water ($\sim$2.8 Å) must be considered in the interpretation of the XRS spectra according to the bond-length-with-a-ruler
principle described previously. It was shown that asymmetrically increasing a donating H-bond distance not only shifts the post-edge to lower energy but also induces an increased intensity in the pre- and main-edge region [51], as is also observed in Fig. 3.1a. However, the spectra of MgCl$_2$ and AlCl$_3$ do not show the expected effect of H-bond elongation by Cl$^-$ although there are more Cl$^-$ ions for the same concentration compared to NaCl. This indicates that the effect of Cl$^-$ may actually be small and it cannot account for the spectral changes in Fig. 3.1a. Therefore, the observed increase in the HDL population is likely caused by Na$^+$. Note that the spectrum calculations by Cappa et al. [38] comparing computed spectra of water donating an H-bond either to Cl$^-$ or to another water were in both cases performed at 2.818 Å which, in the case of Cl$^-$ gives strong Pauli repulsion with ensuing distortions of the electronic structure of the water molecule due to the nearly 0.3 Å too short distance.

The interpretation for Mg$^{2+}$ and Al$^{3+}$ is even more obvious, and the increased fraction of shorter and stronger H-bonds suggests that the effect of the cations is much greater and the effect of Cl$^-$ can be assumed to be negligible. Therefore, it can be concluded that the increased fraction of strongly H-bonded water is caused by the presence of Mg$^{2+}$ and Al$^{3+}$, with the latter having a stronger effect. This is in agreement with data from various x-ray diffraction and molecular dynamics studies that determined that the water O-O distances between the first and second shell of Mg$^{2+}$ and Al$^{3+}$ are shorter than in bulk water (an average of $\sim$2.66 Å for Al$^{3+}$ and $\sim$2.71 Å for Mg$^{2+}$, compared to 2.8 Å in bulk water) [19, 37, 54–56].

At high concentrations, solvated ions are known to form ion pairs (see, e.g., Ref. [57] for Na-Cl ion pairing). In addition, the strength of the ion pairing between acetate and various cations (Na$^+$, Li$^+$, K$^+$, and NH$_4^+$) was found to follow the
Hofmeister series except for Li$^+$ [58]. Therefore, assuming that Na$^+$, Mg$^{2+}$, and Al$^{3+}$ ions follow a similar trend, then the strength of the ion pair interaction is expected to be Al$^{3+} >$ Mg$^{2+} >$ Na$^+$. The XAS spectra were measured at relatively high concentrations (i.e. 4 M for NaCl and 2.8 M for MgCl$_2$ and AlCl$_3$), where ion pairs are likely formed. However, the trends in the difference spectra at high concentrations are consistent with those at lower concentrations (e.g. 1 M); therefore, the ion pairs at high concentrations likely have insignificant effects on the XAS spectra.

**Small Angle X-ray Scattering**

![SAXS data of (a) NaCl, (b) MgCl$_2$, and (c) AlCl$_3$ solutions compared with pure water (black dashes). The solution concentrations from the top are: 1 M, 0.5 M, 0.25 M, 0.1 M for NaCl; 1 M, 0.5 M, 0.25 M, 0.13 M, 0.06 M, 0.03 M for MgCl$_2$; and 0.5 M, 0.25 M, 0.08 M, 0.04 M, 0.019 M, 0.0095 M for AlCl$_3$.](image)

SAXS data for NaCl, MgCl$_2$, and AlCl$_3$ solutions at various concentrations (solid curves) compared to pure water (dashed curves) are displayed in Fig. 3.3 where the scattering intensity $I(Q)$ is plotted as a function of momentum transfer $Q$ (note the
different intensity scales between the three figures). For NaCl solutions (Fig. 3.3a), other than the increased scattering intensity as more ions are solvated, the overall shape of the scattering curve closely resembles that of pure liquid water. The absence of any notable features in the scattering curve indicates that the density profile of NaCl solution is very similar to that of pure water. In light of the interpretation of the XRS spectra, this is not surprising since only the weakening of H-bonds through the hydration of NaCl is observed in XRS. It has been found that the Ornstein-Zernike correlation length of liquid water is reduced significantly by the presence of NaCl salts at supercooled temperatures [59], which is in agreement with the pressure-effect. In contrast, both MgCl$_2$ (Fig. 3.3b) and AlCl$_3$ (Fig. 3.3c) solution scattering is dominated by the development of a “pre-peak” in the intermediate $Q$ region, i.e. the peak located before the first scattering maximum related to the nearest-neighbor distance in the system. Similar pre-peaks have been observed in concentrated aqueous solutions [60, 61] and melted salts [62], and were determined to be largely due to the correlation between cations. The contribution from anion-anion and cation-anion correlations can be neglected in MgCl$_2$ and AlCl$_3$ solutions as indicated by the absence of pre-peaks in the case of NaCl solutions even up to a high concentration of 2 M (not shown). Fig. 3.4 compares the SAXS data of NaCl, MgCl$_2$, and AlCl$_3$ at the same concentration with the data for bulk water to emphasize the intensity enhancement caused by the multivalent cations.

Apart from the pre-peaks, MgCl$_2$ and AlCl$_3$ solutions show much larger scattering signals at low $Q$ compared to pure water and NaCl solution. We hypothesize that the enhanced low-$Q$ scattering signals are attributable to the presence of well defined H-bonded hydration shells around multivalent cations with different local density
Figure 3.4: SAXS data of 0.5 M NaCl (blue), MgCl$_2$ (green), and AlCl$_3$ (red) compared with pure water (black dashes).

compared to pure water, and the pre-peak is due to the interaction between cations that form an ordered quasi-lattice structure. Our hypothesis is consistent with the observation of strongly H-bonded water molecules near the Mg$^{2+}$ and Al$^{3+}$ ions as shown in XRS spectra (Fig. 3.1). In the following, we perform a more detailed analysis of MgCl$_2$ and AlCl$_3$ SAXS data, which can reveal important information about the hydration shells of Mg$^{2+}$ and Al$^{3+}$ cations.

In Fig. 3.5, the dashed curves were obtained by subtracting the water contribution from the scattering signal of each solution and normalizing each subtracted curve with the concentration. This is done under the assumption that the water molecules
outside the hydration shell, including those near the anions, have similar H-bonding environment as bulk water. The scattering at higher $Q$ overlaps very well within statistical errors and the scattering deviates at $Q < 0.5$ Å$^{-1}$ to a degree depending on the concentration. The form factor of one individual unit structure (i.e. cation with hydration shells) is then derived by fitting the scattering for the most dilute solution (0.03 M for MgCl$_2$ and 0.0095 M for AlCl$_3$) from the peak maxima to the high $Q$ limit (solid black line). The Cl$^-$ anion is assumed to have a negligible contribution. The measured deviations from the SAXS form factor of solvated cations are indicative of repulsive interactions between the cations. As the salt concentration increases, the repulsion is magnified resulting in a larger deviation.
The pre-peak position is related to the distance between the solvated cations. The shift of the pre-peaks to higher $Q$ with increasing concentration suggests that the distance between the solvated cations decreases as the concentration increases. The $Q$ offset between the MgCl$_2$ and AlCl$_3$ pre-peaks at the same concentration is attributable to the different widths of the pre-peaks. More specifically, the narrower AlCl$_3$ peak is less affected by the slowly increased small angle scattering signal, and is therefore more reliable for the cation-cation distance estimation.

![Figure 3.6: The plot of estimated cation-cation distance vs. concentration for Mg$^{2+}$ (blue) and Al$^{3+}$ (red) from the pre-peak $Q$ position in Fig. 3.5. For comparison, the calculated distance is displayed as the black line.](image)

Determination of distance from the $Q$ value should ideally be performed using the structure factor. However, for these aqueous solutions, the true structure factor cannot be trivially obtained. Therefore, the peak positions in Fig. 3.5 can be used for a rough estimation. From the $Q$ values of the pre-peak maxima in Fig. 3.5, we
plot the distance $d$ between cations ($d = \frac{2\pi}{Q}$) as a function of concentration, shown in Fig. 3.6. As a comparison, the expected distance between two cations is also displayed, obtained by taking the cubic root of the inverse of the number density of cations (i.e. the volume occupied by each cation). It is readily apparent that the estimated distances for $\text{Al}^{3+}$ are very close to those of the calculated values within 7% uncertainty. However, the distances for $\text{Mg}^{2+}$ deviate by up to 25% particularly at low concentrations. Small uncertainties in the concentration cannot explain this large deviation.

The disparity between $\text{Al}^{3+}$ and $\text{Mg}^{2+}$ can be explained using the following simple
Figure 3.8: A plot of the correlation between Gaussian peak widths and the offset of the peak positions between the original and multiplied peaks.

model. We arbitrarily generated four Gaussian peaks with the same arbitrary position of the maxima but different widths (Fig. 3.7, dashed lines). These peaks can be considered as a representation of the pre-peaks in the structure factor. They are then multiplied with the form factor of solvated Mg$^{2+}$ from Fig. 3.5a, and the resulting curves (solid lines) represent the total scattering analogous to the dashed lines in Fig. 3.5. There is an obvious correlation between the original peak widths and the position of the multiplied curves, displayed in Fig. 3.8. When the width is zero, the peak remains at the same $Q$ position after multiplication with the form factor. Increasing the width of the Gaussians increases the $Q$ offset before and after the multiplication with the form factor. Therefore, since the pre-peaks of MgCl$_2$ solutions are generally wider than those of AlCl$_3$, the $Q$ positions in Fig. 3.5a do not accurately reflect the distance between cations, as observed from the deviations in Fig. 3.6. From the
estimated cation-cation distances of Al$^{3+}$ solution, we found that the cation-cation distance is in good agreement with the quasi-lattice model in salt solutions [60].

Figure 3.9: Comparison of the experimentally determined form factors (thick solid lines) from Fig. 3.5 with calculated form factors of the cations with one (dashed lines) and two hydration shells (dot-dashed lines) obtained from the Debye scattering equation. All red lines are for MgCl$_2$ and all blue lines are for AlCl$_3$. The form factors of only the cations are shown as the thin solid lines at the top of the figure.

In Fig. 3.9, the form factors of solvated Mg$^{2+}$ and Al$^{3+}$ from experimental data are compared with calculated form factors of Mg$^{2+}$ and Al$^{3+}$ with one and two hydration shells (6 water molecules in the first shell and 12 in the second shell), obtained from the Debye scattering equation [63]:

$$ I(Q) = \sum_{m=1}^{N} \sum_{n=1}^{N} f_m(Q) f_n(Q) \sin \left( Q r_{mn} \right), $$

(3.1)

where $N$ is the number of atoms, $f_m(Q)$ and $f_n(Q)$ are the atomic scattering factors.
of atoms \(m\) and \(n\), and \(r_{mn}\) is the distance between atoms \(m\) and \(n\). The atomic scattering factor \(f\) is calculated using the analytic expression

\[
f(\lambda^{-1} \sin \theta) = \sum_{i=1}^{4} a_i \exp(-b_i \lambda^{-2} \sin^2 \theta) + c, \tag{3.2}
\]

where \(a_i\), \(b_i\), and \(c\) are coefficients from Ref. [64] and \(\lambda^{-1} \sin \theta = Q/4\pi\). For oxygen and hydrogen, a modification of the atomic scattering factor was introduced as a correction for the covalent bonding in a water molecule, according to Ref. [65, 66]

\[
f'(Q) = \left[1 + \alpha \exp\left(-\frac{Q^2}{2\delta^2}\right)\right] f(Q), \tag{3.3}
\]

where \(f'(Q)\) is the modified atomic scattering factor, \(\alpha\) is the scaling factor for charge redistribution (0.15 for O and -0.6 for H [66]) and \(\delta\) is a parameter for the delocalization of electrons due to chemical bonding (2.2 Å\(^{-1}\) [65, 66]).

For comparison, the form factors of the cations only (Na\(^+\), Mg\(^{2+}\), and Al\(^{3+}\)) are displayed as the thin solid lines at the top of Fig. 3.9. It is evident that the cations alone cannot account for the experimental form factor of solvated cations in these solutions and their hydration shell(s) must, therefore, play an important role in the scattering. The experimental form factor of Mg\(^{2+}\) is close to the calculated form factor of Mg\(^{2+}\) with one hydration shell, while the form factor of solvated Al\(^{3+}\) is located in between the calculated form factors of Al\(^{3+}\) with one and two hydration shells. As a first approximation, the solvated cation structures can be simplified as a homogeneous sphere and its scattering intensity is described by the sphere radius \(R\) [67]

\[
P(Q) = \left[\frac{3}{(QR)^3}\right]^2 [\sin(QR) - QR \cos(QR)]^2. \tag{3.4}
\]
Fitting the experimental data yields a radius of \( \sim 2.71 \, \text{Å} \) and \( \sim 3.18 \, \text{Å} \) for solvated Mg\(^{2+}\) and Al\(^{3+}\), respectively. These numbers are consistent with the radius of an Mg\(^{2+}\) cation with one hydration shell and Al\(^{3+}\) with 1.5 hydration shells, in agreement with the comparison in Fig. 3.9. These values reflect the density contrast given by the hydration shells of Mg\(^{2+}\) and Al\(^{3+}\) and they are not necessarily associated with the actual number of hydration shells of the cations. For both cations, it can be clearly concluded that the water in the first hydration shell has different density from bulk water. For Mg\(^{2+}\), the density of water in the second hydration shell becomes very similar to bulk water and the second shell does not appear as a density contrast in SAXS although it is quite strongly H-bonded to the first hydration shell (O-O distance of \( \sim 2.71 \, \text{Å} \) vs. 2.8 Å in bulk water [19, 55, 56]). Water in the second hydration shell of Al\(^{3+}\), however, can be considered as having a local density that is between that of the first shell water and bulk water, with an even stronger H-bonding to the first hydration shell compared to Mg\(^{2+}\) (O-O distance of \( \sim 2.66 \, \text{Å} \) [19, 37, 54–56]).

From the SAXS data, we can also estimate the electron density difference between the solvated ions and the surrounding water using the expression

\[
I(Q = 0) = r_0^2 n \Delta \rho^2 v^2,
\]

(3.5)

where \( I(Q = 0) \) is the scattering intensity at \( Q = 0 \) (0.00084 cm\(^{-1}\) for Mg\(^{2+}\) and 0.00072 cm\(^{-1}\) for Al\(^{3+}\)), \( r_0 \) is the Thomson radius of an electron \((2.82 \times 10^{-13} \, \text{cm})\), \( n \) is the number density of the solvated cations, \( \Delta \rho \) is the electron density difference between the solvated cations and the surrounding bulk water, and \( v \) is the volume of the solvated cations from the radii \( R \) determined through equation 3.4. Equation 3.5 yields \( \Delta \rho \) of \( 2.95 \times 10^{23} \, \text{cm}^{-3} \) for Al\(^{3+}\) and \( 2.90 \times 10^{23} \, \text{cm}^{-3} \) for Mg\(^{2+}\). Compared to the
electron density of pure water ($\rho_{(H_2O)_{bulk}} = 3.31 \times 10^{23} \text{ cm}^{-3}$), these values represent an increase of $\sim 88 \pm 1\%$ in electron density for the unit structure consisting of the cation and hydration shell(s).

We can then roughly estimate the local density given by water in the hydration shells $\rho_{(H_2O)_{hyd}}$ using

$$\rho_{tot} = \frac{V_{ion}}{V_{tot}} \rho_{ion} + \frac{V_{tot} - V_{ion}}{V_{tot}} \rho_{(H_2O)_{hyd}},$$

where $\rho_{tot} = \Delta \rho + \rho_{(H_2O)_{bulk}}$ and $\rho_{ion}$ is the electron density of the cation ($\rho_{ion} = 10$ electrons/$V_{ion}$). $V_{ion}$ is the volume occupied by the cation in the ion-hydration shell structure, estimated using one half of the cation-oxygen distance as the radius ($d_{Al-O} = 1.9 \text{ Å} \rightarrow r_{Al^{3+}} = 0.95 \text{ Å}$, and $d_{Mg-O} = 2.1 \text{ Å} \rightarrow r_{Mg^{2+}} = 1.05 \text{ Å}$) and $V_{tot}$ is the volume of the entire ion-hydration shell structure from the radius previously determined using equation 3.4 ($r_{Mg^{2+}+shell} = 2.71 \text{ Å}$ and $r_{Al^{3+}+shell} = 3.18 \text{ Å}$). From equation 3.6, the electron density of water in the hydration shells is estimated to be $5.65 \times 10^{23} \text{ cm}^{-3}$ for Al$^{3+}$ and $5.32 \times 10^{23} \text{ cm}^{-3}$ for Mg$^{2+}$, reflecting $\sim 71\%$ and $\sim 61\%$ increase of electron density from bulk water.

Although these numbers seem large, we must consider how water molecules are arranged in the first hydration shell of the cations compared to bulk water. In ice (Fig. 3.10, right), four water molecules are H-bonded to a central water molecule with O-O distance of 2.75 Å; in liquid water, the O-O distance is even longer (an average of $\sim 2.8$ Å) and the H-bonding network fluctuates from tetrahedral to disordered. However, around Mg$^{2+}$ and Al$^{3+}$ (Fig. 3.10, left), six water molecules are arranged in an octahedral geometry with Mg$^{2+}$- O distance of 2.1 Å and Al$^{3+}$- O distance of 1.9 Å [19]. Therefore, in Mg$^{2+}$ and Al$^{3+}$ hydration shells, more water molecules are...
Figure 3.10: Depiction of the arrangement of water molecules in: (left) the first hydration shell of Al$^{3+}$ ion, and (right) the tetrahedral network in ice.

packed in a smaller volume compared to bulk water, which explains the large increase in electron density.

Although an increase of electron density also suggests an increase in molecular density, we should emphasize here that this is different from the HDL species in bulk water or NaCl solution. The HDL classification in bulk water and NaCl solution is based on a disordered H-bonding network resulting in a more packed structure compared to the LDL species, in which the ordered tetrahedral H-bonding network leaves interstitial spaces, resulting in a lower local density. In the case of water in a cation hydration shell, it was discussed previously based on the XRS spectra that the water H-bonds between the first and second hydration shells are shorter than those in bulk water, confirming the result of various diffraction and molecular dynamics studies [19, 37, 54–56]. In combination with the short cation-oxygen distance, this allows a higher density of ordered water molecules to be present in the hydration shells without introducing interstitial spaces such as those found in LDL water and ice. In addition, whereas the proposed LDL and HDL species in bulk water should
interconvert continuously, the hydration shells of Mg$^{2+}$ and Al$^{3+}$ are stable on a long
time scale albeit with exchange of water molecules occurring.

Our interpretation of the SAXS data is supported by the residence time of wa-
ter molecules in hydration shells, which is another aspect of ion hydration related
to the relative strength of hydration shells. Nuclear magnetic resonance (NMR),
quasi-elastic neutron scattering (QENS), and molecular dynamics studies have deter-
mined the lifetime of a water molecule in the hydration shells of various cations [19].
Although the exact numbers vary, most studies agree that the residence time of wa-
ter in the first hydration shell is $\sim 10^{-12}$ s for Na$^+$, $\sim 10^{-6}$ s for Mg$^{2+}$ and 1-6 s for
Al$^{3+}$ [19, 36, 37]. Therefore, the weak hydration shell around Na$^+$ allows water
molecules in the first hydration shell to exchange with those outside the hydration
shell on time scale comparable to H-bond breaking and reforming in bulk water. How-
ever, the structures formed by Mg$^{2+}$ and Al$^{3+}$ are relatively stable, and the strongly
bound first hydration shell appears as a density contrast in the SAXS data; thus,
the exchange of water molecules between the first and second hydration shells occurs
much more slowly, particularly for Al$^{3+}$. The residence time of the water molecules in
the second hydration shell of cations is not well known; however, it has been suggested
to be on a picosecond time scale for Al$^{3+}$ from molecular dynamics simulations [37].
In addition, an $^{17}$O NMR study has determined that the lifetime of the second hy-
dration shell of Cr$^{3+}$ ion is 128 ps [68]. Since the first shell lifetime of Cr$^{3+}$ is five
orders of magnitude longer than that of Al$^{3+}$ and eleven orders of magnitude longer
than that of Mg$^{2+}$ [69], the lifetime of the second shell of Al$^{3+}$ is expected to be much
shorter than 128 ps and for Mg$^{2+}$ it should even closer to the value for water H-bond
breaking and reforming. This implies that the second shell water molecules of Al$^{3+}$
are more stable than those of Mg$^{2+}$, although much more mobile than those in the first hydration shell of both cations. In connection to our SAXS data, this indicates that the density of the second hydration shell is very similar to the density of bulk water for Mg$^{2+}$ and in between the densities of bulk water and first hydration shell water for Al$^{3+}$. This is what we observe in Fig. 3.9, where Mg$^{2+}$ and Al$^{3+}$ appear to have one and one and a half hydration shells, respectively.

Therefore, half a hydration shell from SAXS data can be interpreted as a gradual change in density between bulk water and the first hydration shell instead of an abrupt change. The first hydration shell of both Mg$^{2+}$ and Al$^{3+}$ with six water molecules in an octahedral geometry and relatively short cation-oxygen distance can be considered as having a high density contrast compared to bulk water. The second hydration shell of Mg$^{2+}$, although quite strongly bonded to the first hydration shell water molecules, has a similar density to bulk water, and, therefore, in SAXS we only observe one hydration shell around Mg$^{2+}$. On the other hand, the second hydration shell of Al$^{3+}$ is more stable and rigid compared to that of Mg$^{2+}$ and it has a density that is intermediate between bulk water and the first hydration shell. Therefore, it appears in SAXS as half a hydration shell.

### 3.2.3 Conclusion

We observe from XRS and SAXS the difference in the way water molecules are structured around Na$^+$, Mg$^{2+}$, and Al$^{3+}$. First, we confirm the FY-XAS study of Näslund et al. [40] that cations cause the restructuring of the water molecules in their vicinity while Cl$^-$ anion has a negligible effect, directly contradicting the TEY-XAS study of Cappa et al. [38]. In NaCl solution, XRS spectra show a weakening of H-bonds
corresponding to a conversion from LDL to HDL due to the presence of Na\(^+\); this is similar to the effect of temperature increase but without inducing increased disorder in the HDL species. The increase in the fraction of the HDL species is also consistent with the effect of an increased pressure, confirming the results of Mancinelli et al. [13]

In contrast, the XRS spectra of MgCl\(_2\) and AlCl\(_3\) unambiguously show the presence of short H-bonds among water molecules in the vicinity of Mg\(^{2+}\) and Al\(^{3+}\) ions, in agreement with the relatively short O-O distance between water molecules in the first and second hydration shells of Mg\(^{2+}\) and Al\(^{3+}\) compared to bulk water from various diffraction and simulations studies.

The SAXS data of NaCl closely resemble that of bulk water, indicating that no structures that give an additional density contrast are formed. The scattering curves for MgCl\(_2\) and AlCl\(_3\), on the other hand, show strongly enhanced signals at low \(Q\) and pre-peaks at intermediate \(Q\) regions arising from structures formed by the cations and water in the hydration shells. Further analysis of the form factors reveals that these structures have a radius of \(\sim 2.71\) Å for Mg\(^{2+}\) and \(\sim 3.18\) Å for Al\(^{3+}\), corresponding to one and one and a half hydration shells for Mg\(^{2+}\) and Al\(^{3+}\), respectively. Electron density estimations suggest that there is \(\sim 61\%\) and \(\sim 71\%\) increase in electron density in the hydration shells of Mg\(^{2+}\) and Al\(^{3+}\) compared to bulk water. This is due to the more compact structure of the hydration shells with six water molecules in the first shell and a cation-oxygen distance of \(\sim 2.1\) Å for Mg\(^{2+}\) and \(\sim 1.9\) Å for Al\(^{3+}\), compared to the average O-O distance of \(\sim 2.8\) Å in bulk water. Since SAXS is a measure of electron density, the observation of half a hydration shell for Al\(^{3+}\) indicates that the change in the density between water inside and outside the hydration shell is not abrupt and is, instead, gradual. Therefore, while the first hydration shells of
both Mg$^{2+}$ and Al$^{3+}$ have completely different densities from bulk water, the second hydration shell of Mg$^{2+}$ is very similar to bulk water and it is, therefore, invisible to SAXS, while the second hydration shell of Al$^{3+}$ has a density that is intermediate between that of the first hydration shell and bulk water and, therefore, appears as half a hydration shell in SAXS. In summary, from a combination of XRS and SAXS, we observed that while Na$^+$ weakens H-bonds in water, Mg$^{2+}$ and Al$^{3+}$ strengthen them by forming stable, highly ordered, high-density hydration shells.

### 3.3 The Effect of Fluoride Anion

#### 3.3.1 Experimental Details

KF, KCl, NaF, and NaCl samples at various concentrations were prepared using commercially available salts (>99% from Fisher Chemicals) dissolved in Millipore-purified H$_2$O (≈18 MΩ cm). XAS spectra were measured in T-mode at SSRL BL 10-1 and SAXS measurements were performed at SSRL BL 4-2. The experimental setup for both T-mode XAS and SAXS measurements is described in Chapter 2.

#### 3.3.2 Results and Discussion

The T-mode XAS spectra of 1, 2, and 4 m KCl and KF solutions compared to that of bulk water, as well as the difference spectra (i.e. solution minus water), are displayed in Fig. 3.11a and 3.11b, respectively. The spectral changes caused by KCl solvation are obvious; the pre-edge (535 eV) and main edge (537-538 eV) increase with concentration accompanied by a decrease in the post-edge (540-541 eV). Since the pre- and main edge are sensitive to weak H-bonds and the post-edge to strong
Figure 3.11: O 1s T-mode XAS spectra of 1, 2, and 4 m KCl (a) and KF (b) solutions. The spectrum of pure water is shown in black. The difference spectra are displayed above each set of spectra, and the inset in (b) shows the enlarged pre-edge region of KF solutions. The difference spectra between 4 m KF and water (green) and between two pure water spectra (black), both multiplied by a factor of 4, are shown in (c). The spectrum of water plus the difference spectrum between 4 m KF and KCl (green) is compared to the spectrum of pure water in (d). All O 1s XAS spectra in (a), (b), and (d) have been normalized by area from 532 to 550 eV.
H-bonds [42, 44, 45], this intensity redistribution from the post-edge to the pre- and main edge is a signature of H-bond weakening, similar to the effect of NaCl solvation [40, 42, 70]. In connection to the fluctuations between the two local favored structures in pure water [46], this can be interpreted as an increase in the fraction of the HDL species caused by the presence of the ions, consistent with the effect of increasing pressure as was also observed from a neutron diffraction study [13]. When the temperature of bulk water is increased, an intensity redistribution from the post-edge to the pre- and main edge is also observed [42, 46, 71]; however, the pre-edge also shifts to lower energy with temperature increase, indicating the increased disorder due to the thermal excitation of the existing HDL species [42, 46], which is not observed for the solvation of NaCl [70] and KCl.

On the other hand, the spectra of KF solutions (Fig. 3.11b) are very similar to that of pure water, and the changes in the difference spectra are very small. There is a slight increase in the pre-edge (inset of Fig. 3.11b) and a very small shift of the main and post-edge to higher energy. In addition, there is a shift of the pre-edge to higher energy as concentration increases. Fig. 3.11c displays the difference spectrum between 4 m KF solution and water multiplied by a factor of 4 (green line) compared to the difference spectrum between two pure water spectra obtained separately (black line, also multiplied by a factor of 4) representing the typical experimental noise, showing that these changes are indeed real and not simply due to noise. In order to understand these minimal spectral changes despite the presence of F⁻ ions, which interact strongly with water, we need to first describe the effect of the K⁺ cation.

Previously, we suggested that the changes in the spectra of NaCl, MgCl₂, and AlCl₃ solutions are mainly due to the cations, and the effect of the Cl⁻ anion is
Figure 3.12: O 1s T-mode XAS spectra of (a) 4 m NaCl (red) and KCl (blue), and (b) 1 m NaF (red) and KF (blue) compared to the spectrum of pure water (black). The difference spectra between the solutions and water are displayed above each set of spectra. Inset: the enlarged pre-edge region of H$_2$O (black), 1 m NaF (red), and 1 m KF (blue). All O 1s XAS spectra have been normalized by area from 532 to 550 eV.
small [70]. To further emphasize the effect of the K\(^+\) cation in KCl solutions, we compare the spectra of 4 m NaCl and KCl to that of pure water in Fig. 3.12. While both salts have a similar effect, i.e. increased pre- and main edge and decreased post-edge, the magnitude of the changes is greater for KCl than for NaCl, which can also be observed from the difference spectra. This trend persists at 1 m concentration, but we show the 4 m spectra where the effect is enhanced to facilitate the comparison. At the same concentration where the Cl\(^-\) can be neglected, this indicates that K\(^+\) has a stronger effect in weakening the H-bonds of water and increasing the fraction of the HDL species. This is in agreement with the previously published fluorescence yield (FY) XAS spectra of NaCl and KCl [40], and it is also consistent with various studies that classify K\(^+\) as a stronger structure-breaker than Na\(^+\) based on their relative size and charge density, viscosity, and hydration entropy [2, 3].

As in KCl, an increase of the pre-edge, albeit very small, in the KF spectra is also observed (inset of Fig. 3.11b), which can be attributed to the effect of K\(^+\). The effect of the F\(^-\) anion must, thus, be the opposite to that of K\(^+\); i.e. F\(^-\) decreases the pre- and main edge and increases the post-edge, thereby cancelling almost all of the effect of K\(^+\), resulting in a spectrum that resembles pure water. The slightly higher pre-edge in KF solutions compared to in water is simply a residual effect of the K\(^+\) cation. Therefore, while K\(^+\) decreases the number of H-bonds in water, F\(^-\) increases them. The enlarged pre-edge peaks of 1 m NaF, 1 m KF, and H\(_2\)O (inset of Fig. 3.12b) show the same trend as NaCl and KCl in which the pre-edge of KF is higher than that of NaF, indicating that there is less residual effect from Na\(^+\) than from K\(^+\). Unfortunately, comparison between NaF and KF at higher concentrations is not possible because NaF reaches its saturation concentration at \(~\)1 m.
CHAPTER 3. THE STRUCTURE OF WATER IN ION SOLUTIONS

Another spectral change observed for KF solutions is the small shift of the pre-, main and post-edge to higher energy, shown in the inset of Fig. 3.11b for the pre-edge and in the enlarged difference spectrum between 4 m KF and water (Fig. 3.11c) for the main and post-edge as the dip at \( \sim 536.4 \) eV and the peak at \( \sim 542.8 \) eV. The shift of the pre-edge to higher energy is similar to the effect of temperature decrease in pure water [42, 46], which is consistent with the previous discussion that F\(^-\) increases the number of H-bonds in the solution. The post-edge in the O 1s XAS spectrum of water can be described as a shape resonance, whose energy position, according to the “bond-length-with-a-ruler” principle, is dependent on the H-bond distance [42, 51]. This has been shown from theoretical simulations [51] as well as experimental XAS spectra of protonated water [50]. In our previous XAS spectra of MgCl\(_2\) and AlCl\(_3\) solutions [70], a shift of the main and post-edge is also observed, especially strongly for AlCl\(_3\), which is attributed to the short H-bonds between water molecules in the first and second hydration shells, in agreement the results of various diffraction and molecular dynamics studies [19].

For hydrated F\(^-\), however, it is unclear whether the short H-bonds are formed between water molecules, between the anion and water in the first hydration shell, or a combination of both since F\(^-\) is able to form relatively strong H-bonds with water. The average distance between fluoride and oxygen, determined from various diffraction studies is \( 2.7 \) Å [19, 25, 33–36], which is shorter than the average O-O distance in liquid water (\( \sim 2.8 \) Å) and close to the H-bond distance in crystalline ice (2.75 Å). In addition, the O-H—F angle was found to be nearly linear [34, 72], indicating that F\(^-\) does indeed form strong H-bonds with water. A combination of vibrational spectroscopy study and \textit{ab initio} calculations of F\(^-\)(H\(_2\)O)\(_{3-5}\) clusters
suggested that there is no water-water H-bonding in the first shell, and the interaction is, instead, dominated by anion-water H-bonding [32]. However, not much is known about the H-bonding between water molecules in the first and second hydration shells of fluoride.

To illustrate the effect of only the F$^{-}$ anion, the spectrum of 4 m KCl was subtracted from that of 4 m KF, and the difference spectrum was then added to the spectrum of pure water. This was done under the assumption that the effect of Cl$^{-}$ is negligible and that the spectrum of the salt solution is the result of a linear combination of the cation and anion. The resulting spectrum (Fig. 3.11d) shows significant changes compared to the pure water spectrum; the pre- and main edge are decreased while the post-edge gains quite a significant intensity, the opposite of the effect of K$^+$. In fact, the spectral features become more ice-like, which is consistent with our observation of the pre-edge shift implying the effect of temperature decrease.

Fig. 3.13 shows the SAXS data of NaF compared to NaCl and of KF compared to KCl at 0.1, 0.25, 0.5, and 1 m concentrations. The data for all of the salt solutions at 1 m concentration are displayed in Fig. 3.14. In all of the graphs, the scattering of pure water is shown as the dashed lines as a reference. The scattering structure factor $S(Q)$, plotted as a function of momentum transfer $Q$, was separated from the total scattering intensity using the weighted sum of the scattering factors of H$_2$O and the individual ions. Note that although the changes in the XAS spectra of KF solutions are minimal due to the opposite effect of the K$^+$ cation and for most salts, 1 m is generally the minimum concentration at which spectral changes become observable, SAXS is very sensitive to the changes in the density variations in the liquid even at very low concentrations; therefore, even with the cancelling effect of K$^+$, the effect of
Figure 3.13: Experimental structure factors $S(Q)$ of (a) NaCl (green) and NaF (purple), and (b) KCl (blue) and KF (red) compared to pure water (black dashed lines). The salt concentrations for each type of solution, from top to bottom, are 1, 0.5, 0.25, and 0.1 m.

$F^-$ is easily observed.

For all salt solutions, the scattering intensity over the measured $Q$ range increases with concentration since more solvated ions are present as scatterers. In addition, at the same concentration KF and KCl have a higher scattering intensity than NaF and NaCl due to the higher number of electrons in $K^+$ than in $Na^+$. The most interesting observation from these SAXS curves is that with the same cation, there is a low-$Q$ intensity enhancement for $F^-$ compared to $Cl^-$ at all concentrations, indicating an increase in the anomalous scattering behavior due to the formation of strongly
H-bonded structures. This enhancement is very similar to the effect of decreasing temperature [46, 59], consistent with the XAS data in Fig. 3.11, which has been interpreted as an increased fraction of the tetrahedral LDL species. In addition, the scattering of Cl\(^-\) solutions shows a plateau at small angles, which was previously found to correspond to reduced correlation length compared to pure water [59], implying a decreasing anomalous behavior of water that is in a similar manner to the effect of pressure increase to break H-bonds [73].

The low-\(Q\) intensity enhancement for F\(^-\) solutions is distinctly different from the enhancement observed in the scattering data of MgCl\(_2\) and AlCl\(_3\), which is dominated
by a pre-peak in the intermediate $Q$ region (before the first scattering peak) related to the scattering from the quasi-lattice structure formed by cations and their hydration shells [70]. It was previously determined that Mg$^{2+}$ and Al$^{3+}$ respectively form an equivalent of one and one and a half hydration shells that have, on average, a higher density than bulk water. This is because there are six water molecules in the first hydration shells of Mg$^{2+}$ and Al$^{3+}$ with cation-oxygen distance of 2.1 Å and 1.9 Å [19], respectively, compared to four in water with O-O distance of $\sim$2.8 Å. However, no such pre-peak is observed for in Fig. 3.13, indicating that, unlike Mg$^{2+}$ and Al$^{3+}$, F$^-$ with its hydration shell does not form a quasi-lattice structure in the solution, presumably due to its lower charge density compared to multivalent cations or due to the cancelling effect of the cations (K$^+$ and Na$^+$) that break H-bonds.

A more detailed analysis of the SAXS data was performed using the method described in Ref. [59], in which the total $S(Q)$ is described as a linear combination between normal scattering $S^{\text{ref}}$ and anomalous scattering $S^{\text{OZ}}$. $S^{\text{ref}}$ is the scattering at intermediate to large angles due to the repulsive interactions in the liquid, which, according to the Percus-Yevick approximation for hard-sphere fluid [74], is given by

\[
\frac{1}{S^{\text{ref}}} \propto 1 - 12\eta \left[ \eta(3 - \eta^2) - 2 \right] j_1(Q\sigma) / (1 - \eta)^4 Q\sigma, \tag{3.7}
\]

where $\eta$ is the volume fraction of water related to number density $n$ by $\eta = \pi n\sigma^3 / 6$, $\sigma$ is the hard-sphere diameter, and $j_1$ is the first-order spherical Bessel function. $S^{\text{OZ}}$ is the anomalous scattering signal at small angles described as a Lorentzian in the Ornstein-Zernike (OZ) theory [75],

\[
S^{\text{OZ}} \propto \frac{1}{\xi^{-2} + Q^2}, \tag{3.8}
\]
where $\xi$ is the OZ correlation length, which is related to the exponential decay of the pair correlation function in the solution. Fig. 3.15 shows the decomposition of the total scattering factor $S(Q)$ into $S^{\text{ref}}$ and $S^{\text{OZ}}$ for NaCl, NaF, KCl, and KF solutions.

The OZ correlation lengths $\xi$ obtained from this method and plotted as a function of concentration are shown in Fig. 3.16. For the same anion, solutions containing Na$^+$ have higher $\xi$ than those containing K$^+$. The reduced correlation length for K$^+$ compared to Na$^+$ is related to a decrease in anomalous behavior, which is in agreement with the XAS interpretation that K$^+$ has a stronger H-bond breaking effect than Na$^+$ (i.e. an enhanced temperature and pressure increase effect). At the same concentration, the $\xi$ values for F$^-$ solutions are higher than those for Cl$^-$ solutions. This is consistent with the observation of an increased anomalous scattering at small angles for F$^-$ compared to Cl$^-$ shown in Figs. 3.13 and 3.14. From the SAXS study of supercooled water [59], it was shown that decreasing temperature results in an increase of correlation length. However, the $\xi$ values of all solutions are lower than water and they decrease as the concentration increases. Comparison between the SAXS data of HCl and NaCl (not shown) reveals that the decrease in correlation length for NaCl solution is due to the Na$^+$ cation while Cl$^-$ has a minor role. Therefore, the decrease in correlation length for NaF and KF solutions, despite the observation of an increased anomalous behavior, is due to the presence of the Na$^+$ and K$^+$ cations, which have the opposite effect from F$^-$. It is likely that although F$^-$ forms a strong first hydration shell due to its strong H-bonding capability, the presence of the counterions weakens the H-bonding between water molecules in the first hydration shell of F$^-$ with those outside, thereby preventing the formation of an extended hydration shell.
Figure 3.15: Decomposition of $S(Q)$ into $S^{\text{ref}}$ and $S^{\text{OZ}}$ for (a) NaCl, (b) NaF, (c) KCl, and (d) KF. For the total $S(Q)$ (both experimental and fit) and $S^{\text{OZ}}$, the concentrations are 1, 0.5, 0.25, 0.1, and 0 (i.e. pure water) m from top to bottom.
3.3.3 Conclusion

In conclusion, from our combined experimental XAS and SAXS data, we observe the increased fraction of LDL species in water due to the solvation of fluoride ions. XAS spectra indicate that $F^-$ increases the number of H-bonds in the solution, likely due to the strong H-bonds between the anion and water. SAXS data show an intensity enhancement at low-$Q$ with increasing concentration for $F^-$ solutions, which is indicative of an increasing anomalous scattering behavior in $F^-$ solutions, similar to the effect of temperature decrease. On the other hand, the small angle scattering for $Cl^-$ solutions with the same cation shows a plateau, suggesting that the scattering becomes similar to that of normal liquid, which is consistent with the effect of temperature and pressure increase. Further analysis to estimate the OZ correlation lengths.
ξ revealed that F⁻ solutions have larger correlation lengths than Cl⁻ solutions; however, the smaller ξ values for F⁻ solutions compared to pure water are likely due to the compensating effect of the Na⁺ and K⁺ cations that weaken the H-bonding network in water. We hypothesize that F⁻ ions act as nucleation centers for the formation of tetrahedral LDL structures in the solution due to its ability to form strong H-bonds with water. However, the presence of the alkali cations likely prevents the formation of a second hydration shell as observed from the smaller correlation lengths of F⁻ solutions compared to water. Therefore, the hydration shell structure around F⁻ is distinctly different from the hydration shells of di- and trivalent cations such as Mg²⁺ and Al³⁺, which were previously found to form extended, high-density ordered structures around the cations [70]. In addition, unlike the first hydration shells of Mg²⁺ and Al³⁺, which persist over a relatively long time scale (10⁶ s for Mg²⁺ and 1 - 6 s for Al³⁺ [19, 37]), the hydration shell of F⁻ is more fleeting (20 - 30 × 10⁻¹² s [24, 35, 36]) and, therefore, the water molecules are involved in normal density fluctuations as in bulk water, albeit at a longer time scale and shorter H-bond distances than in pure water.

3.4 XAS of Alkali Halide Solutions

3.4.1 Experimental Details

Aqueous solutions of alkali halide (KF, RbF, CsF, LiCl, NaCl, KCl, RbCl, CsCl, NaBr, KBr, NaI, and KI) at various concentrations were prepared using commercially available salts dissolved in Millipore-purified H₂O (∼18 MΩ cm). XAS spectra were measured in T-mode at SSRL BL 10-1 using the experimental setup described in
3.4.2 Results and Discussion

The O 1s T-mode XAS spectra of alkali halide solutions (KF, RbF, CsF, LiCl, NaCl, KCl, RbCl, CsCl, NaBr, KBr, NaI, KI) at various concentrations and their difference spectra are displayed in Figs. 3.17-3.19. The effect of alkali and halide ions on the structure of water has been extensively studied using experimental methods, such as infrared [27, 76–78] and Raman [28, 79] spectroscopies, neutron and x-ray diffraction [13, 23, 69, 80–85], and femtosecond pump-probe spectroscopy [16, 22, 86, 87], as well as theoretical methods such as molecular dynamics [15, 24–26, 36, 82, 88] and reverse Monte Carlo [82, 89, 90]. Although XAS has also been used to study certain alkali halide solutions [38–40], to date, the data presented here represent the most extensive systematic XAS study of a large range of alkali halide solutions. This was made possible by the improvements in the feasibility and reproducibility of T-mode XAS measurements described in Chapter 2.

To facilitate the following discussion, the spectra of solutions with the same cations (i.e. KCl, KBr, KI, and NaCl, NaBr, NaI) and those with the same anions (i.e. LiCl, NaCl, KCl, RbCl, CsCl, and KF, RbF, CsF) at the same concentration are shown in Figs. 3.20 and 3.21. While the spectral changes are consistent over the whole range of concentration, even at 1 m, solutions at 4 m concentration were chosen specifically because the spectral changes are more pronounced than at lower concentrations while being the highest common concentration for all of the solutions.

The effect of F$^-$ has been discussed extensively in the previous section as similar
Figure 3.17: O 1s T-mode XAS spectra of KF, RbF, CsF, and LiCl solutions at varying concentrations compared to the spectrum of pure water. All spectra have been normalized by area from 532 to 550 eV. The difference spectra (i.e. salt solution minus water) are displayed above each set of spectra.
Figure 3.18: O 1s T-mode XAS spectra of NaCl, KCl, RbCl, and CsCl solutions at varying concentrations compared to the spectrum of pure water. All spectra have been normalized by area from 532 to 550 eV. The difference spectra (i.e. salt solution minus water) are displayed above each set of spectra.
Figure 3.19: O 1s T-mode XAS spectra of NaBr, KBr, NaI, and KI solutions at varying concentrations compared to the spectrum of pure water. All spectra have been normalized by area from 532 to 550 eV. The difference spectra (i.e. salt solution minus water) are displayed above each set of spectra.
to the effect of temperature decrease, which increases the fraction of tetrahedral low-density structures in the solution due to the formation of strong H-bonds between water and the anion. In Fig. 3.20, we focus the discussion on the effect of larger halide anions (i.e. $\text{Cl}^-$, $\text{Br}^-$, and $\text{I}^-$). The X-O distances between the halide ion $\text{X}^-$ and water in the first hydration shell are, on average, $\sim 3.15$ Å for $\text{Cl}^-$, $\sim 3.3$ Å for $\text{Br}^-$, and $\sim 3.6$ Å for $\text{I}^-$, which are longer than the average O-O distance in bulk water ($\sim 2.8$ Å). Although the anions should have the similar effect as H-bond elongation, it is argued in Section 3.2 that the spectral changes caused by $\text{Cl}^-$ anion are actually small compared to the effect of the cation. From Fig. 3.20, it is clear that, regardless of the cation, the spectra of $\text{Br}^-$-containing solutions closely resemble those of $\text{Cl}^-$-containing solutions; there is only a very small shift of the main edge to lower energy and small intensity variations that can be attributed to uncertainties in the concentration. For $\text{I}^-$ solutions, however, the spectra change dramatically, especially the main edge peak, which becomes very sharp and prominent and is shifted to lower energy, and the pre-edge is slightly increased. In addition, while the intensity above 542 eV is not changed, the region of the spectra between 539 eV and 541 eV is decreased, which is different from the post-edge decreased normally seen in NaCl and KCl solvation or temperature increase. These spectral changes cannot be simply attributed to longer I-O distance ($\sim 3.6$ Å) since there are only small changes when $\text{Cl}^-$ ($\text{Cl-O} = \sim 3.15$ Å) is replaced with $\text{Br}^-$ ($\text{Br-O} = \sim 3.3$ Å). Therefore, $\text{I}^-$ must contribute to the H-bond breaking effect, although the nature of this contribution is unclear from the present data.

In Fig. 3.21, the effect of the alkali cations is studied by comparing the spectra of solutions with the same anions ($\text{Cl}^-$ in Fig. 3.21a and $\text{F}^-$ in Fig. 3.21b). From Fig.
Figure 3.20: O 1s T-mode XAS spectra of salt solutions at 4 m concentration with the same cation and different anions: (a) NaCl, NaBr, and NaI, (b) KCl, KBr, and KI. The spectrum of pure water is shown as the black line. All spectra have been normalized by area from 532 to 550 eV. The difference spectra (i.e. salt solution minus water) are displayed above each set of spectra.
3.21a, it is apparent that all alkali cations increase the fraction of weak/distorted H-bonds as evidenced by the intensity redistribution from the post-edge to the pre- and main edge; this is true even for Li$,^+$, which is often considered as a structure maker due to its small size. However, the magnitude of the spectral changes varies for different cations. The enlarged pre-edge peaks for these spectra are shown in the inset of Fig. 3.21a. From LiCl to RbCl, the intensity of the pre-edge clearly shows a dependence on cation size; however, this effect is reversed for CsCl, where the pre-edge is between those of NaCl and KCl. The same reversal effect is also observed when the Cl$^-$ anion is replaced with F$^-$, shown in Fig. 3.21b. From the discussion in Section 3.3, we proposed that although F$^-$ has the opposite effect from K$^+$, resulting in a total spectrum that is largely similar to the spectrum of pure water, the residual effect of K$^+$ can be observed as the slightly higher pre-edge that increases with concentration. Similarly, the pre-edge peaks shown in the inset of Fig. 3.21b can be used to compare the relative effect of the cations, where it is shown that the pre-edge intensity of CsF is lower than those of KF and RbF, confirming that these spectral changes are real and reproducible.

The experimental and theoretical FY-XAS study of alkali halide solutions by Cappa et al. proposed that alkali cations have no observable effect [38, 39]. However, in Fig. 3.21 we can directly observe from experimental data that there are cation-dependent spectral changes associated with H-bond weakening. As mentioned in Section 3.2, Cappa et al. suggested, based on their DFT calculations, that the changes in the XAS spectra of alkali halide solution are, instead, caused by the electronic perturbation of water molecules by the anions [38, 39]. However, the anion-water distance used in their calculations was too short (Cl-O distance of 2.818 Å instead
of 3.15 Å) [38, 39], leading to the distortion of the electronic structure of water due to Pauli repulsion. In addition, even if there were electronic perturbations to the water by the anions, these effects should be decreased when the anion-water distance is elongated instead of enhanced, which is observed for I\(^-\) in Fig. 3.20.

In general, our observation that alkali ions have H-bond breaking effect on water is consistent with the existing literature, except for small differences. Although Li\(^+\) is often classified as a structure maker based on its small size, a reverse Monte Carlo study has proposed Li\(^+\) as a structure breaker [91], which agrees with our results. In addition, the number of water molecules bound to Li\(^+\) determined from size exclusion chromatography is less than one, whereas structure making ions such as F\(^-\), Mg\(^{2+}\), and Al\(^{3+}\) have \(\sim\)5, \(\sim\)6, and \(\sim\)9 water molecules, respectively [8]. However, our results for halide ions slightly contradict the literature, where the structure-breaking properties of halides have been shown to have a systematic dependence on size [2]. We observe only small differences between Cl\(^-\) and Br\(^-\), and only I\(^-\) shows an indication of an increased ability to break H-bonds.

Cs\(^+\) as the largest alkali cation has been proposed to behave like a neutral hydrophobic particle where the electrostatic interaction between ion and water becomes less important than water-water interaction, leading to the formation of a hydration cage around it [88]. Indeed, water molecules are known to form ice-like cages around small hydrophobic molecules [92]. This may explain the reversal effect observed in Fig. 3.21, where the pre-edge systematically increases from Li\(^+\) to Rb\(^+\) but decreases for Cs\(^+\). Water molecules in the first hydration shell of Cs\(^+\) may form H-bonds with each other, thereby compensating for some of the structure breaking effect, although
Figure 3.21: O 1s T-mode XAS spectra of salt solutions at 4 m concentration with the same anion and different cations: (a) LiCl, NaCl, KCl, RbCl, and CsCl, (b) KF, RbF, and CsF. The spectrum of pure water is shown as the black line. All spectra have been normalized by area from 532 to 550 eV. The difference spectra (i.e. salt solution minus water) are displayed above each set of spectra. The insets show the enlarged pre-edge region.
the extent of this effect is not known. For smaller alkali cations, the ion-water electrostatic attraction dominates; therefore, water cannot form a hydration cage around the cations.

3.4.3 Conclusion

In conclusion, we observe that generally alkali halide salts (excluding fluoride) have similar effect on the structure of water (i.e. breaking H-bonds), but the magnitude varies depending on the type of cation and anion. The spectral changes of alkali halide solutions can be mainly attributed to the H-bond breaking effect of the cations. As the size of an alkali cation increases from Li$^+$ to Rb$^+$, its ability to break H-bonds also increases. This effect, however, is reversed for Cs$^+$, probably because Cs$^+$ behaves like a hydrophobic particle due to its large size, resulting in the formation of H-bonded cage around it. In addition, we classify Li$^+$ as a H-bond breaker despite its small size. For halides, we see negligible differences between Cl$^-$ and Br$^-$, confirming our previous hypothesis that the H-bond elongation effect between anion and water only has a small effect on the overall XAS spectrum. On the other hand, I$^-$ as the largest anion seems to show a H-bond breaking effect.
3.5 References


CHAPTER 3. THE STRUCTURE OF WATER IN ION SOLUTIONS


CHAPTER 3. THE STRUCTURE OF WATER IN ION SOLUTIONS

Chapter 4

The Structure of Confined Water in AOT Reverse Micelles

This chapter is based on a paper titled *Increased fraction of weakened hydrogen bonds of water in aerosol OT reverse micelles* by I. Waluyo, D. Nordlund, U. Bergmann, L.G.M. Pettersson, and A. Nilsson (published in the Journal of Chemical Physics 131 (2009) 031103)*. My contributions as the first author in this paper include performing the experiments, analyzing the data, and writing most of the manuscript.

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CHAPTER 4. WATER IN REVERSE MICELLES

4.1 Introduction

The presence of water in nanoscopically confined environments is important in many biological and chemical processes. For example, water confined in chaperonins was found to influence their ability to assist in protein folding processes [1]. Also, the structure of proteins in a silica matrix is affected by confined water in the silica pores [2]. Confined water is also found in zeolites, aluminosilicate minerals that are used as catalysts in the petrochemical industry [3]. In addition, the study of confined water in artificial environments such as carbon nanotubes [4–6] and Nafion [7–9] membranes is important in the development of nanofluidic devices and proton exchange membrane (PEM) fuel cells, respectively. It is widely believed that nanoscopically confined water has different structural and dynamical properties compared to bulk water.

Reverse micelles have been used as a model system for studying the properties of nano-confined water. Reverse micelles are formed when an amphiphilic surfactant consisting of a polar headgroup and a nonpolar hydrocarbon chain is added to a mixture of polar (e.g. water) and non-polar solvents (e.g. isooctane). The amphiphilic surfactant molecules form aggregates where the polar headgroups face inward surrounding a nanoscopic pool of water molecules while the nonpolar side chains are pointed toward the nonpolar phase. The surfactant can contain either a cationic headgroup (e.g. cetyltrimethylammonium bromide), an anionic headgroup (e.g. sodium bis(2-ethylhexyl)sulfosuccinate) or a neutral molecule (e.g. Triton X100 or Igepal).

Sodium bis(2-ethylhexyl)sulfosuccinate (also called aerosol OT or AOT) is by far the most commonly used surfactant. The structure of AOT reverse micelles has been
extensively characterized using various scattering techniques and they were found to form monodispersed, spherical reverse micelles [10–13]. The size of the aggregates can be controlled by varying the ratio, $w_0 = [\text{H}_2\text{O}]/[\text{AOT}]$, of water to AOT concentration, and the diameter of the water pool (in nanometers) can be determined from the relationship: $d_{wp} = 0.29w_0 + 1.1$ for $2 < w_0 < 20$ [14]. Fig. 4.1 shows an illustration of a spherical reverse micelle and the molecular structure of AOT.

Molecular dynamics simulations [15], as well as various experimental techniques [16–22], have identified two types of water molecules in AOT reverse micelles: interfacial water near the interior surface and bulk-like water in the core. Interfacial water molecules are bound to the hydrophilic headgroups and, therefore, their structure and dynamics differ from core water molecules that behave similarly to bulk water. The ratio between interfacial and core water is correlated to the size of the reverse
micelles; decreasing the reverse micelle size increases the fraction of interfacial water. Due to the restricted mobility of the interfacial water molecules, it was found that larger reverse micelles exhibit bulk water-like dynamical properties while smaller ones have significantly slower dynamics. However, it has been disputed whether the two species of water inside a reverse micelle can be experimentally distinguished. Fayer and coworkers proposed that all water molecules in an AOT reverse micelle are connected through H-bonding network and, therefore, must be considered as having homogeneous dynamics [23]. Later, they found that while this is true for small AOT reverse micelles (i.e. \( w_0 = 2 \) and \( w_0 = 5 \)), water molecules in larger reverse micelles (i.e. \( w_0 = 10 \)) can be separated into the two components [24]. However, Bakker and coworkers used ultrafast pump-probe infrared spectroscopy to spectrally distinguish the OH stretch bands of interfacial and core water and concluded that the dynamics of confined water in reverse micelles is inhomogeneous, even for \( w_0 = 2 \) [18].

Reverse micelles formed by other surfactants have also been studied although not as extensively as AOT. Bakker and coworkers measured the dynamics of cationic reverse micelles formed by cetyltrimethylammonium bromide (CTAB) surfactant using mid-infrared ultrafast pump-probe spectroscopy and found that water in CTAB reverse micelles has different orientational dynamics compared to water in AOT reverse micelle mainly due to water-bromide H-bonding interaction [25]. Another notable study by Fayer and coworkers, who studied water in nonionic reverse micelles (Igepal CO 520 surfactant), also using ultrafast infrared pump-probe spectroscopy, suggested that the orientational dynamics of water in anionic (i.e. AOT) and nonionic reverse micelles are similar and concluded that the dynamics of confined water is largely determined by the confinement itself and not by the nature of the surfactant [26, 27].
CHAPTER 4. WATER IN REVERSE MICELLES

While the dynamics of water in reverse micelles has been extensively studied [28], its interpretation in terms of the effects of nanoconfinement on the local hydrogen (H-) bond structure is under debate. Whereas the slower dynamics of water in small reverse micelles indicates a more rigid H-bond network (i.e. more ice-like), the infrared OH stretch mode shows a shift to higher energy (blue-shift) [16–18, 20]. In bulk water, a blue-shift in the OH stretch mode is commonly associated with an increased fraction of broken or weakened H-bonds. However, it has been argued that this conventional interpretation, while widely accepted for bulk water, may not necessarily apply for water in reverse micelles and that the blue shift may, instead, be caused by the presence of interfacial water, which likely has a different OH stretch frequency compared to bulk water [20]. Others, however, have observed that while the blue component of the OH stretch band does indeed arise from interfacial water, the hydrogen bonds of the interfacial water molecules are systematically weakened as the size of the reverse micelle is decreased [18]. In addition, they found that the core water molecules also have slightly weaker H-bonds compared to bulk water [18]. This interpretation is supported by the study of the OH librational band of AOT confined water, in which a red-shift, attributed to weaker H-bonds, was observed [29].

In this work, x-ray absorption spectroscopy as measured by x-ray Raman scattering was used to probe the H-bonding environment of water in AOT reverse micelles. While vibrational spectroscopy is, by far, the most commonly used technique for studying this system, it often involves complicated data processing that can influence the interpretation, as evidenced by some of the conflicting conclusions summarized previously. XAS, as described in Chapter 1, is a direct and powerful tool for probing the H-bonding environment of water and it has never been used to study this system.
prior to the publication of this work [30]. Therefore, this work offers a simple, yet unambiguous, evidence that water in AOT reverse micelles has weaker H-bonding compared to bulk water.

4.2 Experimental Details

The reverse micelle solutions were prepared using Millipore-purified water (∼18 MΩ cm), AOT surfactant (Sigma-Aldrich, ≥99%) and isooctane as a nonpolar solvent (Fisher Chemical, HPLC-grade). The amount of water was varied to prepare reverse micelles at $w_0 = 5$ and $w_0 = 10$, corresponding to diameters of 2.6 and 4.0 nm, respectively [14]. The XRS data were recorded at the x-ray wiggler beamline (BL) 6-2 at SSRL equipped with a Si(111) double crystal monochromator. The monochromator energy was scanned from 6970 to 7020 eV with a flux of ∼1 × 10^{12} photons/s, a 0.1 × 1 mm² spot size at the sample, and an energy resolution of about ∼0.9 eV. Further details of the experimental setup are described in Chapter 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th># Scans</th>
<th>Total Count</th>
<th>Background</th>
<th>Signal and % Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M AOT</td>
<td>93</td>
<td>∼44000</td>
<td>∼37000</td>
<td>∼7000 ± 3%</td>
</tr>
<tr>
<td>$w_0 = 10$</td>
<td>52</td>
<td>∼25000</td>
<td>∼16000</td>
<td>∼9000 ± 1.8%</td>
</tr>
<tr>
<td>$w_0 = 5$</td>
<td>118</td>
<td>∼56000</td>
<td>∼41000</td>
<td>∼15000 ± 1.6%</td>
</tr>
</tbody>
</table>

Total count and background were measured at ∼7000 eV and ∼6995 eV photon energies (energy transfer of ∼538 eV and ∼533 eV), respectively. Signal is total count subtracted by background and % error is measured by dividing the square root of total count by the signal.

During measurement, scans were taken with energy step sizes of 1 eV from 6970 to 6989 eV, 0.2 eV from 6989 to 7008 eV, and 1 eV from 7008 to 7020 eV. The elastic peak was measured at 6461.8 eV, corresponding to an energy transfer range of 508.2
eV to 558.2 eV. In order to calibrate individual spectra when adding them up, the spectra were splined by linear interpolation to an energy step size of 0.05 eV. Table 4.1 summarizes the photon statistic of the measured scans for 1 M AOT and reverse micelle samples.

### 4.3 Results and Discussion

![Figure 4.2: O 1s XRS spectra of (a) $w_0 = 10$ (left) and $w_0 = 5$ (right) AOT reverse micelles, (b) 1 M AOT in isooctane (without added water), (c) subtracted spectra after 40% (left, $w_0 = 10$) and 55% (right, $w_0 = 5$) of spectrum (b) is subtracted from spectra (a). In spectra (c) the 532.3 eV $\pi^*$ resonance peak is gone, indicating that the spectral contributions are only from water O atoms. All spectra are normalized by area and include error bars given by the thickness of the lines. The energy scale corresponds to energy transfer in XRS.](image)

Figure 4.2: O 1s XRS spectra of (a) $w_0 = 10$ (left) and $w_0 = 5$ (right) AOT reverse micelles, (b) 1 M AOT in isooctane (without added water), (c) subtracted spectra after 40% (left, $w_0 = 10$) and 55% (right, $w_0 = 5$) of spectrum (b) is subtracted from spectra (a). In spectra (c) the 532.3 eV $\pi^*$ resonance peak is gone, indicating that the spectral contributions are only from water O atoms. All spectra are normalized by area and include error bars given by the thickness of the lines. The energy scale corresponds to energy transfer in XRS.
Figure 4.3: O 1s XRS spectrum of bulk liquid water (black) compared with spectra of confined water in AOT reverse micelles at $w_0 = 10$ (red) and $w_0 = 5$ (blue). The spectral contributions of AOT O atoms have been subtracted from the raw spectra, leaving only the spectral contributions from the confined water molecules. All spectra have been area normalized from 533 to 545 eV and the thick lines include error bars. Inset: Difference spectra between $w_0 = 10$ and water (red), and $w_0 = 5$ reverse micelles and water (blue).

Fig. 4.2 shows the O 1s XRS spectra of the $w_0=10$ (left) and $w_0 = 5$ (right) AOT reverse micelle solution (1 Molar AOT in isooctane). The total O 1s XRS spectrum contains contributions from all oxygen-containing species in the probed volume, i.e. both from the water and the AOT surfactant where the latter contains seven oxygen atoms per molecule. We measured the O 1s XRS spectrum of 1 M “dry” (without water) AOT in isooctane (Fig. 4.2b), which was subtracted from the total spectrum in order to obtain the XRS contribution from water (Fig. 4.2c). A previous study has
determined from Karl-Fisher titration that the ratio of water to AOT in the “dry” sample is 0.15 [21]. Therefore, the amount of water in the “dry” AOT is assumed to be negligible compared to the amount of water added to prepare reverse micelle solutions. Due to the low Raman scattering cross section for XRS in general, and the low amount of liquid water in AOT reverse micelles in particular, the data is flux-limited with large Poisson error bars. In addition, the subtraction procedure mentioned previously introduces more uncertainty to the resulting liquid water spectrum in Fig. 4.2c. In Fig. 4.2(right) for \( w_0 = 5 \) reverse micelle, in particular, there are artifacts from the subtraction procedure below the pre-edge. However, they do not change the region of interest from \( \sim 533 \) to 545 eV.

Fig. 4.3 compares the O 1s XRS spectrum of bulk liquid water with those of confined water in AOT reverse micelles at \( w_0 = 10 \) and \( w_0 = 5 \) (after AOT subtraction). The difference spectra for the confined water relative to bulk water are shown in the inset. Despite the large error bars (as indicated by the thick lines), it is evident that the pre-edge intensity of water in the reverse micelles increases compared to that of bulk water. Also, the smaller reverse micelles \( (w_0 = 5, \text{ blue}) \) give a stronger pre-edge compared to the \( w_0 = 10 \) reverse micelles (red).

The pre-edge feature in liquid water XAS/XRS spectrum is attributed to orbitals localized along the weak donor bond of water molecules with asymmetric H-bond configurations [31], i.e. single-donor (SD) species [32]. In a system with a large number of uncoordinated hydrogen bonds, e.g. the surface of ice, this spectral feature is very strong [32]. On the other hand, the post-edge region is attributed to strong H-bonds, which are abundant in a sample with a large number of tetrahedrally coordinated water molecules such as bulk ice [32]. The increased intensity of the pre-edge peak
as observed in Fig. 4.3 thus indicates that the confinement of water in AOT reverse micelles results in an increased fraction of weak (or broken) H-bonds compared to bulk water, and that decreasing the size of the reverse micelles enhances this effect. Further smoothing of the spectra (not shown) indicates that the pre-edge increase is accompanied by a decrease in the post-edge for both $w_0 = 10$ and $w_0 = 5$ reverse micelles, although the quality of the current data does not warrant a detailed discussion of the spectral profile. Despite the uncertainty in the data, we note that the difference spectra in the inset of Fig. 4.3 show the same trend as the spectral changes due to an increase in temperature.

The data presented here are consistent with the interpretation of Dokter et al. where a blue-shift was observed, indicating weaker H-bonds in reverse micelles although the dynamics is slower than bulk water [18]. The weakening of the H-bond in the interfacial layer has been attributed to the hydrophilic nature of the surfactant headgroup, which can form H-bonds with water molecules [18]. A water molecule at the interface can either donate one or both hydrogen atoms. The latter case is unlikely, since the water molecule then would have two strong donor H-bonds, in which case we would see an increase in the post-edge feature and a decrease of the pre-edge peak, which is the opposite of the recorded spectra in Fig. 4.3. Therefore, the most probable scenario for the water-surfactant interaction would involve one donor H-bond from the water, which is consistent with the results of simulations by Faeder and Ladanyi [15]. From the pre-edge increase seen in Fig. 4.3, it is apparent that the other hydrogen atom remains free. One possible explanation for this is that the geometrical restrictions imposed by the spherical curvature of the reverse micelle prevent interfacial water molecules from forming H-bonds with other water molecules.
In addition, the role of the Na\(^+\) counterion must be considered. While simulations have predicted that Na\(^+\) ions are located near the headgroups and do not interact with core water molecules [15], they may have some effects on the interfacial water. Solvated NaCl in bulk water has been shown to break or weaken H-bonding of water (see Chapter 3), resulting in an increased pre-edge peak due to the presence of the Na\(^+\) ion. Furthermore, MD simulations have been used to study the effect of different counterions in AOT reverse micelle (i.e. Na\(^+\), K\(^+\), and Cs\(^+\)) found that the mobility of interfacial water molecules shows a dependence on the counterion [33]. Therefore, the interaction between interfacial water and Na\(^+\) ions may hinder H-bonding to other water molecules.

It can thus be hypothesized that, from a dynamical point-of-view, water molecules appear ice-like and have slower dynamics since they are immobilized by the surfactant headgroups, but from a structural point-of-view, there is less H-bonding among water molecules. It should be noted, however, that the XRS data presented here represent the overall effect on the structure and cannot distinguish the structure of interfacial water from core water nor estimate the ratio of the two species.

### 4.4 Conclusion

The structure of water in AOT reverse micelles was studied using x-ray absorption spectroscopy through x-ray Raman scattering to obtain information about the H-bonding network. Analysis of the spectra shows an increase in the pre-edge compared to bulk water, indicating that the fraction of weakened H-bonds increases upon confinement, similar to the changes resulting from temperature increase and NaCl solvation. This interpretation is consistent with the work of Dokter et al., in which
the blue-shift of the OH stretch peak was assigned to weaker H-bonding [18]. The presence of increased fraction of weakened H-bonding is likely caused by the immobilization of the interfacial water molecules where one OH group is hydrogen bonded to the surfactant head groups and the other remains free.

4.5 References


Chapter 5

Ice on Hydrophobic

Methyl-terminated Si(111) surface

This chapter is based on a paper titled Direct Interaction of Water Ice with Hydrophobic Methyl-Terminated Si(111) by I. Waluyo, H. Ogasawara, M. Kawai, A. Nilsson, and T. Yamada (published in the Journal of Physical Chemistry C 114 (2010) 19004-19008).* This paper is a result of a collaboration between our group and Dr. Taro Yamada from RIKEN, Japan. My contributions as the first author in this paper include performing the measurements, analyzing the data, and writing most of the manuscript. Dr. Yamada prepared the CH$_3$-Si(111) samples.

CHAPTER 5. ICE ON HYDROPHOBIC SURFACE

5.1 Introduction

Hydrophobicity is often described when the interaction between water molecules is stronger than the interaction between water and the hydrophobic interface. In nature, water exists in close proximity to hydrophobic interfaces. The minimal interaction between water and hydrophobic interfaces has a wide significance in many biological and geological processes. For example, hydrophobic amino acid side chains in proteins significantly influence the protein folding process [1], and the hydrophobic surface of aquaporin membranes allows them to easily transport water across the cell membrane [2]. In the environment, naturally occurring hydrophobic coatings on soil can prevent vegetation growth and increase the rate of soil erosion [3].

Various experimental and theoretical techniques have been used to study the interaction between water and hydrophobic interfaces [4]. On surfaces, temperature-programmed desorption and infrared studies suggested that ice layers have a tendency to form three-dimensional clusters on hydrophobic self-assembled monolayer (SAM) surfaces in order to minimize contact with the surface [5]. X-ray reflectivity studies have shown the presence of a depletion layer in a few Ångströms thickness between water and hydrophobic SAM surfaces [6, 7]. Additionally, vibrational sum frequency generation spectroscopy suggested that water molecules form weak but strongly oriented hydrogen (H-) bonds at a hydrophobic interface [8]. These studies agree with the traditional notion of hydrophobicity mentioned previously, where water molecules preferentially form strong interactions among themselves while minimizing interactions with the hydrophobic interface.

In aqueous solutions containing small hydrophobic molecules, the hydrophobic effect is manifested in a different way. Frank and Evans proposed the iceberg model [9],
in which water forms ice-like cages around small hydrophobic solutes, which can be easily integrated in the H-bonding network of water. Experimentally, this has been observed from femtosecond vibrational spectroscopy where water molecules around hydrophobic solutes experience slower dynamics compared to bulk water and the number of these “immobilized” water molecules is linearly correlated to the number of methyl groups in the solute [10]. Therefore, water molecules can be present around the hydrophobic moiety of a molecule although they only form weak interactions.

Here we focus on the weak interaction of water in its frozen form with a hydrophobic methyl-terminated Si surface. We observe a weak direct interaction that leads to a significant perturbation of the first excited state on the carbon atom of the hydrophobic group. This implies that the water-methyl distance should be shorter than in condensed methane due to the formation of a weak hydrogen bond.

Methyl (-CH$_3$) terminated Si(111) surface [hereafter denoted CH$_3$:Si(111)] was chosen as the substrate because it is the best defined organic monolayer deposited on Si surfaces. The -CH$_3$ groups, terminating every outermost Si atom on Si(111) as the smallest organic moiety, form a (1 × 1) adlattice. The structure of this ideal monolayer has been investigated using STM [11–13] and vibrational spectroscopy [12]. The surface is hydrophobic with a contact angle of 78°. In addition, alkyl-terminated Si(111) is generally an ideal substrate for water deposition due to its resistance to oxidation in water as well as in air [14].

We used x-ray absorption spectroscopy (XAS) to investigate the electronic states of CH$_3$:Si(111) both with and without adsorbed water. As described in Chapter 1, XAS is an element sensitive technique for probing the unoccupied electronic states of a system through the excitation of a core electron to an unoccupied orbital. The
sensitivity to the interface is maximized since all of the carbon atoms are present only at the surface, making full contact with the adsorbed ice film. In addition, surface-sensitive electron detection modes of XAS are particularly suited and have been used to extensively study various adsorbate-substrate systems such as hydrocarbons [15–17], glycine [18], and water [19, 20] on metal surfaces. The XAS process is governed by the dipole selection rule in which a core electron from a 1s orbital can only be excited to orbitals with $p$ character. With the development of elliptically polarized undulator beamlines at synchrotron radiation facilities, the polarization of the incident beam can be easily controlled to probe electronic orbitals in different orientations.

5.2 Experimental Details

Samples were prepared in RIKEN, Japan. CH$_3$:Si(111) substrate was prepared by Grignard reaction between CH$_3$MgBr and Cl:Si(111) surface. In short, hydrogen-terminated Si(111) pieces were treated in Ar-diluted Cl$_2$ in ambient light, and then subjected to heating in CH$_3$MgBr in tetrahydrofuran. The final samples were then stored in Ar-charged containers for transportation to SSRL. Further details of the sample preparation can be found in Ref. [12].

Experiments were performed using the ultra-high vacuum (UHV) surface science endstation at elliptically polarized undulator beamlines 5-1 and 13-2 at Stanford Synchrotron Radiation Lightsource (SSRL), which was equipped with an electron analyzer for x-ray photoelectron spectroscopy (XPS) and a partial electron yield detector for XAS. A more detailed description of the endstation can be found in Chapter 2. We used XPS to confirm sample cleanliness and to choose a clean and homogeneous area of the sample to be used for XAS measurements. The sample was heated to 350
K for 15 minutes to remove carbonaceous contaminants. D$_2$O ice films were deposited at varying thicknesses at a deposition rate of ~0.1 layers/second at a temperature of 100 K. We minimized beam damage by using D$_2$O and scanning the sample continuously in front of the spectrometer during the measurements. C 1s XPS and C 1s XAS spectra measured before the deposition and after the removal of ice films were identical, indicating that neither beam damage nor water-induced oxidation had occurred.

5.3 Results and Discussion

![C 1s XAS spectra of (top) condensed CH$_4$ (from Ref. [21]) and (bottom) gas-phase CH$_4$ (from Ref. [22]). The 3a$_1$ peaks are indicated by the dotted line. Inset: the orbital plot of the symmetric LUMO 3a$_1$ orbital of CH$_4$ (from Ref. [21]).](image)

First, we describe the orbitals of CH$_4$, a simpler but closely related system that
has been extensively characterized. Fig. 5.1 shows the C 1s XAS spectra of gas-phase (bottom, from Ref. [22]) and condensed phase CH$_4$ (top, from Ref. [21]). The strongest absorption peak of gas-phase CH$_4$ at 288 eV arises from the 2t$_2$ LUMO+1 orbital. Features at higher energies originate from transitions to Rydberg orbitals. The spectrum of condensed CH$_4$ only shows small changes from the gas-phase spectrum; specifically, peaks due to excitations to LUMO and LUMO+1 orbitals are preserved, although they are slightly broadened, and the Rydberg fine structures are replaced with broad resonances. The C-C distance in condensed CH$_4$ is large ($\sim$4.16 Å [23]); therefore, only higher energy orbitals such as Rydberg orbitals overlap with neighboring molecules, leading to the broad resonances observed in Fig. 5.1 (top), while the 3a$_1$ and 2t$_2$ orbitals remain unperturbed. The 3a$_1$ LUMO orbital has a totally symmetric character (shown in the inset of Fig. 5.1); therefore, the excitation of a 1s electron to this orbital is symmetry-forbidden according to the dipole selection rule. However, a small peak corresponding to a transition to this orbital can be observed at 286.9 eV, which is explained by asymmetrical C-H bond vibrations resulting in dynamic symmetry distortions, thereby allowing the orbital to gain a small $p$ character making it dipole selection rule active. It has been shown that when a CH$_4$ molecule is adsorbed on Pt surface, the LUMO symmetry is broken through orbital mixing with the metal substrate, thereby increasing the $p$ character in the direction towards the surface and enhancing the intensity of the LUMO peak in the XAS spectrum with the E-vector polarization perpendicular to the surface [15, 24].

A similar phenomenon is observed in polarization-dependent C 1s XAS spectra of bare CH$_3$Si(111) surface displayed in Fig. 5.2. The out-of-plane E-vector (perpendicular to the sample surface) mainly probes the Si-C bond with some contributions
Figure 5.2: C 1s XAS spectra of (top) CH$_3$:Si(111) with in-plane (parallel to the surface) E-vector, and (bottom) CH$_3$:Si(111) with out-of-plane (perpendicular to the surface) E-vector. The A$_1$ peaks are indicated by the dotted line. Both spectra were normalized at the maximum intensity.

from the C-H bonds of the -CH$_3$ groups. The shoulder at 285.5 eV corresponds to the LUMO orbital, analogous to the gas-phase CH$_4$ 3a$_1$ orbital, whose symmetry has been broken through the formation of Si-C bond. This orbital is, therefore, denoted A$_1$ orbital. Since in a -CH$_3$ adsorbate the Si-C bond is strongly covalent, this orbital involves more p character as evidenced by the relatively strong intensity compared to the physisorbed CH$_4$ on Pt where all C-H bonds are still intact [15, 24]. In addition, the A$_1$ peak is shifted by 1.4 eV from the 3a$_1$ peak of gas-phase and condensed CH$_4$ while the analogous peak on the spectrum of CH$_4$/Pt(111) is unshifted [15, 24].
The rest of the out-of-plane spectrum is also broadened compared to gas-phase and condensed CH$_4$. Therefore, it is reasonable to conclude that the energy shift and broadening are caused by the strong interaction between -CH$_3$ groups and Si atoms.

The in-plane spectrum [Fig. 5.2 (top)] is of particular interest in investigating the electronic effect of adsorbed D$_2$O ice, since the $p$ character is very weak and any orbital modifications of the surface -CH$_3$ groups could cause an increase in the $p$ character to the A$_1$ orbital and enhance the intensity of the peak. A weak peak at 285.0 eV corresponding to the LUMO excitation is also present in the in-plane spectrum (E-vector parallel to the surface plane), although the orbital should be symmetry-forbidden since this polarization only probes the symmetric orbitals along C-H bonds. Similar to gas-phase CH$_4$, asymmetrical vibrations of C-H bonds can explain the appearance of the LUMO A$_1$ peak. The intensity is much lower compared to the out-of-plane spectrum due to the inherently weaker nature of asymmetrical distortions through vibrational motions compared to covalent bonding. Also, different chemical bonding environments account for the slightly different energy positions of the A$_1$ peak (285.5 eV for out-of-plane and 285.0 eV for in-plane). The broad appearance of the spectral features is likely caused by a wide distribution of structures across the substrate and/or shorter C-C distance between -CH$_3$ groups (3.8 Å, the lattice constant of Si(111)-(1x1) surface) compared to the C-C distance in condensed CH$_4$ (4.16 Å).

The adsorption of D$_2$O ice on CH$_3$:Si(111) induces quite dramatic changes to the C 1s XAS spectra, as displayed in Fig. 5.3, specifically in the A$_1$ peak, which is enhanced in both in-plane and out-of-plane spectra. The changes in the in-plane spectra [Fig. 5.3 (top)] are especially interesting since the hydrophobic -CH$_3$ groups
Figure 5.3: C 1s XAS spectra of CH$_3$:Si(111) with adsorbed D$_2$O ice layers (red - 3 layers, green - 5 layers, blue - 8 layers) compared with the bare surface (black) measured with in-plane (top) and out-of-plane (bottom) E-vector polarizations. The $A_1$ peak intensity is dramatically enhanced by ice adsorption for both polarizations. The dotted line indicates the $A_1$ peak for the bare surface while the dashed lines indicate the $A_1$ energy shift. All spectra were normalized at the maximum intensity.
are not expected to electronically interact with water. However, the dramatic increase in the intensity of the $A_1$ peak as the coverage of water increases suggests that the presence of the ice overlayer enhances the $p$ character of the $-\text{CH}_3$ orbitals on the surface. Further evidence of the orbital modification is seen in a shift of $\sim 0.3$ eV and $\sim 0.55$ eV towards lower excitation energies from 0 to 8 layers ice for the in-plane and out-of-plane polarizations, respectively. Both these observations are a clear indication that there is an orbital interaction between water and $-\text{CH}_3$ groups despite the hydrophobicity of the surface. The changes in the $A_1$ peak of the out-of-plane spectra [Fig. 5.3 (bottom)] are less dramatic than the in-plane spectra, but the same trend is observed. The rest of the spectral features in both out-of-plane and in-plane spectra do not seem to be significantly influenced by the ice overlayer.

It should be noted that for both in-plane and out-of-plane polarizations, the increase of the $A_1$ peak intensity is not linearly correlated with the number of ice layers; i.e. the change from 5 to 8 layers is greater than 0 to 3 or 3 to 5 layers. This is likely caused by the morphology of the ice, which can be determined from the O 1s XAS spectra of the ice films (Fig. 5.4). At all coverages, the polarization dependent XAS spectra are isotropic, indicating that three dimensional non-wetting ice clusters were formed instead of flat wetting layers. This is similar to the case of ice monolayer grown on Cu(111) surface [25]. If flat layers were formed, the polarization dependent spectra would show anisotropy as observed for ice monolayer on Pt(111) [26]. In addition, we can determine that amorphous ice was formed from the absence of the fine structure beyond the post-edge that is present in crystalline ice due to multiple scattering (see Chapter 6 and Ref. [21]). The thickness stated here is the equivalent thickness if the ice were assumed to form flat uniform layers. Since this is not the case, some areas
Figure 5.4: O 1s XAS spectra of ice films grown on CH$_3$:Si(111) substrate at different coverages. The solid lines represent in-plane polarization while the dotted lines represent out-of-plane polarization.

of the surface are not covered with ice at low coverages, but the fraction of the area exposed to vacuum decreases with increasing coverage. We expect that as more water was dosed and the size of the clusters increased not only in height but also laterally, more of the -CH$_3$ groups would become covered with water. This is also observed in the growth of ice on the hydrophobic first water monolayer on Pt(111) [27, 28]. Eventually at high enough coverage, the whole surface would be covered with water and the C 1s XAS spectra would stop changing. Unfortunately, at much higher water coverages, measurements became more difficult since fewer electrons could escape through the thick layer, resulting in a low quality spectrum. This is distinctly different from the ice grown on other hydrophobic surfaces such as Au(111) [29] or
graphene/Pt(111) [30], which were shown to form two layer crystalline films that maximize the number of water-water H-bonding. However, the hydrophobic nature of Au(111) and graphene/Pt(111) is different from that of CH$_3$:Si(111) since no free C-H groups are available to form C-H—O H-bonds with water.

The electronic effect of adsorbed ice on the excited state orbital of -CH$_3$ group is surprising considering the hydrophobic nature of the substrate. The interaction between -CH$_3$ groups and the water molecules perturbs the -CH$_3$ A$_1$ orbital in such a way that it gains p character in both in-plane and out-of-plane directions so that the orbital shape is no longer spherically symmetric in the excited state. However, the observation of a direct interaction between a hydrophobic system and water is not unprecedented. For example, experimental vibrational Raman spectra of methane hydrates, a rigid high pressure system in which CH$_4$ molecules are trapped in ice-like cages, show a red-shift of the C-H stretching band from gas-phase CH$_4$ [31, 32].

Furthermore, we speculate that the direct interaction between CH$_3$:Si(111) surface and adsorbed D$_2$O ice results in the formation of weak H-bonding. Although X-H—O H-bonds are more often observed with highly electronegative atom X (i.e. X = N, O, or F), C-H—O H-bonding has been observed numerous times in literature [33]. For instance, DFT simulations of adsorbed glycinate on Cu(110) showed that a model in which neighboring molecules form C-H—O H-bond was the best model to reproduce experimental XAS data [34]. C-H—O H-bonds were also observed from the nuclear magnetic resonance and infrared studies of 1,4-dioxane and water mixtures [35]. However, in our study, C-H—O H-bonding likely occurred between water and the -CH$_3$ groups despite the hydrophobic nature of the surface. The formation of three-dimensional ice clusters as shown in Figure 5.4 results from the
strong water-water H-bonding in order to minimize contact with the hydrophobic surface. Nevertheless, at low temperatures where the mobility of water molecules is restricted, a direct interaction in the form of weak H-bonding is formed between the water molecules in ice and the methyl C-H bonds. We estimated the surface density of -CH$_3$ groups and of water in ice films to be 7.7 nm$^{-2}$ [12] and 5.6 nm$^{-2}$ at a maximum (derived from the lattice constant of 4.5 Å for the (0001) plane of $I_h$ ice [36]), respectively. Therefore, one H$_2$O molecule can be weakly H-bonded to at least one -CH$_3$ group at the interface covered by ice islands. The strength of C-H—O H-bonds is generally in the range of 0.3 to 3.5 kcal/mol depending on the hybridization of the C atom [33], compared to 5 kcal/mol for O-H—O H-bond in water [37]. For CH$_3$:Si(111), it is expected to be close to the value of 0.3 kcal/mol for the C-H—O H-bond between CH$_4$ and H$_2$O as obtained from *ab initio* calculations [38]. Though obviously much weaker than the H-bonds between water molecules, it was shown that the C-H—O H-bond between CH$_4$ and H$_2$O shows linearity [38], which, indeed, is one of the defining characteristics of a hydrogen bond.

As mentioned previously, the condensation of gas-phase CH$_4$ does not significantly change the XAS spectra due to the large C-C distance. A similar sample such as methanol (CH$_3$OH) also displays only small changes in the C 1s XAS spectra between gas and liquid phases [39], and the overall spectra resemble CH$_4$ spectrum despite the different symmetry. Therefore, the electronic interaction between -CH$_3$ groups and water implies that the C-H—O distance between a water molecule and a surface -CH$_3$ group is likely shorter than the C-C distance in condensed CH$_4$ (∼4.16 Å) or liquid CH$_3$OH (∼3.8 Å [40]). In addition, for glycinate ions on Cu(110), the C-H—O distance was determined to be less than 2.68 Å [34]. However, since the CH$_2$ group
in a glycinate ion is a more acidic H-donor than the CH$_3$ groups on Si(111) surface, the C-H—O H-bond between two glycinate ions is likely stronger than the similar H-bond between H$_2$O and -CH$_3$. Therefore, we deduce that the C-H—O distance in our sample is between 2.68 Å (glycinate H-bonding [34]) and 3.8 Å (C-C distance in liquid methanol [40]). This is also in agreement with the expected value for C-O distance of 3.1-3.5 Å in C-H—O H-bonded systems [33]. However, at higher temperatures, the entropic contributions most likely will lead to a substantial increase in C-H—O distance, resulting in the formation of a depletion layer.

5.4 Conclusions

In conclusion, we present clear evidence from experimental XAS that adsorbed D$_2$O ice directly interacts with hydrophobic -CH$_3$ groups on Si(111). The ground state of the LUMO A$_1$ orbital of the -CH$_3$ groups is spherically symmetric and, therefore, is symmetry-forbidden for XAS excitation. Upon D$_2$O ice adsorption, the excited state of the A$_1$ orbital is asymmetrically distorted by the ice overlayer, thereby increasing the $p$ character and enhancing the absorption intensity in both in-plane and out-of-plane directions. We propose that weak H-bonds are formed between the methyl C-H bonds and the water molecules in the first layer of the ice films. This is an indication that macroscopic observations of hydrophobicity (e.g. contact angle, formation of three-dimensional ice clusters) do not necessarily preclude a molecular orbital interaction at low temperatures.

5.5 References


Chapter 6

The Growth and Structure of Ice on Pt(111)

This chapter is adapted from two publications:


In the first paper, my contributions as the first author include performing the experiments, analyzing the data, and writing most of the manuscript. The second paper is


a collaborative review paper and my contributions that are included in this chapter can be found in Section 4.1 of the paper where I performed the XAS measurements of ice on Pt(111), analyzed the data, and wrote a part of the manuscript.

6.1 Introduction

Due to the important role of ice and ice surfaces in a variety of areas ranging from the search for water on astronomical objects [1–5] and the study of stratospheric chemical reactions [6–9] to the investigation of the structure of hydrogen bonded systems, e.g. liquid water [10, 11], the growth of flat and homogeneous crystalline ice films on metal surfaces is desirable as a highly ordered model system. Platinum single crystal with a (111)-terminated surface [Pt(111)] has long been considered as a good substrate for crystalline ice growth due to its good lattice match with hexagonal ice [12, 13]. Crystalline ice can thus be grown directly on Pt(111) by keeping the substrate in ultra high vacuum (UHV) conditions and at temperatures above 135 K, as has been reported in several studies (see e.g. Ref. [14, 15]).

Crystalline ice can also be formed when amorphous ice films (grown at temperatures below 120 K) are heated to a higher temperature (typically 140 - 160 K), where crystallization occurs simultaneously with water desorption [16–20]. The crystallization process has often been controlled through isothermal desorption and monitored through mass spectrometry. As the temperature is kept constant at ~150 K, the transformation of amorphous ice to crystalline ice causes a characteristic 50% drop in the water desorption rate [19]. It has been demonstrated that the subsequent region of the isothermal desorption shows a constant desorption rate, which can be associated with zero-order kinetics claimed to be indicative of a smooth and homogeneous
crystalline ice film [12, 19–21].

However, the homogeneity of crystalline ice formed by the isothermal heating of amorphous ice films on Pt(111) has recently been questioned [16, 17, 22]. A recent temperature programmed desorption (TPD) study of rare gases adsorbed on crystalline ice prepared by isothermally heating amorphous ice grown on Pt(111) suggested that, although a constant desorption rate was observed after crystalline ice was formed, a significant fraction of the first monolayer was exposed, as indicated by the rare gas desorption temperature [16]. This behavior was attributed to the structure of the first water monolayer, which forms a nearly flat hydrogen bonding network bonded to Pt(111) alternately via the hydrogen atom and the oxygen lone pairs [23]. The formation of the first water monolayer would then result in a flat and hydrophobic surface without dangling O-H groups [16, 22]. Low energy electron diffraction (LEED) has also shown that crystalline ice films need to grow thicker than 40 layers before the LEED pattern from the ordered first monolayer, which shows registry with the Pt(111) substrate, vanishes [22]. Hence, there is an ongoing debate whether it is possible to grow homogeneous crystalline ice on Pt(111).

In the present study, infrared reflection absorption spectroscopy (IRAS) combined with x-ray photoelectron spectroscopy (XPS) were used to investigate the formation of crystalline ice from a uniformly thick film of amorphous D₂O ice upon isothermal heating under UHV conditions. IRAS is receptive to changes in the intramolecular O-D vibrations, and the sensitivity of the O-D stretch frequency to the local geometrical arrangement was used to distinguish amorphous and crystalline ice [24]. Since IRAS is a bulk-sensitive technique, the integrated intensity of the O-D stretch peak was used to determine the thickness of the ice film. XPS is an element-specific technique
that is sensitive to the local environment of the probed atoms [25]. In particular, the O 1s peak from the first water monolayer adsorbed to Pt(111) is shifted from that of the multilayer, which is hydrogen-bonded to other water molecules and not directly interacting with the surface. This sensitivity is used together with IRAS to provide evidence for a large exposure of the first monolayer when amorphous ice on Pt(111) is isothermally heated at 150 K, suggesting that 3-D crystallites are formed in the crystallization process.

The XAS study of ice is important in the fundamental understanding of the unique features in the O 1s XAS spectra of liquid water and their interpretation in terms of hydrogen bonding. The pre-edge peak, in particular, has been debated whether it truly arises from uncoordinated O-H groups. Crystalline ice is an ordered system where most, if not all, of the water molecules are involved in tetrahedral H-bonding network. However, the O 1s XAS spectra of crystalline ice still show a pre-edge peak, even when measured using bulk sensitive techniques such as XRS [26, 27]. The origins of the pre-edge in ice are explored in this study, and we found that while a significant amount of the pre-edge comes from free O-H groups on the surface of ice, there are also contributions from the bulk, possibly due to the presence of high-density amorphous ice phases.

6.2 Experimental Details

The experiments were performed at the surface science endstation at the elliptically polarized undulator beamline 5-1 at SSRL. Further details about the endstation are described in Section 2.3.1 of Chapter 2.

Pt(111) single-crystal was mounted on a liquid nitrogen (LN₂) cooled rod at a 6°
grazing incidence angle relative to the incoming photon beam, which gave an illuminated area of $100 \times 670 \, \mu m^2$ on the sample surface. To heat the sample, a 0.15 mm thin thoriated tungsten filament was mounted near the back-side of the Pt crystal; the filament had a shape that gave uniform heating of the whole crystal. For temperatures above 400 K, the heating power was increased through electron bombardment obtained by a sample bias of 400 V. The temperature was monitored using an alumel/chromel thermocouple spot-welded via a small piece of tantalum foil on the side of the Pt crystal. The crystal surface was cleaned by cycles of Ne$^+$ ion sputtering, annealing to 900 K, and O$_2$ dosing onto the surface at elevated temperatures during cool down (from 800 K down to 370 K). Additional O$_2$ treatments were repeated until a carbon-free surface was obtained, as confirmed by the absence of CO contamination in TPD and XPS. A final heating of the crystal to 600 K removed residual oxygen. The absence of C and O signals in XPS indicates less than 1% of a monolayer of carbon and oxygen contaminations.

Amorphous D$_2$O ice films of $\sim80$ layer thickness ($\sim300 \, \AA$) were grown on the clean Pt(111) surface at $\sim100$ K at a deposition rate of $\sim0.08$ layers/s using a pulsed gas delivery system (deposition rate calibrated using TPD and XPS). Amorphous ice has been shown to grow layer-by-layer on Pt(111) for up to 3 layers [28]. We investigated the thickness uniformity of a 5-layer-thick film (film thickness confirmed through IRAS) at 30 spots within a $9 \times 3.4 \, \text{mm}^2$ area using the Pt 5$p_{3/2}$ and O 2$s$ photoemission peaks (the 2$a_1$ molecular orbital of H$_2$O is predominantly O 2$s$). Since the binding energy of Pt 5$p_{3/2}$ and O 2$s$ are close, 52 (Ref. [29]) and 31 eV (Ref. [30]), respectively, the probing depths of the two photoemission peaks are similar, which, for the combination of 5 layer thickness and 670 eV excitation energy, results in
a 1:1 intensity ratio between these two photoemission peaks. The change in the photoemission peak intensity ratio as a function of thickness provides a sensitive probe of inhomogeneity. A constant peak ratio was observed over 30 spots on the sample; therefore, we confirmed a uniform 5-layer-thick amorphous ice film throughout the investigated sample area, and assumed that the layer-by-layer growth continues for up to 80 layers of uniform thickness.

In this work, the first layer of water adsorbed on Pt(111) is referred to as the first monolayer, whereas the subsequent layers are collectively called the multilayer. One layer in the multilayer ice film is defined as the corrugated slab in a hexagonal ice lattice, also referred to as ice bilayers, separated by 3.7 Å (Ref. [13, 31] and references therein). D$_2$O was used instead of H$_2$O in order to separate the desorption signal of the sample from that of residual H$_2$O vapor in the instrument, to avoid the contribution from condensed water on windows to the O-D stretch frequency peak of the sample, and to minimize the sensitivity to beam damage. D$_2$O with 99.9 atom-% D was purchased from Sigma-Aldrich, and contamination was reduced by repeated pump-freeze cycles.

Crystalline ice was prepared by the isothermal heating at 150 K of the amorphous ice film described above; changes in the water desorption rate were monitored through mass spectrometry. The crystallinity and thickness of the ice film was confirmed and measured by IRAS. The relationship between the ice film thickness and the integrated O-D stretch intensity was calibrated using the intensity ratio of the multilayer and the first monolayer desorption peaks, which appear separately for ice films of less than 10 layers thickness. A calibration curve was then obtained through extrapolation for up to 80 layers thickness.
O 1s and Pt 4f XPS spectra were measured in normal emission (with E-field out-of-plane and parallel to the electron spectrometer lens) using 660 eV photon energy at \( \sim 0.1 \) eV resolution. The electron spectrometer was operated at better than 0.1 eV resolution giving a total energy resolution of \( \sim 0.2 \) eV.

O 1s XAS spectra of the initial amorphous ice and the resulting crystalline ice after isothermal heating were measured using Auger electron yield detection method. NH\(_3\) films were deposited on the crystalline ice surface and their presence was confirmed by IRAS. The NH\(_3\) multilayer was removed by heating up the sample to 114 K, leaving a monolayer of NH\(_3\) terminating the ice surface. O 1s XAS spectra were taken for multilayer and monolayer NH\(_3\) coverage on crystalline ice. To avoid beam damage, the sample was scanned continuously at 15 \( \mu \)m/s during the XPS and XAS measurements.

### 6.3 Results and Discussion

#### 6.3.1 Formation of 3-D Ice Crystallites

Fig. 6.1(top panel) shows the O-D stretch region of the IRAS spectra from 20 layers of (a) crystalline and (b) amorphous ice. The former has three distinct features located at 2340, 2440, and 2485 cm\(^{-1}\), whereas the latter has a broader appearance with a peak maximum at 2520 cm\(^{-1}\). Hence, IRAS is a very suitable tool for determining which form of ice, amorphous or crystalline, is present on Pt(111). Furthermore, the comparison shows that the integrated intensity of the O-D stretch peak of crystalline ice is larger than that of amorphous ice of equal thickness, which is due to different absorption cross sections in the two cases. Fig. 6.1(lower panel) shows the plot of ice
Figure 6.1: (Top panel) IRAS spectra of a 20-layer-thick (a) crystalline and (b) amorphous ice films. (Bottom panel) Ice film thickness versus O-D stretch region integrated intensity for amorphous ice (full circles) and crystalline ice (open circle) and their respective fitted lines (dashed line for amorphous ice and solid line for crystalline ice). Using the fitted calibration line, the thickness of crystalline ice that remained after isothermal heating for 6 minutes (squares) and 16 minutes (triangles) can be determined. Each marker corresponds to one of four separate preparations of ice crystallization (two square markers overlap each other).
film thickness as a function of integrated O-D stretch peak intensity of amorphous (dashed line) and crystalline (solid line) ice where the latter has a comparatively smaller slope. The integrated O-D stretch peak intensity is linearly proportional to the ice film thickness in the range of interest for this study, which is up to 80 layers; the prepared thicknesses of amorphous ice are 5, 10, 20, 40, and 80 layers (full circles).

Crystalline ice, formed through the crystallization of 80 layers amorphous ice, is assumed to show a linear behavior of the integrated intensity with film thickness similar to the amorphous case. A calibration line for the crystalline ice is thus established through the single point at 7 layer thickness (open circle), where the thickness was determined through TPD. The apparent linearity of the two calibration lines manifests the bulk sensitivity of the probe and the reliable growth conditions (the calibration line is fitted through the origin). Fig. 6.1(lower panel) further shows four separate preparations where the calibration line is used to plot the crystalline ice total thickness that remains from an initial $\sim$80-layer-thick amorphous film after isothermal heating ($\sim$150 K) for 6 minutes (squares) and an additional 10 minutes (triangles). The spread of the obtained data within each group is due to slightly different experimental conditions (e.g. slightly different starting thicknesses mainly due to vapor back pressure, small differences in temperature ramping speed, constant temperature resolution ($\pm$ 0.1 K) and exact timing of the isothermal conversion of the amorphous ice to crystalline ice).

Another method to estimate the ice film thickness is to record the substrate photoelectron intensity, which is determined by the finite electron mean free path of the photoelectrons. Fig. 6.2 shows the Pt 4f XPS intensity of the Pt(111) substrate at 660 eV photon energy recorded during growth up to 80 layers of amorphous ice.
Figure 6.2: Pt 4f XPS intensity as a function of amorphous ice thickness (circles) and its exponential fit (solid line). The Pt 4f intensity is defined as 100% for clean Pt(111) and it approaches zero for 80 layers; i.e., no Pt 4f signal is detected. The Pt 4f intensities after isothermal heating for 6 minutes (squares) and 16 minutes (triangles) are shown versus the thickness determined by IRAS in Fig. 6.1. (Inset) Already at 45 to 52 layers (squares), the Pt 4f intensity shows slightly higher intensity than expected from a film with uniform thickness.

film (same preparation as in Fig. 6.1). Unlike the linear dependence in IRAS that represents the total ice coverage independent of the sample homogeneity, the attenuation of photoelectrons is exponential and the Pt 4f intensity is thus sensitive to the uniformity of the ice film. For the growth of amorphous ice films up to 80 layers, the relationship between the ice film thickness and the Pt 4f XPS peak intensity shows an exponential decrease of the signal down to zero intensity, which is consistent with the expected layer-by-layer growth of amorphous ice.

The integrated O-D stretch peak intensity of the obtained crystalline ice film, after
isothermal heating to the point where the desorption rate levels out after the drop in intensity due to crystallization (i.e. after 6 min at 150 K), indicates that 80 layers of amorphous ice films generate crystalline ice with an average thickness of 48 ± 3 layers, as measured by IRAS, shown by the square markers in Fig. 6.1(lower panel).

A careful examination of Fig. 6.2(inset, square markers), on the other hand, reveals that the Pt 4f XPS intensity is slightly higher than expected for a homogeneous ice film of the same uniform thickness. We also observe that the line shape of the O-D stretch peak (not shown) indicates that, at this point, a small fraction of the sample is still amorphous.

Additional isothermal heating for 10 minutes at 150 K decreases the average thickness to 23 ± 4 layers, as measured by IRAS [triangular markers, Fig. 6.1(lower panel)]. However, the Pt 4f XPS intensity is now much higher than expected (triangular markers, Fig. 6.2). The large deviation from the expected Pt 4f intensity is only possible if some areas of the sample are covered with much thinner ice films, thereby generating a significantly stronger XPS intensity from the Pt(111) surface. Moreover, the slightly higher than expected Pt 4f XPS intensity immediately after the drop of the desorption rate (6 min, square markers) indicates that, already before complete crystallization, the ice film is slightly inhomogeneous.

More conclusive evidence for inhomogeneous crystallization can be observed in the O 1s XPS spectra presented in Figs. 6.3(a-c) (see also corresponding measurements in Figs. 6.1 and 6.2), which show O 1s XPS spectra recorded for 80 layers of amorphous ice, ice near completion of crystallization (6 min, 48 layers), and ice after further isothermal heating (16 minutes total, 23 layers). The amorphous ice shows one single peak at ∼533.7 eV binding energy, assigned to the ice multilayer. After
Figure 6.3: (Left panel) O 1s XPS spectra of (a) 80 layers amorphous ice before heating, (b) ice after 6 minutes of isothermal heating at 150 K (∼48 layers, as measured by IRAS), (c) ice after additional 10 minutes of isothermal heating at 150 K (∼23 layers, as measured by IRAS). (Right panel) O 1s XPS spectra of 7 ± 1 layers crystalline ice (as measured by TPD) prepared by isothermally heating 80 layers of amorphous ice at 150 K for ∼40 minutes recorded at three different spots on the sample (separated by ∼2 mm or more) which give varying intensity ratios of the multilayer (533.7 eV) and first monolayer (532.2 eV) peaks such as (d) equal intensity, (e) higher multilayer peak, and (f) higher first monolayer peak.
crystallization, the O 1s XPS spectrum is largely unchanged except for a slight increase of the full width at half maximum (FWHM) attributed to charging effects [32]. After further isothermal heating, a second, clearly distinguishable peak can be seen at 532.2 eV, which corresponds to the binding energy of the O 1s peak from the first water monolayer [23, 33].

Assuming a homogeneous sample with a uniform thickness $d$, we can calculate the contribution of the first monolayer using the escape depth probability $P$ of an electron with a mean free path $\lambda$ following an exponential decay,

$$P = \frac{1}{\lambda} \int_{d-1}^{d} e^{-x/\lambda} dx.$$

(6.1)

With an electron mean free path of $\sim 13$ Å ($\sim 3.5$ layers) [34], the first water monolayer of a 23-layer-thick homogeneous crystalline ice sample would contribute 0.05% to the O 1s XPS signal, which would be undetectable in the experimental spectrum. Consequently, the fact that the O 1s XPS spectrum in Fig. 6.3(c) displays a clearly resolved first monolayer peak is a strong indicator that a significant area of the first monolayer is exposed to vacuum, consistent with the Pt 4f XPS data (Fig. 6.2).

To complement these crystalline ice preparations, thin ice films were generated with an even more extended isothermal heating time ($\sim 40$ min at $\sim 150$ K), leaving an equivalent of $7 \pm 1$ layers crystalline ice as confirmed by TPD. The O 1s XPS spectrum for this case is displayed in Fig. 6.3(d) and the intensity ratio between the first monolayer and multilayer peak is almost 1:1. This ratio unambiguously shows that a significant fraction of the first monolayer is exposed to vacuum and 3-D crystallites are formed, which is in agreement with Kimmel et al. [16, 17] There is
a slight variation of the relative intensity of the multilayer and first monolayer peak across the sample, and Figs. 6.3(e) and 6.3(f) capture the two extreme cases. Thus, some areas of the sample were covered with more crystallites while other areas had more exposed first monolayer. We found that the inhomogeneous distribution of the crystallites is likely caused by a temperature gradient during the heating process. This is not surprising for this relatively large sample (investigated area is $9 \times 3.4 \text{ mm}^2$ of a 10 mm diameter sample), in particular since a change in desorption rate is observable for only a 0.1 - 0.2 K variation in sample temperature. However, the complete data set shows that on a sub-mm scale the inhomogeneity was negligible.

Based on the XPS spectrum in Fig. 6.3(d), we can roughly estimate the relative area of the exposed first monolayer and the average height of the crystallites. The photoelectron peak ratio $R$ between the first monolayer and the multilayer can be expressed in terms of the fraction $a$ of the total area of the exposed first monolayer, average crystallite height $n$ in numbers of layers, and electron mean free path $\lambda$ (expressed in ice layers):

$$R = \frac{a + \left(1 - a\right) e^{-\left(n-1\right)/\lambda}}{\left(1 - a\right) \sum_{j=2}^{n} e^{-\left(n-j\right)/\lambda}},$$

(6.2)

where we have assumed equal detection probability for the top-most layer whether terminating a crystallite containing $n$ layers or being the exposed first monolayer. Equation 6.2 does not include photoelectrons reaching the detector through the walls of the crystallites, which leads to an underestimation of the fraction of exposed first monolayer; the possibility that electrons are captured by the surrounding crystallites when emitted from first monolayer patches introduces some uncertainty. Furthermore, the equivalent number of layers $V_{\text{total}}$ (determined from IRAS in Fig. 6.1) is related
to the crystallite height $n$ and fraction of exposed monolayer $a$ through

$$V_{total} = n \times (1 - a) + a. \quad (6.3)$$

In Fig. 6.4 we plot the value of $a$ as determined from equations 6.2 and 6.3 (solid line and dashed line, respectively) using various values of $n$ for the case of $R = 1:1$ and $V_{total} = 7$ [Fig. 6.3(d)], and $R = 1:5$ and $V_{total} = 23$ [Fig. 6.3(c)]. From Fig. 6.4, one can observe that for $n$ greater than 15 layers, the value of $a$ estimated from equation 6.2 (solid line) asymptotically approaches

$$a = \frac{R}{1 - e^{-1/\lambda} + R} \quad (6.4)$$

The point at which both lines intersect reflects the fraction of the exposed first monolayer and the height of the crystallites on the sample. For the $R = 1:1$ case [Fig. 6.4(a)], the intersection point between equations 6.2 and 6.3 gives 80% as the fraction of exposed first monolayer and $\sim 31$ layers as the average crystallite height. For the $R = 1:5$ case [Fig. 6.4(b)], we estimate that the fraction of the exposed first monolayer area is $\sim 46\%$ with an average crystallite height of $\sim 41$ layers. Thus, a decrease in the amount of ice from an equivalent thickness of 23 layers down to 7 layers results in a 74% increase in the fraction of exposed first monolayer but only a 24% decrease in crystallite height. However, although the average height and area of exposed monolayer can be estimated from the experimental data, the number of crystallites per unit area and their lateral extent, i.e. the size in the plane of the Pt(111) surface, cannot be determined from the data presented here.
Figure 6.4: Graphs of the fraction of exposed first monolayer $a$ versus crystallite height $n$ calculated from equations 6.2 (solid line) and 6.3 (dashed line) for (a) $R = 1:1$ and $V_{total} = 7$ layers, and (b) $R = 1:5$ and $V_{total} = 23$ layers.
6.3.2 The Structure of Ice on Pt(111) by XAS

Figure 6.5: Auger electron yield (AEY) XAS spectra of 80 layers of amorphous ice on Pt(111) grown at \( \sim 100 \) K (red) and 48 layers of crystalline ice prepared by isothermally heating amorphous ice at \( \sim 150 \) K (black). Both spectra have been normalized to the same area from 532 to 550 eV.

Fig. 6.5 shows the XAS spectra of \( \sim 80 \) layers of amorphous ice (prepared by dosing D\(_2\)O on Pt(111) surface at 100 K) and \( \sim 48 \) layers of crystalline ice (prepared by isothermally heating the amorphous ice at 150 K) measured using Auger electron yield with a detection depth of 20 Å [35]. There are significant differences between the spectra of the two ice forms. The post-edge of crystalline ice is higher in intensity, more structured, and slightly shifted to higher energy. In addition, there is more fine-structure beyond the post-edge for crystalline ice, which has been attributed
to multiple-scattering resonances due to long-range order [36–38]. The pre-edge of crystalline ice is also lower than that of amorphous ice.

The broader and less structured post-edge of amorphous ice can be explained by a broader distribution of H-bond distances that results from the more disordered water molecules in amorphous ice compared to crystalline ice. According to the “bond-length-with-a-ruler” principle (Chapter 1, Section 1.2.4), the energy position of the post-edge is dependent on H-bond distances. Therefore, a broad distribution of H-bond distances will result in a broad distribution of post-edge energies, as observed in Fig. 6.5. In addition, further broadening of the post-edge is caused by internal O-D stretch vibrational motion since the post-edge energy also depends on internal O-H (or, in this specific case, O-D) distance according to the Franck-Condon principle [36].

Fig. 6.6 shows the changes in the XAS spectra of crystalline ice after a multilayer of NH$_3$ is deposited on the ice film and subsequently annealed to desorb the NH$_3$ multilayer, leaving a monolayer of NH$_3$ on the ice surface. In the same preparation, IRAS spectra of the O-D stretch region were measured. The free O-D stretch is observed as the small peak at $\sim$2700 cm$^{-1}$ (visible after multiplying the spectrum by a factor of 70) that originates from the dangling O-D groups on the surface of ice [39]. After ammonia is deposited on the ice film, this peak disappears, indicating that all free O-D groups on the ice surface have been terminated by H-bonding with NH$_3$. The corresponding XAS spectra (left panel) show that the pre-edge peak in NH$_3$-terminated ice only appears as a shoulder. However, the fact that a pre-edge feature is still clearly seen, albeit less sharp, after NH$_3$ adsorption leads to the question of whether the pre-edge in ice only arises from the free O-H/O-D on the surface of ice.

To answer this question, we need to examine the surface-sensitive ice XAS spectra
Figure 6.6: AEY-XAS (left) and IRAS (right) spectra of (a) crystalline ice prepared by heating 80 layers of amorphous ice on Pt(111) to ~150 K for 16 minutes, (b) crystalline ice covered with multilayer of NH$_3$, and (c) NH$_3$-terminated crystalline ice after heating to 114 K for 5 minutes, leaving one layer of NH$_3$ on the ice surface. The region for the surface O-D stretch on the IRAS spectra has been multiplied by a factor of 70.

measured by Nordlund et al. [35] The spectra were obtained using AEY detection with the electron analyzer positioned such that the emitted electrons were detected at an extreme grazing angle to give maximally surface-sensitive spectra. The spectra before and after ammonia adsorption (Fig. 6.7) were fitted with Gaussian curves, and it can be observed that the pre-edge is shifted by 0.45 eV to higher energy upon NH$_3$ adsorption, becoming a part of the onset of the main absorption edge. In addition, the intensity of the main edge is decreased while the post-edge is increased. This is an indication that the pre-edge peak observed in the ice spectrum before ammonia adsorption comes from free O-D groups on the surface of ice.
Figure 6.7: Surface sensitive grazing AEY XAS spectra of (top) clean crystalline ice and (bottom) NH$_3$-terminated crystalline ice. Both spectra are area-normalized and fitted with Gaussian peaks (dashed lines). The red dashed peak in each spectrum indicates the pre-edge fit, which is shifted by 0.45 eV as the surface O-D groups are saturated with ammonia.

Fig. 6.8 shows the Gaussian-fitted XAS spectra of crystalline ice before and after NH$_3$ adsorption measured with AEY at normal emission angle, which means that these spectra are more bulk sensitive than those in Fig. 6.7. The spectrum of liquid water measured by T-mode XAS is displayed at the top of the figure for comparison. The right panel of Fig. 6.8 displays the enlarged pre-edge region. The pre-edge of clean crystalline ice can be fitted with two Gaussian curves; one is located at the same energy position as the surface-sensitive pre-edge in Fig. 6.7 and is, therefore, associated with free O-D groups on the ice surface, while the other is located at 0.4 eV
Figure 6.8: XAS spectra of (top) room temperature liquid water (transmission mode), (middle) 45 layers crystalline ice (AEY), and (bottom) NH\textsubscript{3}-terminated crystalline ice (AEY). All spectra are area-normalized and fitted with Gaussian peaks (dashed lines). The left panel shows the spectra in the whole near edge energy region (532-554 eV) while the right panel shows the enlarged pre-edge region (533-536 eV).

higher energy, which is associated with free O-D groups in the bulk ice not present in the surface-sensitive spectrum. Upon NH\textsubscript{3} adsorption, the bulk pre-edge component is located at the same energy position, while the surface component is shifted by 0.45 eV to higher energy, the same energy shift as the surface sensitive spectrum in Fig. 6.7. This is exactly what we would expect as the adsorbed NH\textsubscript{3} molecules only affect the surface O-D groups. Therefore, the pre-edge feature seen in the bulk-sensitive XAS spectrum of NH\textsubscript{3}-terminated ice is attributed to the free O-D in the bulk. Note
that the number of Gaussians used to fit the spectra in Figs. 6.7 and 6.8 is arbitrary and that the Gaussians do not reflect discrete transitions. The goal is to determine the pre-edge position and in order to do this reliably, the whole spectrum had to be fitted.

Tse et al. also observed a pre-edge in their spectra of various forms of ice measured using XRS [26]. The spectrum of high-density amorphous ice (HDA), in particular, closely resembles the spectrum of liquid water, which is attributed to the highly distorted H-bonding in HDA [26]. The spectra of low density amorphous ice (LDA), ice $I_c$, and ice $I_h$ look more similar to the ice spectra in Fig. 6.5 with a lower, but still noticeable, pre-edge intensity than HDA [26]. Tse et al. suggested that since the pre-edge is present in all forms of ice as well as in liquid water and it is (from their spectra) unvaried in energy, then it cannot be sensitive to the local structure of water [26]. However, in Fig. 6.8 we have shown that the pre-edge is, indeed, sensitive to the local structure, as evidenced by the different energy positions of the pre-edge components corresponding to the surface of ice (534.7 eV), bulk ice (535.05 eV), and NH$_3$-terminated surface (535.15 eV).

The presence of a pre-edge associated with bulk ice is particularly puzzling since crystalline ice, in theory, should have tetrahedral H-bonding between water molecules in the bulk. Zubavichus et al. prepared ice films on Au(111) at 90 K and 153 K [40], where the XAS data resemble the amorphous and crystalline ice spectra in Fig. 6.5, respectively. Therefore, we assume that their ice film grown at 153 K is structurally similar to our crystalline ice. Their EXAFS data, however, cannot be satisfactorily fit only with ice $I_c$ structural model; higher density ice structures such as ice II, ice III, and HDA must be included to obtain a good fit [40]. Therefore, the “crystalline” ice
prepared on metal surfaces, whether by direct deposition at high temperatures (∼150 K) or by isothermal heating of amorphous ice, is actually not purely crystalline in nature and it likely contains various forms of higher density ices, giving rise to the pre-edge and main edge. Similarly, the ice samples used in Tse’s XRS measurements [26] likely contain a significant amount of HDA ice.

6.4 Conclusions

The combined XPS/IRAS study of ice on Pt(111) shows that a large fraction of the first monolayer of water on Pt(111) is exposed to vacuum at a relatively high total coverage when crystalline ice is formed by isothermally heating 80-layer-thick amorphous ice at 150 K. Using the relative intensities of the monolayer and multilayer O 1s XPS peaks together with the total coverage, we have quantified the fraction of the exposed monolayer and the average crystallite height. We show that at a total coverage of 23 layers, 46% of the monolayer is exposed and the average height of the crystallites is ∼41 layers. Further isothermal heating to 7-layer thickness (∼91% decrease in total coverage) results in only a ∼61% decrease in crystallite height (∼31 layers), leaving 80% of the monolayer exposed. The study adds spectroscopic evidence for the hydrophobic nature of the first water monolayer on Pt(111), consistent with a recent TPD study of rare gas adsorption on the crystalline ice film [16] and with a recent LEED study of the direct growth of crystalline ice on Pt(111) [22], showing a significant exposure of the first monolayer at multilayer coverage.

The XAS spectra of amorphous and crystalline ice show that the pre-edge does indeed arise from uncoordinated/broken O-H groups in water. The pre-edge contains contributions from free O-H groups on the surface of ice, which is shifted to higher
energy as these O-H groups are terminated by H-bonding to NH$_3$, and from disordered H-bonding in the bulk due to the presence of high-density amorphous ice. A pure crystalline phase of ice is an ideal model system of ordered H-bonding; however, this study shows that preparing such a single crystal of ice in UHV conditions is nontrivial.

### 6.5 References


