Molecular Interaction in Aqueous Solutions

Effects of Temperature and Solutes on Surface Structure and Hydrogen Bonding in Water

CLARA-MAGDALENA SAAK
Intermolecular forces in liquids can give rise to complex emergent structures, particularly in water, where hydrogen bonding causes the formation of extended networks, and surfaces, where intermolecular structures can be distinctly different from the bulk, leading to unique properties and behaviours. While such structures have been studied in detail, it is still relatively unknown how such structures respond and adapt to external changes to their environment. In this thesis, the structure formation behaviour, particularly at the water interface and in the hydrogen bond network, in response to external tunable parameters are investigated using a combination of spectroscopic techniques. Surface-sensitive X-ray photoelectron spectroscopy and Auger spectroscopy are employed to study samples of different sizes, ranging from single gas-phase water molecules where intermolecular interactions are negligible, to the infinite liquid bulk with its fully extended hydrogen bond network. Particular emphasis is placed on the influence of temperature on structural aspects of the studied systems, how they affect the hydrogen bond network as well as the surface enrichment of solutes.

The first part focuses on structure formation at surfaces, and in the case of solutes in water we find that elevated temperature increases the surface enrichment of halide ions, and a diverse set of behaviour for cations depending on the nature of the counter ion. These results are surprising since it was previously predicted that surface enrichment should decrease with temperature, and our results superficially appear to contradict the notion that any emergent structure should become washed out at higher temperature as entropy and disorder begin to dominate. In addition, results on the differences between the surface composition of wet and dry saline aerosols are presented, where we find notable structural differences linked to the different efflorescence points of salts during the drying process.

In the second part, results from studies exploring different aspects of the hydrogen bond network are presented, which are probed via the post-ionisation decay observed in the Auger spectrum. Firstly, the hydrogen bond network of water is studied at different temperatures and system sizes. We find both temperature, and confinement in the form of clusters, to measurably weaken the hydrogen bond network compared with the bulk liquid. Secondly, the influence of hydrophobic functional groups is studied in liquid methanol and mixed liquids containing the cryoprotectants glycerol and dimethyl sulfoxide. The presence of the hydrophobic groups leads to a fracturing of the intermolecular network into smaller domains of hydrophilic and hydrophobic groups.

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urn:nbn:se:uu:diva-391083 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-391083)
Snatching the eternal out of the desperately fleeting is the great magic trick of human existence.

- Tennessee Williams
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Temperature dependent surface propensity of halide salts
C.M. Saak, J. Kirschner, I. Unger, G. Gopakumar, C. Goy, H. Bakker, N. Ottosson, C. Caleman and O. Björneholm
Manuscript in preparation

II The surface of sea spray aerosol under scrutiny: An X-ray photoelectron spectroscopy study
I. Unger, C.M. Saak, M. Salter, P. Zieger, M. Patanen and O. Björneholm
Manuscript in preparation

III Temperature dependence of X-ray induced Auger processes in water
C.M. Saak, I. Unger, G. Gopakumar, C. Caleman and O. Björneholm
Manuscript in preparation

IV Signature of ultrafast proton transfer in the Auger spectrum of amorphous ice
C. Richter, C.M. Saak, M. Mucke, I. Bidermane, T. Leitner, O. Björneholm, N. Mårtensson, S. Svensson and U. Hergenhahn
Manuscript in preparation

V Probing the hydrogen bond strength of solvent clusters using proton dynamics
Manuscript in preparation

VI Competition between proton transfer and intermolecular Coulombic decay in water
C. Richter, D. Hollas, C.M. Saak, M. Förstel, T. Miteva, M. Mucke, O. Björneholm, N. Sisourat, P. Slavíček and U. Hergenhahn
Nature Communications, 9,4988 (2018)
DOI: 10.1038/s41467-018-07501-6
VII  Site-specific X-ray induced dynamics in liquid methanol  
  C.M. Saak, I. Unger, B. Brena, C. Caleman and O. Björnholm  
  *Physical Chemistry Chemical Physics*, 21, 15478-15486 (2019)  
  DOI: 10.1039/c9cp02063b

VIII  Specific probing of the hydrogen bonding network in aqueous mixtures of glycerol and dimethyl sulfoxide  
  C.M. Saak, C. Richter, I. Unger, C. Caleman, O. Björnholm and U. Hergenhahn  
  *Manuscript in preparation*

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Other Papers

**Shifted equilibria of organic acids and bases in the aqueous surface region**  
J. Werner, I. Persson, O. Björnholm, D. Kawecki, C.M. Saak, M.M. Walz, V. Ekholm, I. Unger, C. Valtl, C. Caleman, G. Öhrwall and N.L. Prisle  
*Physical Chemistry Chemical Physics*, 20, 23281-23293 (2018)  
DOI: 10.1039/c8cp01898g

Comments on my contribution

I have actively contributed to the experimental work presented in all the listed Papers. The order of authorship on each individual paper accurately reflects my level of contribution to the respective projects. Where I am first author, I was also the main person involved in the analysis of the acquired data, and wrote the manuscript.
Populärvetenskaplig Sammanfattning

Vatten finns överallt på vår planet, i form av floder, hav, glaciärer och istäcken, som regn och moln i vår atmosfär. Det har format vår miljö genom att karva ut dalar ur berg och mala sten till sand, till den grad att vattnets förmåga att skulptera jorden har blivit ordspråksmässig. Vi är alla medvetna om hur central vatten är för livet, eftersom det är ett av de grundläggande behov som alla levande organismer har gemensamt för att hålla sig vid liv. Vatten är en av huvudkomponenterna i vår kropp, där det finns i cellers och kärls små reservoarer. Det är det essentiella lösningsmedlet som förmedlar biokemin, vilken är grunden för cellernas funktion, central inte bara för transport av komponenter, utan också för processer som proteinväckning och andning.

Med tanke på att vatten är centralt i våra liv på så många olika sätt antar vi ofta att vetenskapen kan ge oss en detaljerad och uttömmande förståelse för dess egenskaper och beteende. Även om de makroskopiska egenskaperna hos vatten har mätts ända sedan naturvetenskaplig forskning började, så är de grundläggande mekanismerna som ger upphov till dessa fenomen fortfarande ett pågående forskningsämne. Många unika egenskaper, till exempel vattens denistetsminskning vid frysning, vilket får is att flyta, har kopplats till dess förmåga att bilda unika växelverkningar mellan de enskilda molekyler som utgör vätskan, de så kallade vätebindningar. För att förstå dessa växelverkningar måste vi först titta på vattnets molekylstruktur, som består av en central syreatom bunden till två väteatomer (H₂O). Dessa väteatomer är inte ordnade linjärt bredvid det centrala syret, utan i vinkel, närmare bestämt en vinkel på 104.5° mellan syret och det två väteatomerna. Medan vattenmolekylens som helhet är elektriskt neutral, vilket betyder att den inte har någon nettoladdning, har vattenmolekylens enskilda atomer så kallade partiella laddningar, varvid syreatomen är delvis negativ (δ⁻) och de två väteatomerna delvis positiva (1/2δ⁺ vardera). Denna laddningsseparation i molekylen ger vattenmolekylens ett permanent dipolmoment, vilket får den att orientera sig i närvaro av ett applicerat elektriskt fält, ungefär som hur en kompass pekar norrut i närvaro av jordens magnetfält.

När många H₂O-molekyler sammanförs, till exempel i flytande vatten, samverkar de positiva och negativa partiella laddningarna hos de enskilda molekylerna med varandra. Detta leder till en attraktiv kraft mellan den partiellt negativa (δ⁻) syreatomen i en molekyl och en delvis positivt (1/2δ⁺) väteatom i en annan. Denna växelverkan drar de två molekylerna mot varandra, vilket leder till bildandet av tidigare nämnda vätebinding. En enskild molekyl kan bilda totalt fyra vätebindingar med sina grannar, genom att donera två

Vätebindningar är inte bara viktiga för växelverkan mellan vattenmolekyler med varandra, utan också för lösning och blandning av andra kemiska ämnen. När ett ämne upplöses i vatten, bildar det starka växelverkningar med de omgivande vattenmolekylerna, som när det gäller organiska ämnen vanligen utgörs av vätebindingar. Salter är mycket lösliga eftersom vattenmolekylernas partiella laddningar kan bilda stark Coulombväxelverkan med laddningarna hos saltets olika joner. Ett exempel är vanligt bordssalt, natriumklorid, där jonerna Na⁺ och Cl⁻ interagerar med vatten. Faktum är att salter är så lösliga att huvuddelen av vattnet på planeten, vilket finns i våra hav och oceaner, är mycket salt. Även sötvatten, som bara utgör 2,5% av planetens totala vatteninnehåll, innehåller fortfarande små spår av salter och mineraler.

Saltvatten hamnar i atmosfären när vågor bryts vid havsytan, vilket ger upphov till en fin dimma av saltvattensdroppar, en aerosol, som är tillräckligt lätta för att tas upp av vinden och transporteras högre upp i atmosfären. En annan källa till atmosfäriskt vatten är stora vegetationsområden såsom skogar, varifrån stora organiska molekyler kommer med i de atmosfäriska vattendropparna. Sådana vattendroppar är kritiska för att förstå atmosfärisk kemi, eftersom salter och molekyler som finns i dem kan delta i en mängd reaktioner med gasformiga komponenter i den omgivande luften. De kan till och med påverka molnbildningen genom att ändra vattendropparnas hygroskopicitet (d.v.s. deras förmåga att absorbera och behålla fukt). I vilken utsträckning dessa dropppar påverkar det globala klimatet är fortfarande i stort sett okänt eftersom de deltar i så många atmosfäriska processer, och dessa aerosolers bidrag till den globala strälningsbudgeten är den största osäkerheten i klimatmodellering. I den här avhandlingen använder jag röntgenfotoelektronspektroskopi för att undersöka egenskaperna hos olika vattenhaltiga system. I denna teknik bestrålas vätskan med så kallad mjukröntgenstrålning, som i det elektromagnetiska spektrumet ligger mellan ultraviolett strålning och de hårda röntgenstrålarna som används för medicinsk diagnos. Energin hos mjukröntgenstrålning är tillräckligt hög för att avlägsna elektroner från materialets atomer, vilket kallas joniserings. Om vi använder en monokromatisk röntgenljukskälla, ger antalet utsända elektroner som en funktion av deras kinetiska energi ett så kallat röntgenfotoelektronspektrum för materialet, vilket innehåller information om bland annat provets relativa kemiska sammansättning. Eftersom fotoelektroner som bildas i provets inre inte kan komma ut utan att spridas (d.v.s. reflekteras eller absorberas) är denna teknik också mycket ytikänslig, vilket gör den väl lämpad för studier av ytanrikning.
När elektroner sänds ut från ett material innebär de hål de lämnar i elektronstrukturen att systemet befinner sig i ett mycket högt energitillstånd, och systemets elektroner kommer att ordna om sig för att sänka energin så mycket som möjligt, en process som benäms som strukturell eller elektronisk relaxation. Efter röntgeninducerad elektronutsändning sker denna relaxation vanligen genom att en elektron från de yttre skalen `faller` in det hål som fanns kvar i den elektroniska strukturen. Denna process frigör energi från systemet, vilket kan leda till utsändande av en andra elektron från de yttre skalen. Denna mekanism kallas Auger-sönderfall och det så kallade Auger-spektrumet innehåller information om hur materialet kan läka den skada som har orsakats av joniseringshändelsen. Auger-processen är också mycket känslig för förändringar i den lokala molekylära strukturen runt jonen, och vi använder därför den för att studera de tidigare nämnda vätebindningarna i vatten och dess lossningar.

I denna avhandling ställs grundläggande frågor om blandade lossningar och deras ytor, och jag försöker svara på dem genom att betrakta problemen ur en molekylär synvinkel och försöka koppla de makroskopiska egenskaperna med deras molekylära drivkrafter.

Först fokuserar jag på anrikning av joner vid vattenytan. Eftersom oorganiska joner såsom natriumklorid och natriumjodid växelverkar så starkt med vatten, brukade det antas att de endast finns i det inre av lossningen där de starkt kan växelverka med vattenmolekylerna. Under de senaste åren upptäcktes emellertid att stora anjoner som jodid kan anrikas vid ytan, ett fenomen för vilket de underliggande drivkrafterna i stort sett var okända. För att undersöka ytanrikning av joner ytterligare undersökte vi ytsammansättningen för halidsalter vid olika temperaturer. Överraskande visade vi att ytkoncentrationen faktiskt ökar vid högre temperaturer, vilket är icke-intuitivt eftersom det vanligtvis antas att eventuella framväxande strukturer slätas ut när temperaturen höjs och systemets oordning ökar. Genom att kombinera tidigare publicerade arbeten från Caleman et al. och Ben-Amotz med våra experiment tillskriver vi denna observation den ökade entropin, som är relaterad till molekylär oordning i jonernas första solvationsskal, vilken är högst när jonen är vid ytan. Vi undersökte också skillnader mellan de torra och våta formerna av en aerosol, och fann att ytons sammansättning skiljer sig väsentligt mellan de två fallen. Detta beror på själva torkningsprocessen, eftersom olika salter bildar kristaller i olika steg i torkningsprocessen, beroende på saltkristallens stabilitet, såväl som saltets hygroskopicitet och löslighet. Detta betyder att joner nära ytan i den våta aerosolen kan begravas i det inre av den torkade aerosolen, om de bildar ett salt snabbare än de andra komponenterna. Genom att kombinera dessa resultat kan vi förutsäga att eventuella atmosfäriska reaktioner med halidjoner kommer att förstärkas vid högre temperaturer, eftersom temperaturen i atmosfären visar hög variation beroende på region och höjd, vilket förväntas ha ett betydande inflytande på ytreaktioner. Ytsammansättningen kommer också att påverkas av den relativa fuktigheten i miljön, eftersom torkningen av
aerosolen signifikant kan förändra hur de olika lösta ämnena fördelas mellan ytan och det inre.

Water is present throughout our planet, as rivers, oceans and streams, as glaciers and the planet’s icecaps, and in the rain and the clouds of our atmosphere. It has shaped our environment, by carving valleys from mountains and milling rocks into sand, to the degree that water’s ability to sculpt the earth has become proverbial wisdom. We are all aware of how central water is to life, since it is one of the basic needs all living things share to stay alive. Water is one of the main components of our body, contained in the small reservoirs of cells and vessels, the essential solvent that mediates the biochemistry which is the basis of cellular function, central not only for transport of components, but also for processes such as protein folding and respiration.

Considering that water is central to our lives in so many different ways, we often assume that science can provide us with a detailed exhaustive understanding of its properties and behaviour, and while the macroscopic properties of water have been measured since the early days of scientific inquiry, understanding the fundamental mechanisms giving rise to these phenomena is still an ongoing topic of research. Many unique properties, such as water’s expansion upon freezing, which causes ice to float, have been linked to its ability to form unique interactions between the individual molecules making up the liquid, which we call hydrogen bonds. To understand these interactions, we must first look at water’s molecular structure, which is comprised of a central oxygen atom connected to two hydrogen atoms (H₂O). These hydrogen atoms aren’t arranged linearly around the central oxygen, but rather at an angle, giving water a slightly bent geometry (\( \angle \text{H-O-H} = 104.5 ^\circ \)).

While the overall molecule is neutral, meaning that it doesn’t carry charge, the individual atoms of water carry so-called partial charges, with the oxygen atom being partially negative (\( \delta^- \)), and the two hydrogen atoms partially positive (\( \frac{1}{2} \delta^+ \) each). This charge separation within the molecule gives water a permanent dipole moment, causing it to orient in the presence of an applied electric field, similar to how a compass points north in the presence of the Earth’s magnetic field.

When many H₂O molecules are brought together, such as in liquid water, the positive and negative partial charges of the individual molecules interact with one another, leading to an attractive force between the partially negative (\( \delta^- \)) oxygen site of one molecule, and one partially positive (\( \frac{1}{2} \delta^+ \)) hydrogen site of another. This interaction draws the two molecules closer together, leading to the formation of the aforementioned hydrogen bond. An individual molecule can form a total of four hydrogen bonds with its neighbours, donating two with
its hydrogen atoms, and accepting two at the oxygen atom, forming a tetra-
hedral arrangement of neighbouring molecules surrounding the central water molecule. The formation of a hydrogen bond between two water molecules also affects the bonds within each molecule in a way that further strengthens the hydrogen bonding. This and partial covalent contributions make the understanding of hydrogen bonding particularly challenging. Hydrogen bonds are not only important for the interaction of water molecules with one another, but also for solvation and mixing of other chemical species. When a substance dissolves in water, it forms strong interactions with the surrounding water molecules, and in the case of organic solutes these are typically realised via hydrogen bonds. Salts are highly soluble because the $\frac{1}{2} \delta^+$ and $\delta^-$ charge of the water molecules can form strong coulombic interactions with the charges of the different ions making up the salt crystal (e.g. Na$^+$ and Cl$^-$ in sodium chloride, commonly known as table salt). In fact, salts are so soluble that the majority of water on the planet, found in our seas and oceans, is highly saline. Even fresh water, which only makes up 2.5% of the total water content of the planet, still contains small traces of salts and minerals.

Saline water finds its way into the atmosphere via the breaking of waves on the sea surface, which produces a fine mist of salty water droplets, an aerosol, which is light enough to be taken up by the wind and transported into the upper layers of the atmosphere. Another source of atmospheric water is from large areas of vegetation such as forests, which is how large organic molecules are introduced into atmospheric water droplets.

Such water droplets are critical to understanding atmospheric chemistry, since the salts and molecules contained within them can engage in a multitude of reactions with the gaseous components in the surrounding air, and even influence the growth of clouds by changing the hygroscopicity of the water droplets (i.e. their ability to absorb and retain moisture). The extent to which these droplets influence the global climate is still largely unknown, since they participate in so many atmospheric processes, and the contribution of aerosols to the global radiative budget of the planet is the largest source of uncertainty in climate modelling.

In this thesis, I use X-ray electron spectroscopy to investigate the properties of different aqueous systems. In this technique, the liquid is illuminated with so-called soft X-ray radiation, which on the electromagnetic spectrum sits between ultraviolet radiation and the hard X-rays used for medical diagnosis. The energy of soft X-ray radiation is sufficiently high to remove electrons from the atoms of the material, which is called ionisation. If we use a monochromatic X-ray light source, tracing the number of emitted electrons as a function of their kinetic energy yields the so-called X-ray photoemission spectrum of the material, which contains information about the relative chemical composition of the sample, amongst other things. Since electrons emitted in the bulk of the sample cannot escape without being scattered (i.e. reflected or ab-
sorbed), this technique is also highly surface-sensitive, making it well-suited for the study of surface enrichment.

When electrons are emitted from a material, the holes they leave in the electronic structure cause the system to be in a very high energy state, and the system’s electrons will rearrange to lower the energy as much as possible, in a process referred to as structural or electronic relaxation. After X-ray induced electron emission, this relaxation usually occurs through the migration of an electron from the outer shells into the hole that was left in the electronic structure. This process releases energy from the system, which can lead to the emission of a second electron from the outer shells. This mechanism is referred to as Auger decay and the so-called Auger spectrum contains information about how the material can heal the damage inflicted by an ionisation event. The Auger process is also very sensitive to changes in the local molecular structure around the ion, and we therefore employ it to study the previously mentioned hydrogen bonds that are formed in water and its solutions. Here, fundamental questions about the nature of mixed solutions and their surfaces have been posed, and I attempt to answer them by considering these problems from a molecular viewpoint, trying to connect the macroscopic properties with their molecular driving forces.

Firstly, I focus on the surface enrichment of ions at the aqueous interface. Since inorganic ions such as sodium chloride and sodium iodide form strong interactions with water, it used to be assumed they reside in the bulk of the solution where they can strongly interact with the water molecules. It was, however, discovered in recent years that large anions such as iodide can be enriched at the surface, a phenomenon for which the underlying driving forces were largely unknown. To explore ion surface enrichment further, we investigated the surface population of halide ion salts at different temperatures. Surprisingly, we found the surface concentration to actually increase at higher temperatures, which is counter-intuitive since it is usually assumed that any emergent structuring becomes washed out when the temperature is raised and the disorder of the system increases. Combining previously published work from Caleman et al. and Ben-Amotz with our experiments, we attribute this observation to the increased entropy, which is related to molecular disorder, of the ion’s first solvation shell, which is highest when the ion resides at the surface.

We also investigated differences between the dry and wet states of an aerosol, finding that the composition of the surface differs substantially between the two phases. This is due to the drying process itself, since different salts form crystals at different stages of the drying process, depending on the stability of the salt crystal, as well as the hygroscopicity and solubility of the salt. This means that ions close to the interface in the wet aerosol can be buried in the bulk of the dried aerosol, if they form a salt faster than the other components. Combining these results, we may predict that any atmospheric reactions involving halide ions will be enhanced at higher temperatures, since the temper-
ature of the atmosphere shows high variability depending on the region and the altitude, which is expected to have a significant influence on surface reactions. The surface composition will also be affected by the relative humidity of the environment, since the drying of the aerosol can significantly change the way the different solutes are distributed into the bulk and surface regions.

In the second part, I shift focus to hydrogen bonding to explore how the networks these interactions form in the liquid are affected by different variable parameters, such as heating the liquid, solidifying it, or confining it into small droplets. We find these changes weaken the overall network of the solvent molecules, and change the way they react to ionisation when irradiated with X-rays. We also investigated the intermolecular network in more complex systems such as methanol and mixtures of water and cryoprotecting molecules. Both methanol and the studied cryoprotectants, glycerol and dimethyl sulfoxide, contain both hydrophobic and hydrophilic groups. In both cases, the presence of the hydrophobic groups disrupts the hydrogen bond network and leads to the formation of local domains, also referred to as micro-segregation. In this scenario, the hydrophobic groups are forced next to each other in order to minimise their disruption to the overall network. Since the molecules still contain other hydrophilic groups that are able to integrate well into the hydrogen bond network, the mixture does not segregate macroscopically, appearing homogeneous to the naked eye.

Overall, the work contained in this thesis contributes to a fuller understanding of water’s enigmatic behaviour, and has uncovered some further unusual phenomena, such as the increased surface enrichment of ions at higher temperature. We have demonstrated that Auger spectroscopy is a useful technique to help us discover new details of water’s intermolecular structure, and discovered subtleties in how such structure reacts and changes under different conditions. There is still much to learn about water and its solutions, but this work adds another piece to the puzzle.
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<tr>
<td>$\Delta G_{ads}$</td>
<td>Gibbs Free Energy of Adsorption</td>
</tr>
<tr>
<td>$\Delta H_{ads}$</td>
<td>Enthalpy of Adsorption</td>
</tr>
<tr>
<td>$\Delta H_{iw}$</td>
<td>Direct (ion/water) contribution to Enthalpy of Adsorption</td>
</tr>
<tr>
<td>$\Delta H_{ww}$</td>
<td>Indirect (water/water) contribution to Enthalpy of Adsorption</td>
</tr>
<tr>
<td>$\Delta S_{ads}$</td>
<td>Entropy of Adsorption</td>
</tr>
<tr>
<td>$\Delta S_{iw}$</td>
<td>Direct (ion/water) contribution to Entropy of Adsorption</td>
</tr>
<tr>
<td>$\Delta S_{ww}$</td>
<td>Indirect (water/water) contribution to Entropy of Adsorption</td>
</tr>
<tr>
<td>%RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>ADL</td>
<td>Aerodynamic Lens</td>
</tr>
<tr>
<td>ArTof</td>
<td>Angular Resolved Time of Flight</td>
</tr>
<tr>
<td>ASW</td>
<td>Amorphous Solid Water</td>
</tr>
<tr>
<td>BE</td>
<td>Binding Energy</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>EDL</td>
<td>Electric Double Layer</td>
</tr>
<tr>
<td>ETMD</td>
<td>Electron Transfer Mediated Decay</td>
</tr>
<tr>
<td>GDS</td>
<td>Gibbs Dividing Surface</td>
</tr>
<tr>
<td>HB</td>
<td>Hydrogen Bond</td>
</tr>
<tr>
<td>ICD</td>
<td>Interatomic Coulombic Decay</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic Energy</td>
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<tr>
<td>LJ</td>
<td>Liquid Jet</td>
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<tr>
<td>MCP</td>
<td>Micro Channel Plate</td>
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<tr>
<td>MD</td>
<td>Molecular Dynamics</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>PE</td>
<td>Photo Electron</td>
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<tr>
<td>PTM-CS</td>
<td>Proton Transfer Mediated Charge Separation</td>
</tr>
<tr>
<td>Tof</td>
<td>Time of Flight</td>
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<tr>
<td>VSFG</td>
<td>Vibrational Sum Frequency Generation</td>
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<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
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1. Introduction

From the first philosophers, then, most thought the principles of the nature of matter were the principles of all things. That of which all things that are consist, the first from which they come to be, the last into which they are resolved, the substance remaining, but changing in its modifications, this they say is the element and this the principle of things [...] Just so they say nothing else comes to be or ceases to be, for there must be some entity - either one or more than one - from which all things come to be, it being conserved. [...] Thales, the founder of this type of philosophy, says the principle is water.

- Aristotle, Metaphysics

Thales of Miletus was considered by Aristotle to be the first philosopher, and therefore the first scientist, who applied reason and observation to explain the nature and origin of the cosmos he found himself in. Here, a brief account of his thinking on water is given, based on the work by A.C. Grayling. Thales postulated there must be a basic substances or principle (an arche) from which the cosmos, all matter, and all forms of life are composed of, from which they come to be, and into which they return. Thales believed that this arche of the cosmos is water. He arrived at this conclusion by the observation that water is omnipresent, both in the inanimate world and in the realm of the living. It forms the rivers and oceans, the rain falling from the sky, and it dampens the soil; water is present in the blood of humans and animals and in the sap of plants, and most importantly all living things die without it, making it essential for life to exist.

Thales proposed that even the earth is borne from water, an assumption that can easily be understood when observing the huge quantities of soil, or silt, washed ashore by the Nile as it annually floods. Water was particularly unique in the mind of classical philosophers due to its metamorphic character. Water was the only substance known at the time to exist in all three material states: solid when frozen, liquid in its fundamental form and gaseous as steam and vapour. Water is also one of the usually four or five elements that have been evoked as the constituents from which the world is formed in many schools of teaching, both in western and eastern cultures: water, air, soil, fire and ether.

While our understanding of the nature of the universe has significantly advanced since the days of Thales’ work, the account of his thinking highlights an important point: Water has been at the heart of western philosophical inquiry since its birth in ~ 600 BCE on the shores of the Aegean Sea.
Even in the modern understanding of our world water is central to many disciplines, since it is present throughout the entirety of our planet. The pervasive forms of our planet’s water content are unified into the so-called hydrosphere,\textsuperscript{15} which describes the entire mass of water on planet earth, and how the different reservoirs are connected. The different forms water takes in the hydrosphere form a continuum of interchangeable states which are connected together in the global water cycle,\textsuperscript{16} encompassing all forms of water in various phases and distinctly different environments of the planet, from high up in the troposphere, to the deep oceans, and even penetrating far below the crust of the planet into the geological mesosphere,\textsuperscript{17} where minerals are formed.

Water also has a central role in enabling life to sustain itself\textsuperscript{18} and all cells and organisms contain water as a major constituent. Its role in biology\textsuperscript{19} is diverse but for example, within the cells water acts as the essential solvent that mediates the biochemical processes that sustain cellular function. In the bloodstream water fulfils the role of a transport medium for compounds such as dissolved gases, e.g. oxygen and carbon dioxide, or larger biomolecules, such as hormones. The entire water content of the body acts as a temperature buffer, to avoid overheating which can lead to protein damage. Water is also essential in facilitating processes such as protein folding, which is essential since the three-dimensional structure of the protein is closely linked to its function.

In the atmosphere water exists as vapour, aerosols, and larger condensed droplets, as well as ice crystals. This constitutes the part of the water cycle that describes cloud formation and precipitation. Most of the water present in the atmosphere originates from the ocean surface, either through direct evaporation of water molecules, or in the form of small aerosol droplets which are cast up into the air when waves break.\textsuperscript{3} Another source of airborne water is through the uptake of groundwater by vegetation and transmission back into the atmosphere through transpiration. This pathway also introduces larger organic compounds into the atmosphere that mix with the aqueous droplets.\textsuperscript{4} Aerosols are of particularly great importance to atmospheric science since they can have both a direct and indirect influence on the radiative budget of the planet.\textsuperscript{5} Their direct effects describe the ability of the aerosol to scatter and absorb solar radiation; the indirect effect covers their ability to change cloud formation processes and precipitation efficiency, but also their effect on the liquid water content of clouds and the ice formation process. Interestingly, the properties of aerosols strongly depend on their particle size, sub-micron particles both scatter more light per unit mass and have a longer lifetime than their larger counter parts. The ability of aerosols to act as cloud condensation nuclei also critically depends on the chemical composition of the droplet.

Since the behaviour of aerosols is so complex and depends on many factors the net influence of aerosols on the climate is the largest source of uncertainty in predictive models,\textsuperscript{5} and a deeper understanding of this unique group of systems is required.
Even when isolated and studied in a lab environment, pure water itself is a highly complex chemical system displaying a number of anomalous properties, the origins of which are still not fully understood. Some examples of its anomalous behaviour include: Expansion upon freezing, high surface tension, high melting and boiling point, high dielectric constant, and high viscosity, to name a few. Most of these properties have been linked to water’s ability to form strong intermolecular hydrogen bonds. Hydrogen bonds can mainly be described as electrostatic interactions, but they do contain a weak covalent contribution. In water hydrogen bonding leads to the formation of a local tetrahedral structure of the nearest neighbours around a given water molecule. In the bulk these individual bonds lead to the formation of strong long range disordered networks that also have a highly dynamic character, with the individual hydrogen bonds being formed and broken on the picosecond timescale.

Water is sometimes referred to as the universal solvent due to its unmatched ability to dissolve a wide variety of substances, both organic and inorganic. As such, it is rarely found in its pure form, and even fresh water, which only makes up 2.5% of the planetary water content, contains significant amounts of ions dissolved in the liquid, with the upper limit of fresh water salinity usually given at 500-1000 ppm. Therefore, it is important to understand not only water itself, but also how different solutes interact with it and affect its properties.

The work summarised in this thesis is predominantly focused on the liquid/gas interface, which is of particular interest in the context of atmospheric science. The aqueous aerosol droplets commonly found in the atmosphere have a particularly high surface-to-volume ratio, which makes their surface especially important in understanding their properties. Aerosol surfaces have also been shown to act as sites for heterogeneous catalysis in the reactions between gas phase molecules and the solutes contained within the droplet. Both of these effects mean that the water-air interface holds particular relevance for atmospheric chemistry.

The termination of the hydrogen bond network that occurs upon surface formation leads to intriguing structural effects, especially in the presence of solutes. Restructuring of the liquid at the surface is driven by the system’s attempt to minimise the so-called surface energy arising from the unsaturated hydrogen bond sites of the water molecules. Solutes can either be attracted or expelled from the interfacial region depending on their specific nature. In particular, surface enrichment of small molecules and ions have been investigated in detail, since the underlying driving forces can go beyond simple hydrophobic expulsion, as even highly soluble ions are sometimes enriched at the surface.

The main text of this thesis is divided into the following parts: After this introduction (Chapter 1), I give a brief introduction to the molecular description of liquids in general and the relevant molecular interactions in water (Chap-
ter 2). The remainder of the thesis is then divided by topic, and contains both summaries of the scientific background, and results and discussion of the Papers presented in this thesis. In (Chapter 3), two different aspects of surface enrichment are presented. Firstly, the influence of temperature on ionic surface enrichment is studied. The changes in surface enrichment we observe are closely linked to the thermodynamic driving forces underlying the effect, which have been debated extensively in the literature. Secondly, the link between dry and wet surface structure and whether the former is a good predictor of the latter is discussed. These effects are relevant for atmospheric aerosols, since the aqueous droplets formed from sea spray often dry out in the different layers of the atmosphere depending on their relative humidity. Chapter 4 focuses on the hydrogen bond network under different conditions, to test how it is affected by external perturbation. First, I summarise work focusing on the hydrogen bond network of pure water at different temperatures (cold and warm liquid), and in different phases (small clusters, amorphous ice). The network is then disrupted by a 'molecular modification' of the liquid, first by going one step along the methylation series from water to methanol (which contains a single methyl group) and then by studying the hydrogen bond network of mixed liquids containing glycerol and dimethyl sulfoxide. The goal of these experiments is to investigate how the network adjusts to and accommodates the more hydrophobic functional groups or molecules. The results from both Chapter 3 and Chapter 4 are then summarised in Chapter 5 and an Outlook is given Chapter 6. The individual experimental components that were used to obtain the results presented throughout this thesis are summarised in Chapter 7. Finally, my collaborators that have contributed to the presented work are acknowledged in Chapter 8.
2. Molecular Liquids

2.1 Introduction to Liquids *

Due to the high mobility and diffusivity of the molecules in the liquid phase, the global structure of the liquid is very hard to characterise. The liquid is highly disordered, and any local structures are transiently formed. This absence of translational symmetry in a lattice-like structure makes it inherently difficult to describe the liquid phase. The structure of the liquid is often described by the radial distribution function.

Liquids are dynamic systems, making their global structure difficult to describe. Liquids are generally characterised as having short-range order and long-range disorder, as described by the radial distribution function (RDF). Such distribution functions are used to reveal the microscopic structure of the liquid, i.e. the arrangement of molecules relative to one another, rather than the global structure, which would be a random distribution of molecules at a constant density. These distribution functions indicate the probability of finding another atom or molecule at a given radial distance, around a given atom/molecule at the centre of the function, averaged over all molecules in the liquid. Examples of the RDF of a gaseous, liquid, and solid compound are sketched in Figure 2.1. Crystalline solids are highly structured, therefore sharp peaks are present in the RDF, even at large radial distance. In contrast, gases are highly disordered, therefore only one peak exists in their RDF, indicating the van-der-Waals diameter. The RDF of the liquid phase resembles an intermediate state between the order of the solid and the disorder of the gas. It is notable that even in the minima between the different solvation shells of the liquid there is a finite particle density, which is related to the larger diffusivity in the liquid compared with e.g. solids.

Even within the liquid phase, an important distinction is made between associated and non-associated liquids. Non-associated liquids, e.g. liquid nitrogen, do not show any highly directional interactions, making it possible to explain their intermolecular structure through the packing of molecules. In associated liquids such as water, the directional interactions of the hydrogen bonds occurring between the molecules leads to a much more defined local structure (i.e. tetrahedral geometry).

*Many of the fundamental properties and effects that characterise a liquid are outlined by D. Chandler in his book Introduction to Modern Statistical Mechanics\textsuperscript{35} and the discussion in this section is based upon his work.
2.1.1 Intermolecular Interactions

Molecules can interact with one another via a multitude of interactions of variable strength. The overall shape of an intermolecular potential is usually characterised by a short-range repulsive contribution and a long-range attractive interaction. The combination of the two leads to the formation of a potential minimum, corresponding with the equilibrium distance between the two units. The depth and position of this valley depends on the delicate balance of the different interactions. Here, the main categories of intermolecular interactions are briefly summarised: van-der-Waals, ion-dipole, and ion-ion interactions. In water, one of the most investigated interactions is the hydrogen bond, which is a unique bonding type that will be discussed separately in Section 2.1.1.1 below.

The term van-der-Waals interactions includes the interactions of uncharged groups, namely dipole/dipole, dipole/induced dipole, and London dispersion interactions (induced dipole/induced dipole). Any interactions that require an induced dipole strongly depend on the polarisability of the molecule. Induced dipole interactions are much weaker than the ones of charges and permanent dipoles, as they arise from the electron distribution of molecules being influenced/polarised by a close-by unit. However, in a highly polarisable medium such as water, their cumulative influence should not be neglected.

In the case of aqueous solutions, additional solute-water interactions also need to be taken into account. These interactions are dominated by strong charge/dipole or dipole/dipole interactions, that are central in the formation and structuring of the first solvation shell around charged solutes.
2.1.1.1 Hydrogen Bonding

The IUPAC Compendium of Chemical Terminology\textsuperscript{37} defines a hydrogen bond as follows:

\begin{quote}
A form of association between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits proximity of the interacting dipoles or charges. [...] 
\end{quote}

The most important example of a molecule with strong hydrogen bonds is water. The water molecule can both donate and accept two hydrogen bonds, leading to a tetrahedral coordination structure, as sketched in Figure 2.2. Water's ability to form hydrogen bonds is the main reason why it can solvate such a wide variety of molecules, even relatively apolar molecules, as long as they possess some protic character. In the simplest terms, a hydrogen bond in water is an intermolecular interaction between partially positive hydrogen and partially negative oxygen atoms. However, even in the early description of hydrogen bonding by L. Pauling in 1939,\textsuperscript{38} it was suggested there is some covalent contribution to the bond (5 to 10\%). This was later confirmed by nuclear magnetic resonance (NMR)\textsuperscript{39} and Compton scattering\textsuperscript{40} studies. The covalent character of the hydrogen bond contributes to the highly directional nature of the interaction, requiring alignment of the molecules along a linear hydrogen bond axis. Even now, difficulties in precisely defining hydrogen bonding still remain.\textsuperscript{26}

Compared with non-associated liquids, the hydrogen bonds that are formed between water molecules bring them closer together, along the hydrogen bond axis. However, the high directionality of hydrogen bonds limits the number of molecules in the first hydration shell to four. These four nearest-neighbour molecules are arranged tetrahedrally around the central molecule, as can be seen in Figure 2.2. The tetrahedral arrangement of the first hydration shell

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{tetrahedral_hydrogen_bond_environment.png}
\caption{Sketch of the tetrahedral hydrogen bond environment of a water molecule in the liquid phase. Water is a double-donor, double-acceptor molecule, donating hydrogen bonds via the OH groups and accepting them with its electron lone pairs.}
\end{figure}
leads to a decreased density of neighbour molecules than would be expected by pure packing of a non-associated liquid. The formation of hydrogen bonds, on average, therefore decreases the density of the liquid, as can be seen in the anomalous expansion of the liquid upon freezing. The formation of a hydrogen bond also leads to changes to the water molecule itself, namely an induced dipole/polarisation of the water molecule, which is reflected in the stepwise changes in the central water’s dipole moment as the number of hydrogen bonds increases. This change in both the molecular dipole and electron distribution when a hydrogen bond is formed is most likely related to the observation of cooperative effects in hydrogen bonding.

2.1.2 Intermolecular Network Formation
The structure and dynamics of associated liquids such as water are unique in the sense that their intermolecular structure cannot be explained purely by molecular packing. As discussed in the previous Section, the very specific and directional attractive interactions of the hydrogen bonds lead to tetrahedral ordering around a given water molecule. If all molecules would adhere to this tetrahedral arrangement, we would arrive at the crystal structure of hexagonal ice (I\(_h\)) (here the term hexagonal refers to the crystal lattice, not the coordination of each molecule). In the liquid however the local tetrahedral order is disturbed by the random fluctuations that characterise the liquid phase, which leads to a rapid loss of ordering effects, approximately within two molecular diameters. This loss of distinct structure can be seen in the radial distribution function of liquid water compared with ice. A comparison between the RDF of a non-associated liquid and the corresponding solid is shown in Figure 2.1. So while each individual water molecule will form close to four hydrogen bonds, the structure of the liquid overall is better characterised as a highly disordered network.

Part of the reason why the barrier for network rearrangement is so low in water is that the molecules of the hydration shell can rearrange via a bifurcation mechanism. In this mechanism, the incoming molecule first associates with an occupied hydrogen bonding site, and the outgoing molecule leaves the site in a second step. This way of exchanging a given molecule in the hydration shell avoids the significant energetic barrier of first breaking the hydrogen bond and then reforming it.

In solutions or mixed systems the presence of solutes can influence the hydrogen bond network of water over multiple molecular diameters. In the case of strong water-solute interactions, this effect can lead to added polarisation in the surrounding water molecules, which in turn affects the other hydrogen bonds this molecule is engaged in. Reorientation of the initial solute can then induce relaxation or reorientation in the other coupled molecules as well. Beyond facilitating collective rearrangement, the hydrogen bond network is
central for fast intermolecular energy transfer in the liquid, e.g. of O-H stretch vibrational excitation along the network\textsuperscript{45} and proton mobility, which is discussed below.

\subsection{2.1.2.1 Behaviour of the Proton in Water}
Liquid water has a notable propensity for autodissociation into hydronium (H\textsubscript{3}O\textsuperscript{+}) and hydroxide (OH\textsuperscript{−}) ions. The behaviour of the excess proton has been debated heavily,\textsuperscript{26} in particular whether it becomes associated with one water molecule (Eigen structure: H\textsubscript{3}O\textsuperscript{+}) or is shared between two water molecules (Zundel structure: H\textsubscript{2}O···H\textsuperscript{+}···OH\textsubscript{2}). These two cases probably represent characteristic structures of the real behaviour of the proton, since it only briefly associates with a single molecule, migrating through the liquid very quickly, and interconversion between the two structures has been observed.\textsuperscript{46}

The high mobility of protons in water is often attributed to be a characteristic of the hydrogen bond network itself: Rather than diffusing through the liquid as a single unit, as ions such as Na\textsuperscript{+} do, the proton can associate with a water molecule, forming H\textsubscript{3}O\textsuperscript{+}, and then liberate a proton on the other side of the molecule. It is therefore not the same proton that diffused along the network, but rather the proton defect, starting a chain reaction of association and liberation. This mechanism is referred to as the Grotthuss or proton-hopping mechanism. It has been suggested in the literature that a single proton transfer can require the collective motion of up to 15 water molecules.\textsuperscript{47}

High mobility through the hydrogen bond network is not only observed for the excess proton, but also the relative structure of the bound hydrogen atoms can fluctuate heavily. In ice, but especially in the liquid phase, the protons of water can migrate \textit{via} concerted collective rearrangement within the network, such as e.g. proton tunneling or switching of hydrogen bonding partners. Any collective rearrangement is most likely facilitated by the synergistic character of the hydrogen bond network. Knowing the oxygen lattice of the liquid or ice is therefore not enough to deduce the positions of the hydrogen atoms, because they migrate quickly between different hydrogen bonding positions representing degenerate microstates.

In the solid different forms of ice, the proton structure leads to an interesting observation: Most ice phases have a proton-disordered structure at higher temperatures and an equivalent proton-ordered structure at lower temperatures. In the case of ice I\textsubscript{h}, which is a proton-disordered phase, the proton-ordered equivalent is ice XI. The protons of ice I\textsubscript{h} still have significant mobility in the ice lattice even when heavy cores are thermally frozen, \textit{via} e.g. proton hopping\textsuperscript{48} or tunneling.\textsuperscript{49} The ordered/disordered phase transition of ice XI to I\textsubscript{h}, which occurs at around 100 K,\textsuperscript{50} is sometimes coined as a melting of the proton structure, while the heavy cores remain fixed.
3. Surfaces

3.1 Introduction to Surfaces

Most simply, a surface or interface can be defined as the boundary between two phases, e.g. solid/liquid, liquid/gas, liquid/liquid etc. In this thesis we focus on the liquid/gas surface, as approximated by the liquid/vacuum surface. Distribution functions are used to describe liquid/gas surfaces, since the liquid surface is not as well defined as in the solid phase. In simulations the density distribution functions are often used to define the Gibbs dividing Surface (GDS) at half the bulk density. This definition averages over any density or height fluctuations of the liquid surface, and defines a flat surface plane that divides the two phases. Alternatively, an instantaneous contact surface can also be defined. The instantaneous surface definition is sometimes used for liquids and considers fluctuations of the interface, this can sometimes make any layer formation or surface structuring of the solvent more apparent. Both of these definitions of the surface are sketched in Figure 3.1 (a).

When the bulk of a dense substance is terminated to form a surface, the atoms or molecules that reside at the newly formed interface have a reduced number of nearest neighbours/intermolecular bonding partners. These frustrated surface molecules can rearrange to minimise their collective surface energy and maximise their coordination, leading to the formation of structural motifs that are absent in the bulk of the material, these effects are described for water and its solutions in the following Sections.

3.1.1 Surface Structure of Water

The water surface itself is subject to significant fluctuations, sometimes referred to as capillary waves. Due to these fluctuations, the average displacement of the water molecules at the surface can be described by the mean-square fluctuations in surface height, relative to the GDS.\textsuperscript{51} The surface contains a significant population of very weakly bound molecules, either in a physisorbed state or as single hydrogen bond acceptor or donor,\textsuperscript{52} and has been described as an intermediate step in the evaporation and condensation process.\textsuperscript{53} Reduction in the number of hydrogen bonds and expansion of the O-O distances in the surface region by 5% relative to the bulk\textsuperscript{54} both indicate there is a much weaker hydrogen bond network at the interface than in the bulk. The dielectric properties of water change in the surface region, which is related to changes in hydrogen bonding.\textsuperscript{55} There is an interconnection between the
formation of hydrogen bonds, the molecular dipole and bulk properties such as the dielectric constant and the permittivity. However, such bulk properties are perhaps not best-suited to describing the surface layer, which is on the molecular scale. Surfaces often react to the loss of bulk translational symmetry by rearranging their structure to compensate for the loss of nearest-neighbour interactions, compared with the bulk. The orientation of individual water molecules in the surface layer has been studied in detail using molecular dynamics (MD) and sum-frequency-generation (SFG) spectroscopy by Götte et al., and the surface structure described therein can be summarised as follows: The outermost water molecules orient themselves such that significant population of molecules have one OH group oriented towards the gas-phase/vacuum, which are commonly referred to as dangling OH groups. The second OH unit of these molecules is strongly hydrogen-bound to other water molecules in the surface region, with the oxygen site of these molecules oriented slightly towards the bulk. The first layer of fully hydrogen-bound molecules below the instantaneous surface are oriented with their dipole pointing the opposing direction, namely with their hydrogen atoms towards the bulk and the oxygen towards the surface. This is followed by another weakly-oriented layer of molecules having the same orientation as the outermost molecules, namely the oxygen pointing towards the bulk. In other experimental SFG work it has also been reported that the molecular orientation of the surface extends over the first three molecular layers of the surface,, meaning most that of the orientational influence of the interface should be lost within approximately three molecular water layers.

3.1.2 Surface Enrichment of Solutes

The term surface enrichment of a given solute refers to a concentration in the surface region that exceeds the bulk concentration. The simple case of surface
enrichment is the hydrophobic exclusion of apolar groups from liquid water, such as in long chain alcohols and other common surfactants. Essentially, the worse a solute is at integrating into the hydrogen bond network, the weaker its water/solute interactions are compared with the water/water interactions, and the more likely it is to be expelled from the bulk and enriched at the interface. The surface enrichment of a long chain alcohol is sketched in Figure 3.1 (b.2). Depending on the bulk concentration of the solute, the surface enrichment of these surfactants usually shows two regimes. At lower bulk concentration the surface concentration is linearly dependent on the bulk concentration and increases strongly when the bulk concentration is increased, which is referred to as the linear regime. Beyond a critical bulk concentration, the surface concentration stays the same, even as the bulk concentration is increased further, this concentration range is referred to as the saturation-regime. Surface enrichment that follows this general behaviour has been described as Langmuir-like surface enrichment in recent publications.\textsuperscript{34,60,61} This can be explained in terms of there being a maximum number of molecules that can populate the surface, and once the surface is saturated with surfactants the remaining molecules cannot be expelled from the bulk and remain fully bulk solvated. The number of available surface spaces, and therefore the maximum surface concentration, depends on the nature of the solute. The bulk concentration at which surface saturation is reached is important, as it can provide information about the Gibbs free energy of adsorption ($\Delta G_{\text{ads}}$) of the solute.

However, well solvated inorganic ions can also be enriched at the interface, as is the case for some monoatomic ions such as iodide and bromide\textsuperscript{9,10,62,63} and some polyatomic ions, e.g. perchlorate\textsuperscript{64} or thiocyanate.\textsuperscript{51,65} These ions are usually large, polarisable, and carry a negative charge. The two types of surface active components influence the structure of the interface differently, since they have inherently different interactions with the solvent. The driving forces for hydrophobic enrichment have been studied in detail before,\textsuperscript{34,60,61} and here we focus on surface enrichment of small inorganic ions. In the case of inorganic ion enrichment the increased concentration of the anions close to the interface leads to a charge buildup, which in turn causes the formation of a charge compensation layer of cations in the deeper layers of the surface region. An example of the density profiles of a surface enriched anion and its counter-ion is sketched in Figure 3.1 (b.1). The two layers of ions lead to a significant electrostatic field, which orients the dipole of the water molecules that separate them, with the oxygen pointing towards the cations and the bulk and the hydrogen atoms to the anions and the surface. This orientational order that the ions impose on the surface region weakens the hydrogen bonding of the water molecules to a certain degree, depending on the nature of the solute and its concentration.
3.1.3 Difference in Ion Solvation at Surface and Bulk

In basic textbooks it is usually assumed that small, inorganic ions are repelled from the liquid/air surface, since they are highly soluble and form strong, favourable interactions with bulk water. This assumption was supported by surface tension measurements which predicted a negative surface excess of inorganic ions at the surface. This effect was modelled by Onsager et al.\textsuperscript{67} by considering the ion as a point charge and the surface as a sharp phase boundary between two dielectrics. In this model, the surface repulsion of the ions was attributed to image charge repulsion.

To understand why some ions do in fact become enriched at the interface\textsuperscript{9, 68} the basic principles of their molecular interactions with the solvent in the surface layer are outlined below. First, the solvation of single ions as they approach the phase boundary is considered, and then how different ions interact with one another in the surface and bulk region: As the ion approaches the surface, the ion-water interaction will decrease on average, as the solvation decreases (i.e. interactions beyond the first solvation shell are weakened or lost) and finally, the solvation shell begins to lose water molecules if the solute moves across the surface plane. This desolvation of the ions acts as a potential wall at the surface,\textsuperscript{69} limiting how close the ions can approach the instantaneous interface of the liquid. The energetic cost of losing solvent molecules in the first solvation shell is so high that most small ions can, at most, be found directly under the outermost surface layer of water molecules. Depending how tightly the water molecules are bound to the ions, as e.g. described for Li\textsuperscript{+} and K\textsuperscript{+} in the literature,\textsuperscript{69} the ions lose solvation shell molecules at different distances from the instantaneous interface, indicating that different ions can approach the instantaneous surface to different degrees.
The disruption of the water/water interaction by the cavity formation around the ion can also be very different depending on the position of the ion relative to the surface.\textsuperscript{10} In the bulk the water/water network is very strong, so the formation of a cavity for the ion comes at significant energetic cost. At the surface, however, the hydrogen bond network is much weaker, due to the decreased density and broken bonds, so as a result the energetic cost of cavity formation is not as high.

The dipole of the water molecules also differs at the interface compared with the bulk, which influences both the ion/water interaction and the screening of the charges. The decreased dipole weakens the ion/water interactions, however the decreased screening of the ion charge would lead the ion to exert a more long range effect on the surrounding water molecules.

The interaction between anions and cations is also affected by their distance from the surface, an effect that is closely related to the changed screening of charges due to the decreased water dipole and dielectric constant in the interfacial region. It has been shown in molecular dynamics simulations of monoatomic ions that cation/anion interactions are more pronounced in the surface layer than in the bulk.\textsuperscript{70} Effects such as increased ion/ion interaction in the surface layer are most likely related to the observation that ion pairing of polyatomic ions is enhanced at the interface.\textsuperscript{71,72} An ion pair is defined as the association of two ions in the liquid, held together by coulombic interaction, without the formation of a covalent bond. The electrostatic interaction is often mediated by water molecules.\textsuperscript{73} Ion pairs can take different forms, and are divided into three general groups: contact ion pairs, solvent-shared ion pairs, and solvent-separated ion pairs.\textsuperscript{74} Both mono- and polyatomic ions that do not form ion pairs in the bulk have been observed to form such ion pairs at the surface.\textsuperscript{56,75} The lifetime of ion pairs are on the order of tens of picoseconds, and they are formed and broken continuously.\textsuperscript{76}

All these effects add to the surface enrichment discussed in Section 3.1, since they all contribute to the total Gibbs energy of adsorption of an ion close to a surface. The decomposition into the different ion/water and water/water contributions to both enthalpy and entropy\textsuperscript{10,51} was outlined by Ben-Amotz,\textsuperscript{11} and a short summary of the work presented in the publication is given here:

The main conclusion of the publication\textsuperscript{11} is that the water/water contribution to enthalpy ($\Delta H_{ww}$) and entropy ($\Delta S_{ww}$) are equal and opposite and therefore cannot be the driving force for ion surface enrichment.

In order to understand what drives the ion’s surface enrichment one has to look at the enthalpy and entropy terms of the remaining ion/water interaction. The direct ion–water enthalpy ($\Delta H_{iw}$) describes the average solvent/solute interaction energy due to dispersion and electrostatic interactions. As previously mentioned, the $\Delta H_{iw}$ potential increases as the ion approaches the surface, which reflects the loss of water/ion interaction.

The entropy term ($\Delta S_{iw}$) describes, in very simple terms, the fluctuations in the solvent/solute interaction energy. This change is related to the fact that as the
ion comes to the surface the interaction energy decreases (enthalpy) which in turn allows for the variability in the interaction energy to increase (entropy). The $T \Delta S_{iw}$ term is largest when the ion is at the interface, and stays constant once the ion is on the vacuum side of the Gibbs dividing surface. The $\Delta H_{iw}$ potential steeply increases once the first solvation shell is weakened, which acts as a barrier hindering the ions from desolvating, and effectively evaporating off the liquid. The ion/water interaction is therefore strong enough to firmly anchor the ions in the liquid phase. From these two terms it becomes apparent that the ion-water interaction enthalpy favours bulk solvation, whereas the entropy term favours surface solvation, with the latter being large enough to drive the surface enrichment of halide ions.
3.2 Surface Sensitive Photoelectron Spectroscopy

3.2.1 Photoelectron Spectroscopy

In X-ray photoelectron spectroscopy (XPS) we study the electronic structure of a material via the electrons emitted from the sample due to the photoelectric effect. The XPS spectrum traces the intensity of emitted electrons as a function of their kinetic energy. If a monochromatic light source is used to emit the electron, its kinetic energy can be related to the binding energy of the electron via:

\[ BE = h\nu - KE - \phi \]  

(3.1)

where \( \phi \) denotes the workfunction of the material, which is used for solid samples.

An important aspect of XPS is its chemical specificity, which is due to the fact that the binding energy of the core levels are unique to the different elements, making the technique well suited for chemical analysis or selectively investigating parts of a mixed system. The exact binding energy of a given orbital does not depend on the nature of the atom alone, but also on the chemical environment the atom is embedded into. This includes effects such as oxidation state, partial charge, nature of the neighbouring atoms, bond hybridisation, and screening effects in the final state. The chemical bond the atoms form will most strongly distort the outer valence orbitals, since they are actually involved in the formation of these bonds, but it also shifts the binding energy of the core levels. This effect on the core level binding energy is referred to as the chemical shift. Usually, the removal of electron density in the valence region, via a bond to a \( \sigma \)-acceptor or an electro negative atom for example, increases the binding energy of the core levels.

To predict the binding energy of a given state, one needs to consider both the initial state of the system at the moment of ionisation and the final state it is excited into. The observed binding energy then corresponds to the total energy difference between the initial and the final state. Final state effects mainly include the electronic response to the vacancy created by ionisation, which occur in concert with the creation of the vacancy. Depending on differences between the potential shapes of the electronic initial and final state, several vibrational states of the final state can be populated, leading to a progression of vibrational lines that can be observed in the XPS spectrum. In our work the initial state is usually in the vibrational ground-state, but if there were a significant population of these states, the energetic difference of these vibrational states would also be observable in the XPS spectrum.

The homogenous lineshape is mainly determined by the lifetime broadening of the state. In the case of the condensed phase, the lineshape of a given peak is considerably broadened in comparison with the gas phase, since the energy of both the initial and final state vary significantly when the atomic coordinates change slightly. This means that even a small change in the intermolecular
Figure 3.3. Schematic of electrons created in the bulk and at the surface of liquid water. The probability for scattering is higher for an electron liberated in the bulk, as it has to travel a longer distance through the dense medium before it reaches the vacuum of the experimental chamber. The orange glow indicates the positive charge of an ionised molecule, and the free electrons are shown in dark blue.

due to the strong changes in interaction energy at slightly different hydrogen bonding geometries, this effect is particularly pronounced in water.

3.2.2 Electron Scattering

The information depth of an XPS experiment mainly depends on two things, firstly how much of the sample is illuminated by the X-ray beam, and secondly how well the electrons that are ionised in the illuminated volume can be detected. For the electrons to be detected, they must first escape the dense medium of the liquid sample and the vapour phase around it. Electrons have a very short mean free path, which is why electron spectroscopy is usually restricted to vacuum environments. The photoelectrons created in the bulk are inelastically scattered and no longer contribute to the measured XPS peaks but to the background at lower kinetic energy. Conversely, it is more likely for the electrons created at the surface of the liquid to reach the electron analyser without being inelastically scattered, and thus for them to contribute to the signal intensity of a peak. The probability of an electron being scattered as it travels in a medium is described by parameters such as the inelastic mean free path (IMFP) or the electron attenuation length (EAL). The latter corresponds to the distance a number of electrons can travel through a medium at a given kinetic energy after which their number of electrons at that kinetic en-
ergy is reduced by 1/e. The IMFP or EAL are not interchangeable, but they both describe the same underlying process, namely the scattering probability of electrons at a certain kinetic energy. The mean free path of an electron strongly depends on its kinetic energy. The often cited universal curve\textsuperscript{8} of the IMFP has a minimum at approximately 70 eV kinetic energy, which means that by using a variable energy photon source and thus tuning the electrons energy we can change the characteristics of an XPS experiment from being highly surface sensitive to bulk sensitive. The IMFP of electrons in water is still largely contended, but it is on the order of 1 nm for kinetic energies around 100 eV.\textsuperscript{77}
3.3 The Influence of Temperature

3.3.1 Temperature-dependent Water Properties

Many of water’s anomalous properties are revealed when observing its behaviour as a function of temperature, such as e.g. the density anomaly,\textsuperscript{21} since a change in temperature is closely linked to corresponding changes in the hydrogen bond network.

From a molecular standpoint, an increase in temperature leads to larger entropy in the system and therefore larger fluctuations and disorder. In the bulk, an increased temperature will increase fluctuations around the equilibrium distances between molecules, and increase diffusion dynamics. This leads to greater variability in the local structures found in the liquid. The increased disorder of the liquid has been observed to manifest both in the hydrogen bond length and angle.\textsuperscript{78} Overall these effects are consistent with a decrease in the hydrogen bond network strength.

On the macroscopic scale, a decrease in the dielectric constant is observed with increased temperature,\textsuperscript{79} which is also likely related to changes in the hydrogen bond network, since a weaker hydrogen bond decreases the induced dipole in the individual water molecules. Another macroscopic property that reflects the change in hydrogen bonding is the viscosity of the liquid, which decreases at higher temperature,\textsuperscript{25} as well as self-diffusion which is increased. Both of these changes reflect the weakening of both the individual hydrogen bonds and the network as a whole.

At the water surface, an increase in vapour pressure is observed at elevated temperature,\textsuperscript{23} as well as a related increase in surface roughness i.e. capillary waves. In a related manner, the surface tension of the liquid is found to decrease.\textsuperscript{22} The trend observed in the surface properties indicates that the energetic barrier and structural difference between the two phases decreases as the temperature is raised.

3.3.2 Temperature-dependent Surface Enrichment

As briefly mentioned in the last paragraph of the previous Section, an increase in the system’s temperature will lead to an increase of the vapour pressure and a decrease in the surface tension of the liquid. Both effects indicate that the water self-interaction at the interface is decreased. This decrease might be attributed to both the increased entropy and the decrease in the dipole of the individual molecules, two effects that are likely related.

The surface enrichment of ions at different temperatures has been investigated in only a limited number of publications. While there is one experimental study on SCN\textsuperscript{−},\textsuperscript{51} there are only MD studies on the surface propensity of halide ions, which found a decrease in surface enrichment with increased temperature.\textsuperscript{80} This was attributed to the fact that the entropy of the system is increased when the ions are in the bulk of the solution. Since the contribution
Figure 3.4. Schematic of the aqueous interface containing an arbitrary surface-enriched salt. The black arrows indicate the most important dynamic processes influenced by a change in temperature. D: Diffusion, EI: First step of evaporation from a hydrogen-bonded state to a physisorbed state in the surface layer, EII: Second step of evaporation from the surface layer into the vapour, $\Delta G_{ads}$: Gibbs energy of adsorption of ions to the interface, $F_c$: Coulombic ion/ion interaction, $S_{cw}$: Entropy of capillary waves, $S_{cf}$: Cavity formation entropy, and $H_{sol}$: ion-water enthalpy of the solvation shell.

of the total entropy to the Gibbs free energy is increased at higher temperature, the surface concentration of ions is predicted to decrease at higher temperature.\(^\text{10}\) The major temperature dependent processes at the water surface and the relevant contributions to surface enrichment that need to be considered when the temperature of the system is changed are summarised in Figure 3.4.

3.3.3 Measuring the Surface Propensity of Halide Salts
In this work, we combined results from vibrational sum-frequency-generation (VSFG) experiments with surface-sensitive XPS measurements to investigate how a change in sample temperature affects the surface enrichment of dissolved alkali-halide salts. We focus on the influence of temperature on the surface properties of chloride, a bulk-solvated ion,\(^\text{64}\) as well as bromide and iodide, both of which have previously been shown to be enriched at the aqueous interface.\(^\text{10,63,68,81–83}\) The two experimental techniques deliver information
Figure 3.5. Left panel: Normalised area of the VSFG difference spectrum of the water and saline solutions (LiI and NaI) at temperatures ranging from 5 to 60 °C. Right panel: Factorial change of normalised XPS peaks, representing the ion:water ratio, of warm and cold liquid jet systems.

on different aspects of the surface structure and are therefore highly complementary. VSFG measurements are sensitive to any ordering effect the ions have on the water molecules at the surface. An increased VSFG response corresponds to an increased population of water molecules with no net centrosymmetry. In the XPS measurements, the ion propensity in the surface region is measured directly and we can determine how the ion distribution changes in relation to the surface region when the sample temperature is changed. This means that, while in principle both techniques are sensitive to changes in ion surface enrichment, the comparison of the two is not straightforward and there might be differences in what the experiments tell us about the structure of the surface. Below, I briefly summarise the results from both experiments separately, before outlining a unified interpretation.

VSFG spectra of NaI and LiI solutions, as well as neat water, were obtained at temperatures ranging from 5 to 60 °C. Both saline samples show a significant deviation from the spectrum of neat water, mainly the intensity of the high frequency side of the bound OH region. This effect is attributed to two effects: Firstly, the water molecules that form hydrogen bonds with iodide have a higher vibrational frequency than water molecules forming hydrogen bonds with other water molecules. Secondly, the different surface propensities of the halide anions and the surface-depleted cations create an electric field that orders the water molecules close to the surface.

To highlight the changes to the VSFG spectrum at different temperatures due to changes in the ion distribution, and not the change of the water surface itself, we focus on the integrated area of the difference spectrum as given by $\text{VSFG}_{\text{ion-solution}}(T) - \text{VSFG}_{\text{water}}(T)$. Any temperature-dependent change in the resulting difference trace can therefore be attributed to changes induced
by the ions. The individual difference traces are shown in Figure 1 of Paper I. For both LiI$_{(aq)}$ and NaI$_{(aq)}$, an increase in the difference between the solution and the water reference is observed as the temperature is raised. The integrated areas of the difference traces, relative to the value at 5 °C, are shown in Figure 3.5. The temperature effect is much more pronounced for LiI$_{(aq)}$ (a factor of 1.5 at 60 °C) than for NaI$_{(aq)}$ (a factor of 1.1 at 60 °C). This result is interpreted as an increase in the surface concentration of iodide ions with increasing temperature for both systems. The nature of the counterion clearly plays an important role in determining the magnitude of the temperature-dependent change, likely by affecting the electric field near the surface.

In the XPS experiments, we evaluate the surface propensity as determined by the ions’ normalised peak area at cold and warm temperature, to obtain a factorial change in the ion:water peak ratio for both the cation and anion. We refer to this factorial change in surface concentration of the ions as $\Delta c_{XPS}$. A factor $\Delta c_{XPS} > 1$ corresponds to a relative increase of the ion’s surface propensity with temperature, and $\Delta c_{XPS} < 1$ to a decrease, with the values obtained for the different ions shown in Figure 3.5.

The surface propensity of bromide and iodide ions was found to increase at higher temperature for all bromide and iodide salt systems studied here. In the case of the chloride ion, no change in the chloride:water ratio is observed when comparing the cold and warm XPS data. Since the chloride ion has been shown to be bulk-solvated, our results indicate that the chloride ion simply remains in the bulk of the solution irrespective of the sample temperature.

In the case of the studied cations, no such uniform trend can be described. The surface propensity of sodium in NaCl$_{(aq)}$ is unchanged by the increased temperature, but decreases to different degrees in the cases of NaBr$_{(aq)}$ and NaI$_{(aq)}$. Conversely, the surface propensity of the potassium ion in KI$_{(aq)}$ is increased at the elevated temperature. The sodium ion’s changed behaviour, depending on the nature of the anion, indicates that the specific cation/anion interaction must play a significant role in guiding the cation’s relative surface enrichment or depletion at different temperatures.

We also extracted iodide:water ratios for LiI$_{(aq)}$, NaI$_{(aq)}$, and KI$_{(aq)}$ in the surface region at cold and warm temperature, as shown in Figure 2 and Table 1 of Paper I. The ratios are normalised to the value of the cold NaI$_{(aq)}$ system and indicate the relative change in surface population of iodide, due to the nature of the cation and the system temperature. In the cold system, the iodide surface concentration is the same for NaI$_{(aq)}$ and LiI$_{(aq)}$, with KI$_{(aq)}$ showing a slightly reduced iodide surface concentration. In the warm system, the increased temperature raises the concentration of anions relative to the cold system, with the iodide concentration of the warm system being lowest in KI$_{(aq)}$, intermediate in LiI$_{(aq)}$ and largest in NaI$_{(aq)}$. These results show that, while the nature of the counterion modulates the magnitude of the temperature effect of iodide, it does not do so to a large degree, and the behaviour of the iodide ion is very similar in all three solutions.
The experimental results of both VSFG and XPS indicate an increase of halide anion propensity at the water interface when the temperature of the system is raised. They also highlight that there is a specific cation/anion interaction which changes the magnitude of the temperature-induced change in surface structure. In particular, the difference in the temperature-dependent surface propensity of the sodium ion in NaCl, NaBr and NaI indicates that the behaviour of the cation strongly depends on the surface propensity of the anion.

### 3.3.4 The Influence of Temperature on Surface Structure

If we compare the main results obtained using the two independent techniques, they agree qualitatively on the fact that there is an unexpected increase in the surface concentration of bromide and iodide ions enriched at the aqueous interface. This result is surprising, since it has been predicted from MD studies that the surface concentration should decrease with increased temperature.\(^8\) The result of increased surface structuring at higher temperature also appears to defy the intuitive assumption that any emergent structure should be lost or decreased when the system is heated and entropy is increased. Since we observe that the nature of the cation and anion influence the magnitude of the temperature change observed (but not the direction/sign of the effect) in both the VSFG and XPS data, the ions cannot be assumed to behave independently at the water interface, and we must therefore consider the effect of the ion/ion interaction to fully describe the surface structure of aqueous solutions.

In the VSFG data, the changes to the water interface are more pronounced in LiI than NaI. This could be interpreted as either a stronger increase in surface concentration of iodide in LiI than NaI, or that the structure of the electric double layer (EDL) is affected differently by increased temperature in the two solutions. We know from the iodide:water peak area ratios extracted from the XPS data (see Figure 2 in Paper I) that the increase in surface propensity of iodide at higher temperature is very similar for all iodide salts that we studied. This means the cation effect observed in the VSFG cannot be explained by a drastically different change to the surface concentration of iodide at higher temperature in the presence of Li\(^+\) or Na\(^+\).

We also observe in the XPS data that, for NaBr and NaI, the surface concentration of the cation decreases and the anion concentration increases with temperature, indicating that the segregation of cations and anions increases at higher temperature. The magnitude of the Na\(^+\) depletion appears to depend on the nature of the anion, since it is more pronounced for NaI than NaBr, whereas no effect is observed in NaCl. An increase in segregation between the anion and cation would lead to a larger number of water molecules being oriented by the EDL, and in turn to a larger VSFG response. We therefore extrapolate that in the case of Li\(^+\) the cation is even more depleted at higher temperatures than Na\(^+\), which would lead to a surface structure exerting a stronger ordering
Figure 3.6. Sketch of NaCl, NaI and KI as model cases for: (a) no surface enrichment, (b) surface enrichment without ion pairing, and (c) surface enrichment with ion pairing.

effect on the surface, therefore giving rise to the larger VSFG response that we observe. Finally, in the case of potassium iodide, we see that both the iodide and potassium concentration increase together with temperature.

As outlined in Section 3.1.3, surface enrichment is driven by the balance between direct ion-water enthalpy and entropy, with the former (enthalpy) disfavouring surface population and the latter (entropy) favouring it. The balance between the two contributions therefore determines if an ion is enriched or not.

The surface enrichment of the larger anions (bromide and iodide) is driven by the increased ion-water entropy achieved when the ion resides at the surface. An increase in the system’s temperature increases the influence of the entropy term to the Gibbs adsorption potential, which in turn deepens the surface minimum in the Gibbs free energy and therefore increases the ion’s surface propensity. The increase in the anion surface concentration with temperature is only mildly affected by the nature of the cation, as we observe clearly in the case of iodide, which behaves very similarly in LiI(aq), NaI(aq) and KI(aq).

The Gibbs free energy of the isolated cation in water (i.e. in the absence of a counter-anion) can mainly be described by the enthalpic ion-water interaction. This means that the isolated cations are preferentially solvated in the bulk due to the enthalpic driving force. This is because the ion-water entropy of the cations is significantly smaller at the interface than for the anions, which can be linked to the solvation shell structure. The cation’s solvation shell is more tightly-bound and structured, whereas an anion’s solvation shell is looser because the water molecules interact with the anion through the hydrogen atom which carries half the partial charge of the oxygen, allowing for greater disorder. However, when anions are present, the cations are drawn from the bulk
into the surface layer by the long-range ion-ion interaction potential formed by the charge build-up of anions preferentially residing close to the surface. The exact shape of this potential depends on the enrichment of the anions, the nature of both the anion and cation, and the dielectric constant of the solvent. Assuming the cations are drawn towards the interface by the surface-enriched anions to form a charge compensation layer, as argued above, then a decrease in cation surface propensity with temperature indicates a reduction in the cation charge compensation layer with temperature. This may be interpreted as an indication that the ion-ion interaction leading to the formation of the charge compensation layer is an enthalpically-driven process, which becomes "washed out" as the entropy contribution to the ion-ion potential becomes dominant at higher temperature, as opposed to the entropically-driven anion surface propensity, which further increases with temperature. In the special case of KI(aq) the ions appear to be 'well matched', since both are considered to be soft ions, and likely form ion pairs at the surface.
3.4 Composition of Wet and Dry Surfaces

3.4.1 Measuring the Surface Composition of Sea Spray Aerosol

Sea spray is one of the main sources of atmospheric aerosol, which is generated via wave breaking and bubble bursting in the marine boundary layer.\(^3\) Once airborne, the water content of the sea spray particles may decrease due to evaporation, effectively increasing the concentration of the non-volatile components. Recent studies indicate that calcium ions can be enriched in small sea spray aerosol particles.\(^8^4\) It has been suggested that the enrichment of calcium ions may be caused by complex formation of calcium with the organic fraction of the aerosol. These complexes would be surface enriched due to the hydrophobicity of the organics in the aerosol particles.\(^8^5\) Later this assumption was challenged by the observation of calcium enrichment in the absence of organics in small inorganic sea salt particles.\(^8^4\) To study the enrichment of calcium ions in a systematic way, the surface of dried aerosols along with the equivalent aqueous surface were investigated using surface-sensitive XPS. To simplify the problem, different model solutions were used, the complete compositions of which can be found in Paper II.

First, aerosols originating from simplified model systems (molar ratios of CaCl\(_2\):NaCl = 1:1 and 1:4) were investigated, to study the interaction of calcium chloride with sodium chloride, the most common salt in sea water. Relative XPS intensities of the corresponding core level peaks can be seen in Figure 1 of Paper II. For both solutions, only Ca 2p and no Na 2s signal was observed in the surface layer of the dried aerosols. This means that even at relatively high concentrations of NaCl in the parent solution the surface of the dried particles are entirely made up of CaCl\(_2\). In the wet (aqueous) surface equivalent of the 1:1 solution, we observe Ca 2p and Cl 2p but no Na 2s signal intensity, in qualitative agreement with the dried aerosol results. These measurements were then compared to an artificial inorganic sea salt mixture, which is standardised to model most of the inorganic components of sea salt, but contains very little calcium. In this case, a clear Na 2s peak was observed in the dried aerosol, but no appreciable Ca 2p signal. When the relative concentration of Ca\(^{2+}\) ions was increased in the parent sea salt solution, the surface was repopulated by calcium ions and no sodium was observed on the particle surface. From this data it can be concluded that, in the dried particles, the cations are in competition for the surface layer and no mixed NaCl/CaCl\(_2\) phase is formed in the samples. Liquid jet results of the calcium-enriched sea salt solution show a small surface contribution of both Na 2s and Ca 2p, which means that in the liquid surface the two cations may coexist in the surface region.

To investigate the influence of organics on the surface composition, different concentrations of acetic acid were added to the calcium-enriched sea salt mixture. In all three cases the same result was observed, namely a strong carbon peak which confirmed the surface presence of acetic acid, accompanied by a
Figure 3.7. Schematic of the sequential crystallisation during the drying process. In the top left the blue core symbolises the aqueous solution containing the inorganic ions. The green shell represents the surface enriched organics. As the relative humidity is decreased (in clockwise order) and the aerosol loses water content the different salts crystallise sequentially when their respective efflorescence points are reached. This sequential crystallisation leads to the formation of multiple shells, with the liquid organic remaining on the surface of the aerosol particle.

Na 2s peak. No calcium was observed on the dried particle surfaces of these systems. In contrast, calcium was found to still be present in the surface layer of the aqueous equivalent, mirroring the results of the inorganic mixtures. From this we can conclude that the added organic did not form a complex with calcium on the surface of the dry aerosol, since no calcium ions were observed in the surface region in the presence of these organics. For the aqueous surface, there is no equivalent competition between the different cations for the surface layer.

3.4.2 Drying as a Structure-forming Mechanism

The comparison of the liquid and dried surface composition indicates that the surface structure of the dried aerosols is not the same as in the liquid, or the wet surface. There must, therefore, be another mechanism altering the structure of these particles. The step of the aerosol particle generation which hasn’t been discussed so far is the drying process. The relative humidity at which a salt crystallises is referred to as the efflorescence point, and efflorescence occurs in the aerosols as the relative humidity is lowered by the diffusion dryer. In the liquid phase, all ions can mix throughout the aerosol droplet, but during the drying process the different salts, NaCl and CaCl$_2$, effloresce separately and sequentially. NaCl is the first salt to crystallise, whereas CaCl$_2$ has a high hydroscopicity and retains water down to a lower %RH, leading to the formation of a core/shell particle with NaCl in the centre surrounded by CaCl$_2$. This model matches well with the observed behaviour in dried aerosols that
only one type of cation is found in the surface layer at any given time. The proposed core-shell formation mechanism is sketched in Figure 3.7. For real sea spray aerosols, the formation of a CaSO$_4$ core has been predicted, since the formation of this phase due to the very low solubility of CaSO$_4$ in water has been observed previously.$^{86}$ For the sea salt mixture we studied, the small calcium content is used up by the efflorescence of the CaSO$_4$ core, and therefore no CaCl$_2$ film is formed on the surface. When the sea salt solution is further enriched in calcium, the efflorescence of calcium sulfate does not remove all calcium from the liquid phase and the remaining excess calcium ions effloresce as CaCl$_2$ at a lower % RH. When the organic acid is then added to the system, it remains liquid even when all of the residual water has evaporated from the particle, forming the outermost layer around the saline particle. The main conclusion of this study is that the composition of the dried and wet systems are not determined by the same mechanism; the dynamic equilibrium that governs the aqueous surface enrichment is not found in the dried particles. In the latter case, the surface composition is determined by the hygroscopicity and efflorescence/solubility of the salts contained in the parent solution.
4. Hydrogen Bonding

Many of the unique properties observed in water and related systems such as alcohols have been connected to hydrogen bonding, which is the strongest intermolecular interaction in these systems. Hydrogen bonding networks are difficult to understand because of the cooperative effects that take place in the network, meaning that it cannot simply be described as a sum of the individual hydrogen bonds, making it important to study hydrogen bonding in the fully formed network.

We study the intermolecular network via its influence on the electronic structure of the liquid, and ionisation-induced proton dynamics. The electronic and atomic structure of a molecular system have a synergistic relationship, as the electronic structure of a molecule both gives rise to and is influenced by the intramolecular structure and the local environment of the molecule. While hydrogen bonding has been studied from a molecular structure and dynamics approach in detail (vibrational and scattering experiments, molecular dynamics simulations), we investigate it from the viewpoint of electronic structure. This is advantageous because the occurrence of ultrafast dissociation along a hydrogen bond can be related to the formation of hydrogen bonds in the ground state, and the structural average that is observed in the Auger spectrum can be linked not only to the existence of hydrogen bonding but also the strength of the collective network.

We mainly focus the analysis of our data on hydrogen bonding, but some conclusions about inter-molecular spacing and packing can also be drawn.

4.1 Auger Spectroscopy

Auger spectroscopy measures the secondary electrons emitted from a molecule due to the decay of the core hole state, that is created by an ionisation event. After core ionisation, of the 1s state for example, the system is left in a highly excited core hole (1s$^{-1}$) state. This excited state is very short-lived, with a lifetime on the order of a few femtoseconds, and will then decay by filling the core vacancy with an electron from the outer valence orbitals. The excess energy is dissipated by either the emission of a photon carrying the equivalent energy (fluorescence, X-ray emission) or by emission of a secondary valence electron, which leaves the molecule in a double valence-vacancy ($v^{-2}$) final state of charge (2+), the Auger process is sketched in Figure 4.1. Auger decay is considered to be a local process, as the core hole is localised on a single
Figure 4.1. Schematic of the electronic transitions involved in (a) photoionisation, (b) Auger decay, (c) ICD and (d) ETMD. The core hole excited state created in (a) is the initial state for the relaxation pathways sketched in (b)-(d). Both ICD and ETMS involve the electronic states of a neighbouring atom or molecule, and are therefore termed non-local autoionisation processes.

atom, which has its greatest overlap with valence orbitals localised on the same atom. The emission of the secondary electron is sometimes also referred to as autoionisation, which is mostly used when the excited system is neutral. The kinetic energy of the Auger electron, i.e. the secondary electron released upon the system’s relaxation, is not dependent on the energy of the photon creating the core hole, and only depends on the energy difference between the intermediate core-hole excited state and the doubly ionised final state. The chemical sensitivity of Auger, not only to the direct chemical environment and element, but also to the binding state e.g. on a surface was discussed in detail by Rye et al.\textsuperscript{88} Therein, the authors show that the analysis of the Auger spectra can be less ambiguous than the core-level chemical shifts observed in direct photoionisation. The same degree of information in terms of intermolecular binding could in principle be obtained \textit{via} the valence levels, however the delocalised nature of these states lead to a complex spatial average and lacks atom specificity. Since Auger electron spectroscopy combines the chemical selectivity of the ionisation that creates the core vacancy and sensitivity to the valence states that participate in any inter- and intramolecular interaction and bonding, it is particularly well suited for studying the local environment of a molecule and its interactions with other molecules. In addition, Auger spectroscopy provides temporal information about processes occurring on the timescale of the core-hole lifetime, i.e. a few femtoseconds.\textsuperscript{87}
The information we obtain from our spectra can be regarded as an average over multiple snapshots of local structures that are combined to yield the measured Auger spectrum. We can therefore only draw conclusions about the network and local structure of the system on average.

4.1.1 Non-local Decay

When the core excited molecule is embedded into a dense medium such as a solid or liquid, or even just in small molecular aggregates, the electronic states of its neighbouring molecules can become involved in the decay process. Such pathways are called non-local decay processes and are categorised, depending on the exact mechanism, into two main families: intermolecular coulombic decay (ICD)\(^{89-92}\) and electron transfer mediated decay (ETMD)\(^{93, 94}\). Schematics of these processes are shown in Figure 4.1.

In the case of ICD the secondary electron is liberated from a neighbouring molecule, and in ETMD the electron that fills the inner shell vacancy also originates from a neighbouring molecule. Because these processes lead to a distribution of the final state charge (2+) over two separate molecules, the energy of the final-state is lower compared with the local decay channel, where both final state charges located on the same molecule. The kinetic energy of the secondary ICD/ETMD electron is therefore increased relative to local Auger decay. The non-local channels we observe are ones with a sufficiently higher kinetic energy that they appear in a region where there are no local contributions. There may however well be more non-local transitions that merge with the continuum of transitions. What we observe and discuss in this work is thus a lower limit to how many non-local transitions there are.

4.1.2 Excited State Proton Dynamics

If the lifetime of the intermediate core hole state is long enough, some nuclear relaxation can occur before the electronic decay into the final state. Nuclear dynamics occurring on this timescale have been described previously in the literature, often under the name *ultrafast dissociation*.\(^{95-97}\) In the case of liquid water a proton transfer during the lifetime of the O 1s\(^{-1}\) intermediate state has been studied in detail by Thürmer *et al.*\(^{98}\) What is unusual about the ultrafast dissociation of water is that the O 1s\(^{-1}\) state is not dissociative in the gas phase, but dissociation becomes allowed in the hydrogen bonded condensed phase.

Any decay process involving such proton dynamics has been termed *proton transfer mediated charge separation* (PTM-CS),\(^{98, 99}\) since the loss of the positively charged proton decreases the total charge on the ionised parent molecule. This charge separation lowers the energy of the final state, which can be observed spectroscopically as an increase in kinetic energy of the sec-
Figure 4.2. Schematic energy diagram of the PTM-CS process, based on the work by Thürmer et al.\cite{Thürmer2015} After the initial core ionisation (green arrow) the (1h/O 1s\(^{-1}\)) system can either: (i) Decay directly via Auger into the (2h/v\(^{-2}\)) final state, denoted here by the purple arrow, or (ii) a proton is transferred to a neighbouring water molecule before the decay, leaving the initial molecule doubly ionised but only singly charged (\(\text{OH}^+ \cdots \text{H}_3\text{O}^+\)), shown by the dark blue arrow. Since in the latter transition the final state is lower in energy the emitted PTM-CS electron carries a higher kinetic energy. Secondary electron and therefore an increase of the relative intensity on the high kinetic energy flank of the Auger spectrum. The PTM-CS process and the involved potential curves are sketched in Figure 4.2.

In order to separate the PTM-CS feature from other non-local decay channels, deuterium is substituted for hydrogen in the sample. The higher mass of the isotope leads to decreased dispersion of the wave packet in the excited state, i.e. a higher percentage of states decays close to the ground state geometry.\cite{Thürmer2015} All other non-local processes that take place in the ground state geometry are unaffected by the isotopic substitution, as the geometric and electronic structure of the system is not significantly altered by the isotopic substitution, since the efficiency of these processes mainly depends on the interatomic distances. During the short lifetimes of the O 1s core-hole (4 fs), the proton is most likely not fully transferred to its nearest neighbour. It is more likely the O-H bond elongates towards a Zundel-like\cite{Zundel1930} structure in which the proton is shared between two molecules. The electronic decay then occurs in this partially proton-transferred geometry. This mechanism is outlined in the scheme below, where we use O 1s ionisation in a water dimer as an example. Non-covalent interactions, such as hydrogen bonds are denoted by ‘\cdots’, and elongated covalent
bonds by ‘···’. The second column shows the equivalent core approximation \((Z+1)\), where applicable:

\[
\begin{align*}
HOH & \cdots OH_2 \\
\downarrow & \text{O1s Ionisation} \\
HO(1s^{-1})H^{+} & \cdots OH_2 \approx (Z+1) HFH^{+} \cdots OH_2 \\
\downarrow & \text{Bond Elongation} \\
HO(1s^{-1}) - H^{+} & \cdots OH_2 \approx (Z+1) HF - H^{+} \cdots OH_2 \\
\downarrow & \text{Shared Proton} \\
HO(1s^{-1}) \cdots H^{+} & \cdots OH_2 \approx (Z+1) HF \cdots H^{+} \cdots OH_2 \\
\downarrow & \text{Electronic Decay} \\
HO(v^{-2}) & \cdots H^{+} \cdots OH_2 \\
\downarrow & \text{Charge Repulsion} \\
HO(v^{-2})^{+} & \cdots H^{+} OH_2
\end{align*}
\]

We may consider the initial elongation of the O-H bond in the intermediate state to initiate a proton transfer that completes after relaxation into the electronic final state. After autoionisation has taken place, the system is left with the final state charge of \(2^+\). In the case of ionisation in a hydrogen bond network, specifically, the ejected proton may then diffuse along the hydrogen bond network via a Grotthuss-like mechanism, further separating the two final-state charges.

The autoprotolysis upon core-level ionisation that takes place in hydrogen bonded systems such as water leads to the creation of additional free protons that are not present in the ground state. This means one can speak of X-ray induced acidity, similar to the photoacidity of X-H bonds reported in connection with HOMO-LUMO excitation.\(^{101}\)

Since the core-ionised state is not dissociative in the gas phase, we can assume that the creation of the core hole alone is not sufficient to drive the proton dynamics that are observed in the condensed phase. The ionised molecule needs to be embedded in an environment which has sufficient electron density \((\delta^-)\) close to the proton to stabilise the positive charge site created by the dissociation event. In the case of water the only possible partially negative site that can receive the proton in the dissociation process is the electron lone-pair orbital of the oxygen site. The proximity of the partial negative charge needs to be sufficient, while the mainly electrostatic interaction with the proton needs to be strong enough to lower the energetic barrier in the excited state to enable proton dynamics to occur. An electrostatic interaction strong enough to alter
the excited state potential to this degree would most likely be characterised as a hydrogen bond in the ground state, which is why we interpret excited state protolysis as an indication of hydrogen bonding. Our experiments therefore contain information about a ground state effect, namely hydrogen bonding, through its influence on the excited state potential and the resulting dynamic processes, since the formation of a hydrogen bond in the ground state brings two molecules into the geometry which is necessary for a proton to be transferred in the excited state.
4.2 Different Phases of Water

In this Section, our results on the influence of system temperature and size on the relative propensity of the different decay pathways, i.e. local, non-local and proton dynamics, are summarised. Using these propensities we attempt to draw conclusions about how the hydrogen bond network is affected when water is exposed to different conditions or environments.

The O 1s Auger spectrum of the water gas phase and of liquid water at low temperature, both H$_2$O and D$_2$O, have been described in the literature before, and the data presented here is used to outline our analysis and as reference spectra, since an absolute efficiency of the different processes was not determined, apart for the inner valence ICD efficiency presented in Paper VI. It is therefore not possible to determine the absolute strength of the hydrogen bond network from our data, but we report the propensity for proton dynamics in the O 1s excited state relative to what is observed for liquid water at low temperature. The propensity for proton transfer can be related to the average strength of the hydrogen bond network in the studied systems relative to one another, as outlined in Section 4.1.2.

We investigate the autoionisation region of amorphous solid water (Paper IV), liquid water at higher temperature (Paper III), and in clusters (Paper V) and (Paper VI) and compare them to the reference gases of gas-phase water and liquid water at low temperatures. Below, the different systems are first discussed individually and then compared to one another. An overview of the systems studied here is sketched in Figure 4.3.

4.2.1 Liquid Water

Our reference case for comparison is liquid water at low temperature, which has been discussed in the literature.\textsuperscript{98} The comparison to liquid water is useful because we can judge how the change in phase or composition disrupts or changes the nature of the hydrogen bond network. To outline how the Auger spectra are analysed and what information can be obtained from them, the case of liquid water is discussed in some detail first.

The Auger spectrum of the gas phase water has been studied in detail in many publications\textsuperscript{88,90,95,102} and can be seen in Figure 4.4. It consists of a main peak, corresponding to a 1b$_1$ - 1s transition and 1b$_1$ ionisation, which yields a secondary electron with the highest possible kinetic energy. The peaks at lower kinetic energy then correspond to transitions successively involving the inner valence states. These different relaxation pathways all occur involving the intramolecular electronic states of the ionised water molecule, and are referred to as \textit{local} transitions.

Local transitions can also take place in the condensed phase, but their spectrum is shifted in kinetic energy and broadened. Both of these effects can be traced back to the additional polarisation screening in the liquid phase: The
shift can be explained as a stabilisation of the final state charges by the polarisable neighbour molecules around the ionisation site that is only possible in the condensed phase. The broadening is related to the structural diversity in the first hydration shells of water, and to how sensitive the interaction between the ionised molecule and the neighbour molecules is to a change in the intermolecular distances. In liquid water the structure of the first hydration shell can fluctuate very strongly (otherwise it would be crystalline ice). The intermolecular interactions, i.e. hydrogen bonds, of water are particularly strong and directional, which means these fluctuations lead to large changes in the interaction between the different molecules. This in turn affects their ability to screen the charge created by the ionisation, leading to a very broad distribution in the strength of the screening effect and a corresponding broadening of the spectral peak.

The contribution of local transitions to the overall Auger spectrum to a condensed phase sample and the influence of screening is often approximated by both shifting and broadening the corresponding gas phase spectrum.\textsuperscript{103, 104} When comparing the gas phase and the liquid phase it becomes apparent that the liquid-phase Auger spectrum of water contains a significant shoulder on the high kinetic energy side of the main peak (local transitions), which clearly cannot be found in the (broadened) local Auger spectrum, see Figure 4.4.

\textbf{Figure 4.3.} Sketch of the different water systems that were studied in Papers III - VI
These transitions involve the electronic states of the neighbouring molecules around the ionisation site and are attributed to non-local transitions. As outlined in Section 4.1.1 the main relaxation pathways that contribute to this region are ICD and ETMD.

The isotopic substitution of deuterium for hydrogen leads to a significant change in the relative signal distribution in the Auger spectrum, namely an increase of the relative signal intensity in the spectral regions attributed to local transition and a corresponding decrease of relative signal intensity in the regions of non-local decay. The structure of heavy and light water does not differ significantly in terms of O-O distances and the propensity for the non-local ICD and ETMD channels is therefore not expected to change due to the isotopic substitution. The isotope effect has been attributed to proton dynamics in the excited state, as outlined in Section 4.1.2. We interpret our liquid water measurements in accordance with the discussion presented therein. Any redistribution of normalised signal intensity in the Auger region between H$_2$O and D$_2$O is attributed to the proton/deuterium migration in the excited state, with the larger mass of the deuterium leading to weaker dynamics. Both local and non-local transitions can occur in conjunction with proton dynamics, however it was highlighted in the initial publication that the change in final state energy due to the proton transfer is most likely more pronounced for local decay, as ICD and ETMD already lead to the spread of the final-state charge over more than one molecule.

4.2.2 Liquid Water at Different Temperatures

When the temperature of the liquid is raised, two effects are observed in the O1s Auger spectrum of water, as shown in Figure 4.4: Firstly, the non-local decay shoulder decreases relative to the local decay, and secondly the isotope effect, and therefore the proton dynamics in the excited state, is decreased. The change in the local/non-local decay propensity can be explained simply by a change in water’s local structure and intermolecular distances due to the increased temperature: The density of the liquid is decreased at larger temperatures, which makes the non-local processes less likely to occur (ICD scales with $\frac{1}{r^6}$, and self-diffusion is also increased in the liquid, making it more likely that the hydration shell around the ionisation site is in a transient non-saturated geometry of weaker net hydrogen bonding.

The influence of the added entropy on the intermolecular structure also manifests itself in the proton dynamics that occur in the system: Since fewer molecules are found in a tetrahedral hydrogen bond environment, the PTM-CS contribution decreases as the temperature is raised. This reflects the weakening of intermolecular coupling via hydrogen bonding, and macroscopic changes related to the hydrogen bonding network of the liquid such as e.g. the decreased viscosity and increased self-diffusion. Even when a molecule is
Figure 4.4. O 1s Auger spectra of (from bottom to top): gas phase H$_2$O, amorphous solid films of H$_2$O and D$_2$O, liquid H$_2$O and D$_2$O, liquid H$_2$O and D$_2$O at elevated temperature, large H$_2$O and D$_2$O clusters, and small H$_2$O and D$_2$O clusters. The dashed light blue lines mark the region used to normalise the traces relative to one another. The data sets were shifted relative to each other to overlap the maximum of their H$_2$O Auger spectrum with the one of liquid water, as indicated by the grey dotted line. This is necessary to correctly normalise their respective area. A gas phase contribution has been subtracted from the two liquid systems. The two cluster phase data sets still contain some contribution from the monomer, that can be seen in the large cluster case as a shoulder on the high kinetic energy side of the main peak.
engaged in a hydrogen bond the intermolecular motion is likely more pronounced, since some of the lower energy intermolecular rotations and librations become more populated with increased temperature. It has been shown previously that both the hydrogen bond length and angle are affected by an increase in the system’s temperature.\textsuperscript{78}

4.2.3 Amorphous Solid Water

Compared to the crystalline structure of ice, amorphous solid water (ASW) shows no long range order, but rather a disordered arrangement reminiscent of liquid water, but lacking the high diffusion found in the liquid phase. ASW has therefore been used as a structural analogue of liquid water in the past,\textsuperscript{106} but the question remains how much the lack of self-diffusion affects the intermolecular structure.

The close resemblance of the oxygen lattice between liquid water and ASW leads to the expectation that the hydrogen bond network is structurally similar in the two phases. It is therefore predicted that the Auger region of ASW also features an isotope effect in the high kinetic energy flank.

The O 1s Auger spectrum of both normal and deuterated ASW is shown in Figure 4.4. The general shape of the spectrum is very similar to liquid water, with a prominent main peak, corresponding to local Auger decay and a significant non-local decay shoulder at higher kinetic energy. The relative intensity of the non-local shoulder is somewhat larger in ASW than in liquid water, indicating that a higher fraction of core holes decay \textit{via} a non-local channel. The isotope effect is very similar to liquid water as well, with more relative signal intensity redistributed to the local Auger spectral region when deuterium is substituted for hydrogen. The magnitude of the effect is however smaller than in liquid water, which means that a smaller fraction of core holes decay in a partially proton-transferred geometry, which we attribute to a weaker overall hydrogen bond network.

The changes in the relative non-local and PTM-CS fraction of ASW compared with liquid water can be explained as follows: In liquid water there is enough diffusion and mobility of the water molecules, which makes the network more flexible to optimise the local hydrogen bond environment. The bulk ASW film was formed by depositing vapour onto a cold surface (98 K), which can be considered to freeze the molecules in the random orientation that they arrive in, allowing for minimal structural relaxation or rearrangement. This means that while the long-range structure of ASW closely resembles the disordered structure of a liquid-like phase (rather than the highly ordered structure of crystalline ice) it is not able to replicate the locally ordered structure that forms when the system relaxes to optimise for strong intermolecular hydrogen bonds. Since the density of ASW is slightly less than that of liquid water (0.94 g/cm\textsuperscript{3}),\textsuperscript{107} the larger non-local contribution cannot simply be assigned to an increased
number density of neighbours around the ionised molecule. Perhaps the more disordered local structure of ASW features a larger spread in O-O distances, i.e. more nearest neighbour molecules at both shorter and longer distances, compared with liquid water. In this case the increased population at short distances would significantly affect the propensity for non-local decay, since ICD scales with \( \frac{1}{r^{105}} \).

In summary, our results show that while ASW is qualitatively a good model for liquid water, in terms of the spectral observation of non-local decay and proton dynamics in the excited state that resemble the liquid phase, the propensity of the different decay channels is somewhat different, an effect we tentatively assign to the absence of tetrahedral ordering in the local structure.

4.2.4 Water Clusters

Clusters show a number of size dependent properties, which affect the hydrogen bond network, mainly due to confinement effects and their high surface-to-volume ratio. Within these confined geometries we can therefore explore how the hydrogen bond network develops at different cluster sizes.

4.2.4.1 Core Hole Decay

We obtained O 1s Auger spectra of two size regimes of clusters, small and large, which are shown in Figure 4.4. Compared to the liquid water spectrum there are some noticeable differences. Firstly, the non-local decay shoulder is less pronounced in the cluster phase; The contribution from non-local decay processes to the total Auger spectrum is smallest in the small cluster conditions, and increases with cluster size. This can be rationalised straightforwardly, as clusters have a large surface-to-volume ratio which means a larger fraction of molecules don’t have a full hydration shell, and hence less neighbour-molecule density around them. This will reduce the probability for non-local decay as a function of the surface-to-volume ratio. Water surfaces are also known to have a lower density than the bulk,\(^{54}\) which means the nearest neighbours in the surface region are further apart, again lowering the probability for non-local decay.

When comparing the O 1s Auger H\(_2\)O and D\(_2\)O cluster traces to those of liquid water, there are qualitatively similar but quantitatively smaller differences in the relative signal distribution. The isotope effect is significantly weaker in small clusters than in large clusters. In the larger clusters we observe an isotope effect which is comparable in magnitude to the effect observed in bulk liquid water. The hydrogen bond network of the clusters is strained both due to the high surface fraction of molecules that have dangling OH bonds, but also due to the confinement effects that occur in the small quasi-spherical cluster shape, which hinders the formation of a strong/liquid-like hydrogen bond network. It does appear, however, that these effects only influence the hydrogen
Figure 4.5. Summary of the two competing relaxation pathways after photoionisation. The water dimer can relax via ICD, or transfer a proton to a neighbouring molecule during the lifetime of the inner valence hole, which is on the order of tens of fs.\textsuperscript{110,111} This transfer closes the ICD channel and the excess energy is emitted via internal conversion. The ICD process is also shown in Figure 4.1.

bond network of smaller clusters, and the network converges to bulk at relatively small sizes. This is in line with the fast convergence to bulk observed for water compared with other solvents, in terms of its valence binding energy,\textsuperscript{108,109} and indicates that the hydrogen bond network forms very quickly in water and is quite robust to the strain the confinement of the cluster geometry introduces.

4.2.4.2 Inner Valence Ionisation Decay

In this study, the size dependent ICD efficiency of water clusters after inner-valence 2a\textsubscript{1} ionisation was investigated. The ICD efficiency is less than unity for all cluster conditions studied, and its value decreases with decreasing cluster size. Furthermore a comparison of heavy and light water clusters shows that the ICD efficiency exhibits a considerable isotope effect, with a higher efficiency in heavy water. This isotope effect is attributed to a dynamic process, reminiscent of proton dynamics upon core level ionisation (PTM-CS), competing with ICD decay.

Before addressing the nature of this competing process, we consider the case of very small clusters (average size $\langle n \rangle < 10$ molecules). In this case the low ICD efficiency can be explained quite readily: For small clusters there are simply much fewer neighbours around any given water molecule compared to large clusters or bulk water. This then lowers the possibility for energy transfer to another molecule to occur, both due to the scaling of ICD propen-
sity with $\frac{1}{25}$ and because of the decreased density of neighbour molecules around the ionised site. This is also why the ICD efficiency for water vapour is 0 by definition; there simply isn’t sufficient molecular density around the excited molecule. This lowering of the efficiency due to lack of neighbouring molecules is estimated to saturate relatively quickly as the cluster size increases, after a few tens of molecules. However, there will always be a fraction of unsaturated molecules at the interface, which will lower the total ICD efficiency for particles with a large surface:bulk ratio.

In order to investigate how proton transfer after ionisation could influence the valence ICD process, the potential energy surfaces of a water dimer along the O-H coordinate were obtained for different electronic states, as shown in Figure 2 of Paper IV. The 2a$_1$ singly ionised state of the dimer has a negative slope, which indicates that the state is indeed dissociative and proton dynamics take place upon ionisation, qualitatively reproducing the dynamic processes observed after O 1s ionisation. It can also be seen that the decay into a doubly ionised state via ICD is only favourable ($\Delta E < 0$) for O-H bond lengths up to 1.3 Å. In other words: the elongation of the O-H bond effectively closes the ICD channel, after which the excess energy of the excited state is dissipated via a different pathway, which does not involve the emission of an electron, as sketched in Figure 4.5. Since the heavy system disperses more slowly along the O-H/D axis$^{112}$ the ICD-capable population is more long lived in D$_2$O than H$_2$O; the ICD channel remains open longer in heavy water, allowing more states to decay and thereby increasing the efficiency of the process.

The proton transfer responsible for the closing of the ICD channel mirrors the dynamics observed in water after O 1s ionisation;$^{98}$ together with the presented experiments, these studies highlight the substantial influence of proton dynamics along the hydrogen bond on the auto-ionisation process in water. In the valence region, the pronounced influence of proton transfer/structure on the energetics of the system becomes clear, since the migration of the proton in the excited state can not only change the energy of a final state, but even close a decay channel. The change in geometry therefore changes the energetic ordering of the states.

4.2.5 The Hydrogen Bond Network of Water under Different Conditions

Here, a short summary and discussion of the results obtained for water studied under different conditions and in different phases (ASW, clusters, and liquid) is provided. As we have seen, the post-ionisation decay of water is highly sensitive even to subtle changes in the structure of the intermolecular network, as manifested in the electronic structure of the liquid. We use the relative propensity for local and non-local decay to evaluate any changes to the average O-O
distance that occur in the different phases and the normalised isotope effect (PTM-CS) to study the strength of the hydrogen bond network.

In ASW, the water molecules cannot relax their local structure to form tetrahedral hydrogen bond structures, as they are frozen as soon as they are deposited, which means there is also no local order, but it is a fully disordered structure more akin to a very dense gas. We observe an increase in the non-local decay contribution, but the lack of short-range tetrahedrality reduces the amount of proton dynamics that can take place in the excited state.

The average strength of the hydrogen bond network in water, as studied by its proton dynamics in the ionised excited state, is decreased by not only the temperature of the sample, but also the strained structure and surface/bulk ratio of cluster systems. Similar influence of proton transfer on the relative energy difference of the different states can be observed in the valence region, however since the states are much closer in energy to begin with, the proton dynamics actually lead to a state crossing which closes an autoionisation channel.

This work indicates that the hydrogen bond network is sensitive to even subtle changes to the system, which is reflected in the propensity for different decay channels after ionisation.
4.3 Amphiphilic Liquids

In this Section we study how a hydrophobic disruption to the hydrogen bonding capabilities of the individual molecules manifests itself in the intermolecular network of the liquid and its postionisation decay.

We choose to study methanol, which is related to water via the substitution of one proton by a methyl group, thereby removing one of the hydrogen bond donor possibilities from the oxygen site of the molecule. When the methyl group is introduced to the molecular environment the remaining alcohol hydroxyl group has been shown to still largely mimic the behaviour of water, both in its acidity (slightly more acidic than water in the gas-phase but almost the same in solution\textsuperscript{113}) and electronic structure,\textsuperscript{88} apart from the new state/orbital introduced by the covalent bond. In the same vein, the methyl group has been shown to be very close in its behaviour to methane.\textsuperscript{88} This means that the methanol molecule can be abstracted to be an ideally hydrophobic (CH\textsubscript{4}) and an ideally hydrophilic (H\textsubscript{2}O) sub-unit, that are linked together by a single bond. Molecules that combine both hydrophobic and hydrophilic properties are referred to as amphiphiles, and we use methanol as a model system for this group of molecules.

The vastly different character of the two functional groups gives rise to a certain tension in the behaviour of the molecule, as it has to optimise the interaction of its two very different subgroups with the environment through the intermolecular structure. The tension between hydrophilic and hydrophobic interaction is known to be responsible for emergent phenomena in larger amphiphiles such as surface or micelle formation,\textsuperscript{114} which segregates the homogeneous bulk into domains of hydrophilic and hydrophobic interaction. In the bulk, liquid methanol forms 2D chains of molecules, with the individual hydroxyl group participating in two hydrogen bonds, both donating and accepting one.\textsuperscript{115}

We want to investigate how the influence of the hydrophobic group is manifested in the average strength of the intermolecular network, and whether the liquid is able to maintain a strong network despite the considerable disruption the methyl groups represent.

4.3.1 Liquid Methanol

We investigate both the O 1s and C 1s Auger spectrum of methanol, to study the behaviour of the two different functional groups in the liquid phase. In these spectra we analyse both the changes in PTM-CS and also the non-local decay channels, as they modulate strongly with the intermolecular distances to the nearest neighbours. The analytic approach is the same as outlined for the water data presented in Section 4.2. We interpret a change in the local to non-local decay ratio as an indication of changes to the local packing density of the molecules, and changes in the PTM-CS propensity as an indication of
Figure 4.6. Possible decay channels discussed in this work. Decay paths after carbon ionisation are indicated in green, and the corresponding channels at the oxygen site are shown in purple. The emitted photoelectrons (PE) and secondary electrons are shown in dark blue. The majority of excited states decay via a local pathway (centre). The static non local decay mechanism (C1 and O1) shown here is ‘interatomic coulombic decay’ (ICD) but this pathway also includes ‘electron transfer mediated decay’ (ETMD). The pink and blue wavy arrows (C1 and O1) indicate the energy transfer of the ICD process. Any decay that occurs in conjunction with proton dynamics is denoted as C2 and O2 here. This figure shows the example of local Auger decay in a proton-transferred structure (PTM-Auger), but proton dynamics can also precede the other non-local decay channels mentioned above.

the average hydrogen bonding around the oxygen or carbon site. The different decay mechanisms we consider in this work are sketched in Figure 4.6. The carbon and oxygen site of methanol show different propensities for local and non-local post-ionisation decay channels. While the main decay channel of C 1s−1 and O 1s−1 vacancies is still the local Auger pathway, a larger subset of the O 1s−1 states decay non-locally through a mechanism that involves the electronic states of its immediate neighbours. This different propensity for local/non-local decay means that the 2+ charge of the final state is either more localised in the case of C 1s ionisation or more delocalised in the case of O 1s ionisation. As previously mentioned, the local structure around the ionisation site determines the relative decay channel propensity. Carbon mainly decays via local pathways because of its weak intermolecular interaction with its neighbours, and the resulting larger distances to the next atom. Conversely the oxygen site decays non-locally to a higher degree, because of its strong, directional intermolecular interactions which decrease the distance to the next atom.
The isotope effect observed in the O 1s Auger of methanol is very similar to the
effect that has been previously described for water. Proton transfer during
the 1s\(^{-1}\) excited state appears to be a general pathway, that is not unique to
water, as long as strong intermolecular interactions such as hydrogen bonding
lower the barrier for a shared Zundel-like proton state to be formed between
both participating molecules. Both in the case of \(\text{-CH}_3\) and \(\text{-OH}\) a significant
isotope effect, and therefore propensity for C-H or O-H bond dissociation,
has been observed. This dissociation allows for a delocalisation of the 2+
final state charge without involving the electron density of the neighbouring
molecules in the decay process.

While water and methanol show different dissociation constants in the ground
state, their behaviour becomes more similar in the core excited state which we
have studied here. An additional driving force for dissociation in the excited
state is present in both methanol and water. Excited state C-H or O-H dissocia-
tion appears not to be dependent on ground state dissociation, but they both
need the same geometry, namely a hydrogen-bond-like arrangement in which
an oxygen lone-pair is positioned on axis with the C-H or O-H bond.

4.3.2 Domain Formation

In methanol an unexpectedly large isotope effect in the C 1s Auger spectrum of
the methyl group is observed. This may be attributed to one of two effects or,
more likely, a combination of both: Firstly, since the proton dynamics in the
excited state have been linked to hydrogen bond formation, one could simply
argue there are more C-H···O hydrogen bonds formed in the liquid than antici-
pated, or that the simple spatial proximity to the hydroxyl group is enough
to lower the barrier for proton transfer. Since each oxygen accepts on average
only one hydrogen bond in methanol, the hydroxyl groups could in principle
accept a dissociating proton \(\text{via}\) the unoccupied hydrogen bond acceptor site.
Secondly, the loss of a proton most likely induces a significant structural rear-
grangement of the carbon site, which would only have three covalently bound
partners upon protolysis. This makes it more favourable for the group to move
towards a planar sp\(^2\) geometry. Since dissociation now involves the dynamics
of not one but three hydrogen sites, one might expect a larger difference in the
excited state dynamics. Such rearrangement has been shown to produce an
isotope effect in solvated ammonia.\(^{116}\)

The change in local environment around the methyl and hydroxyl groups, as
reflected in the changed non-local decay propensity, can be explained by the
differences in molecular interaction of these two functional groups: As previ-
ously outlined, the hydrophilic hydroxyl group still largely behaves like wa-
ter, and forms strong intermolecular hydrogen bonds with the neighbouring
sites, which reduce their intermolecular distance. In contrast, the hydrophobic
methyl group cannot form the same strong intermolecular bonds, and behaves
essentially like a methane molecule. The absence of any strong interactions with the neighbouring sites is reflected in the large intermolecular distances around this group.\textsuperscript{115}

The O-H···O hydrogen bonds are the strongest mode of inter-molecular interactions in liquid methanol. The system will therefore adjust its structure to optimise for these hydrogen bonds and minimise the disruption from the methyl groups to the forming hydrogen bond network. It has been shown in both experiment and simulation\textsuperscript{115,117,118} that this favouring of hydroxyl self-interaction leads to the formation of transient chains and rings of -OH groups that have strong but small local hydrogen bond networks. The methyl groups are therefore expelled from these regions, making them very oxygen-dense compared to the average composition of the bulk. The clustering of the hydroxyl groups also has the result that the methyl groups will form carbon dense layers around the hydrogen bond regions. We refer to these two different local regions as hydrophilic (-OH) and hydrophobic (-CH\textsubscript{3}) domains. When the system is at low temperature, and there is only weak thermal excitation and no diffusion, i.e. methanol ice, these local domains grow into the long-range 2D chains that characterise the crystal structure.\textsuperscript{119}

The described liquid structure clearly deviates from the structure that would be predicted by pure molecular packing, which disregards specific, directional interactions effectively treating the system as a non-associated liquid. Compared to water, the introduction of a methyl group into the liquid is therefore a significant disruption to the molecular network. As a result, the hydrogen bond network of methanol is not as extensive as the one found in liquid water, where almost all molecules are essentially part of the same network, but rather consists of a collection of local, transient domains of hydrogen bound hydroxyl groups, which take the form of small aggregates of molecules arranged as rings and chains.\textsuperscript{115,120} These emergent structures are formed to enable the liquid to maintain strong intermolecular hydrogen bonds. The ordering these structures introduce to the liquid goes beyond the hydration shell structure that is also found in liquid water, but the liquid remains effectively homogeneous, since the domain formation is both microscopic and transient.

4.4 Micro Segregation in Mixed Liquids

4.4.1 Dimethyl sulfoxide and Glycerol

Cryoprotectant molecules are known to strongly affect the macroscopic properties of water, most prominently its freezing point\textsuperscript{121,122} and viscosity,\textsuperscript{123–125} two properties that are commonly linked to the hydrogen bond network of the solution. Since cryoprotectants have such a pronounced colligative effect on the macroscopic freezing behaviour of the liquid, there should be a related change to the microscopic hydrogen bonding network of the solution. Here we have studied the influence of two common cryoprotectants,
Figure 4.7. Difference traces of the O 1s Auger spectra of DMSO and glycerol, compared with their non-deuterated analogues. Panel (a) shows the glycerol/water and (b) the DMSO/water mixtures. In both panels the pure water trace is shown in dark blue. Panel (c) summarises the relative isotope effect ($\Delta_{PTM-CS}$).

Dimethyl sulfoxide$^{122}$ and glycerol$^{121}$ on the hydrogen bond network, through their influence on the postionisation processes observed in the O 1s Auger spectrum.

O 1s Auger spectra were obtained for both glycerol (6 mol% and 11 mol%) and DMSO (10 mol% and 50 mol%) in water, to compare with the equivalent spectra of pure water. We observe an isotope effect in all systems, but the magnitude of the PTM-CS feature varies strongly across the different samples. For comparison, the normalised difference traces are shown in Figure 4.7 (a) and (b). The addition of cryoprotecting molecules reduces the propensity for proton dynamics to occur in the excited state, while the shape of the difference trace is unaffected by changes of the molecular composition. The normalised absolute value of the area under the difference trace is used to compare the average strength of the hydrogen bond network in these systems, see Figure 4.7 (c). Both glycerol concentrations and the lower DMSO concentration have a similar influence on the hydrogen bond network of the solution, lowering the observed isotope effect by approximately 20%. The 50% DMSO solution, however, has a much more pronounced influence, lowering the observed isotope effect by almost 80%.

For mixed systems, a major contribution to the decrease of the isotope effect relative to water is most likely the reduction of possible O-H⋯O hydrogen bonds that can be formed per oxygen site in the mixed sample. Since the number of hydrogen bond acceptors (oxygen lone pairs) is larger than the number of hydrogen bond donors (-OH groups) in the mixed systems, we focus on the latter to estimate the reduction in the number of possible hydrogen bonds. However, the reduction in the number of possible hydrogen bonds in the mixed systems compared with pure water is not sufficient to explain the decrease in
the relative isotope effect we observe in our experiments, indicating there must be additional effects contributing to the lowering of the excited state proton dynamics. The fraction of possible hydrogen bonds formed in the liquid is therefore further reduced by some other effect the co-solvents introduce. This additional effect is most likely connected to the disruption introduced to the hydrogen bond network by the apolar functional groups of the cryoprotecting molecules, effectively reducing the number of hydrogen bonds that can be formed in the liquid. We refer to this additional effect as the *steric hindrance* of the apolar groups. Under the term 'steric hindrance' we include any effect obstructing hydrogen bond formation by keeping the donor and acceptor groups from coming into spatial proximity, due to e.g. the cavity formation around apolar groups.

4.4.2 Microsegregation and Incomplete Mixing

Aggregate formation in mixed aqueous liquids are hypothesised to be driven by the water hydrogen bond network, which tries to exclude hydrophobic groups to optimise for water/hydroxyl interactions.\(^{126}\) Such segregated geometries minimise the disruption to the hydrogen bond network caused by the co-solvents, compared with a homogeneous distribution of molecules, meaning that the better a co-solvent can integrate into the hydrogen bond network, the fewer aggregates will be found in the solution and the smaller they will be. For glycerol, it has been shown that in mixtures as dilute as 5 mol%, only 40% of the glycerol molecules are found as monomers, with the remaining 60% forming dimers or larger aggregates.\(^{127}\) The molecules forming these aggregates maintain strong hydrogen bonding with the surrounding water via their hydroxyl groups, and arrange their hydrophobic backbone towards the centre of the aggregate.\(^{126}\)

In DMSO/water mixtures similar effects were observed, namely the formation of complexes in which the DMSO molecules align along their S=O bond and the oxygen sites form hydrogen bonds with the surrounding water molecules, whereas the \(S(CH_3)_2\) groups aggregate together,\(^{128}\) only weakly interacting with the surrounding water molecules.\(^{129}\) In the case of the 10 mol% DMSO solution studied here, most DMSO molecules will accept one hydrogen bond from water.\(^{130}\) At higher concentrations of DMSO, such as the 50 mol% solution studied here, the self-interaction of the DMSO molecules is even more enhanced, leading to the formation of dimers that only interact with each other via intermolecular O⋯S interactions and don’t participate in any hydrogen bonds with water.\(^{130}\) The aggregates are then excluded from the hydrophilic phase, forming DMSO domains. The aggregation of the DMSO molecules can therefore lead to the formation of a surface-like layer of water molecules around the hydrophobic aggregates.\(^{131,132}\) In the case of true phase boundaries, such hydrophilic/hydrophobic interfaces often lead to the formation of
so-called dangling -OH groups of the water molecules residing on the interface, and thus unable to form hydrogen bonds.\textsuperscript{32,133} The formation of hydrophilic/hydrophobic interfaces on the molecular scale leads to a strong increase in the steric hindrance. This micro-segregation of hydrophilic entities from the hydrogen bond network is reminiscent of the behaviour we observed in methanol. Combining the observations of these two studies we can speculate that any groups or molecules that cannot integrate well with the hydrogen bond network are expelled from it, forming small transient domains or aggregates, in order to minimise their disruption to the hydrogen bond network. This pronounced preference of the system to optimise its intermolecular structure for hydrogen bonding is what drives the formation of these domains and aggregates.
5. Summary and Conclusions

In this thesis, results from spectroscopic studies of surface structure and hydrogen bonding in aqueous and related systems using surface-sensitive XPS and Auger spectroscopy have been presented. Perhaps the most surprising result of this work is the finding that the surface propensity of halide anions in water is increased at raised temperature. This is unexpected, since it was previously predicted by molecular dynamics simulations that the surface enrichment of ions should decrease at higher temperature, and also because the idea that an increase in entropy is found to accompany increased solute surface structuring is somewhat counter-intuitive. We also find an influence of the specific anion/cation interaction on the temperature-dependent surface propensity of cations, which has not been observed before. The ion/ion interaction has often been disregarded as negligible when describing the driving forces of ion surface propensity, but our results show the ion-ion interaction plays an important role in determining the surface propensity of alkali metal cations as a function of temperature.

When comparing the surface structures of wet and dry aerosols derived from the same parent solution, we found these can show very different ion distributions. In liquids, different surface-enriched compounds can co-exist at the interface, whereas in dry systems typically a single species becomes favoured. We link this observation to the fact that different salts effloresce at different relative humidities as the aerosol dries, leading to the formation of core-shell type structures in the dry solid particles. Wet surface structure is therefore not always a reliable indicator of dry surface structure.

In the second part of the thesis, a summary of projects regarding the hydrogen bond network of water in different environments, as well as methanol and solutions of cryoprotecting molecules were presented and discussed. The O 1s Auger spectra of different hydrogen bonded systems were studied, with emphasis on the proton dynamics that can occur during the lifetime of the core hole. These dynamic processes were linked to the strength of respective system’s hydrogen bond network. In the case of water, the average strength of the hydrogen bond network was studied in different environments, namely clusters of different sizes, liquid water (at two different temperatures), and amorphous solid water. The normalised isotope effect, and therefore the strength of the hydrogen bond network, was compared with liquid water. While many of the results confirm existing predictions in the literature, namely that heating water decreases its hydrogen bond network strength while in clusters the hydrogen bond network is weakened by their constrained geometry, it
is noteworthy that the postionisation decay processes observed in the Auger spectrum are sensitive to these changes in intermolecular interaction, making it well-suited to study the subtle changes that can occur in the liquid phase, as a complementary approach to other more well-established techniques. In special cases, knowing the phase of an aqueous system is not sufficient to predict the strength of the hydrogen bond network, for example in amorphous solid water the lack of local ordering/tetrahedrality makes the hydrogen bond network weaker than the liquid, even though there is no thermal disorder. The effect of excited state proton dynamics along a hydrogen bond was also studied after inner valence (as opposed to core-level) ionisation of different-sized water clusters. It was found that the change in the O(2a−1)-H distance distorts the electronic structure of the system to the point that the electronic inner valence decay (i.e. ICD) becomes energetically unfavourable and the ordering of the states is inverted.

In methanol and mixtures of cryomolecules with water, we found that the network is surprisingly robust, even when hydrophobic groups are admixed with the liquid. In these systems, a hydrogen bond network is able to form even when there is significant disruption, however the preferred self-interaction of water gives rises to unique transient/dynamic local structures such as microsegregation.

Hydrogen bonding in water is both a strong intermolecular interaction that imposes ordering on the local molecular environment, but not strong enough that it restrains the system into one rigid geometry (at room temperature). This allows for both order (local structure) and disorder (diffusion and dynamics) to influence the system approximately equally. When the balance of order/disorder is disrupted (e.g. by addition of solutes or surface formation) counter-intuitive or anomalous effects such as transient microsegregation in a homogeneous mixture, or increased surface structuring at high temperature can occur.
6. Outlook

This work has uncovered further questions about the nature of hydrogen bonding networks in water and surface enrichment of solutes. In particular, our investigation of temperature-dependent surface enrichment highlights the previously overlooked role of the counterion on the surface propensities of cations in the case of alkali halides dissolved in water. This raises the question to what extent ion-ion interactions near the interface may be more important than previously appreciated in other similar systems. Future work in this area could look at whether ion pairing occurs to any significant degree near the interface, and whether the driving forces for ion pairing might be an important factor determining surface propensities at different temperatures. Since we have seen that increased entropy can actually increase apparent structuring at the surface, perhaps entropy also plays a major role in driving such ion pairing as well.

A major future goal would be to construct a general model for describing and predicting ion surface enrichment across a range of different systems, incorporating all the necessary driving forces including those uncovered and discussed here. It would also be instructive to test whether the temperature effect observed in the case of alkali halides is also seen in different systems such as enrichment of polyatomics and organic molecules. For the work covered in the second part of the thesis exploring hydrogen bonding, our work on PTM-CS could also be extended to other phases of ice to see whether similar effects can be observed there, and if so, whether and how the behaviour differs. It will be necessary to quantify the PTM-CS response relative to hydrogen bond strength, with the eventual goal that the technique could be used as a quantitative measure of hydrogen bonding in a range of condensed systems. We will also need to test the limits of the PTM-CS technique, where it is applicable and where it fails, in order to fully appreciate its utility as a technique and help place it alongside other existing techniques in the toolbox of complementary methods for probing hydrogen-bonded systems.
7. Experimental

7.1 Electron Detection
Electrons are routinely detected using a microchannel plate (MCP) detector, which is based on the impinging electron triggering an electron cascade in the channels of the detector. This cascade acts as an amplifier so that the signal can be detected on either an anode or a phosphor screen. In the case of a delay line detector, the anode has the shape of a grid, which allows the detection of all three dimensions of the electron’s velocity, if the impinging electron rate is sufficiently low. What distinguishes the methods discussed below is not so much the method of electron detection, they are in fact all using MCP detectors, but the way electron kinetic energies are resolved. This can be achieved by resolving the electrons temporally as in a time-of-flight spectrometer or spatially as in the hemispherical analyser. Below, three different electron spectrometers are presented. The Hemispherical Analyser is used in Papers I, II, III, V, VII and VIII. The magnetic bottle and ArTof Spectrometers are both well suited to record electron/electron-coincidences. They are used in Papers VI and IV; however only the former makes used of the coincidence capability of the spectrometer.

7.1.1 Hemispherical Electron Energy Analyser
The hemispherical electron energy analyser consists of two concentric hemispherical electrodes (inner and outer hemispheres) held at fixed voltages. The electrons that enter the hemisphere are linearly dispersed along the axis connecting the entrance and exit aperture based on their kinetic energy. This spatial dispersion of the electron distribution is then mapped using an MCP coupled to a fluorescence screen. The fluorescence signal is recorded by a CCD camera and converted into a 2D map of the electrons recorded as a function of the kinetic energy.

7.1.2 Magnetic Bottle Spectrometer
The magnetic bottle spectrometer is, in essence, a time-of-flight (ToF) spectrometer in that the information about the electron kinetic energy is contained
The important distinction between these two spectrometers is the mechanism of resolving the kinetic energy of the electron: (a) spatial dispersion in the field of the hemisphere and (b) temporal resolution via the flight time in the spectrometer tube. Another important difference is that (a) allows for continuous operation, while (b) requires a pulsed light-source.

in the temporal distribution of the electrons arriving at the detector. However, it differs from the typical Wiley-McLaren ToF setup\textsuperscript{135} as the gaseous sample is ionised in the presence of a strong inhomogeneous magnetic field, which helps to collect a very large solid angle of the emitted electrons, and not an electric extraction field. The magnetic bottle spectrometer also uses a weak homogeneous magnetic field in the drift tube to guide the electrons.

To be able to obtain information on the efficiency of the ICD process one needs to be able to relate the ICD electron back to its parent photoelectron. This is possible if one performs an electron-electron coincidence experiment. In this experiment a pulsed light source is used and the light intensity is lowered, such that only one photoelectron is created per light pulse. Any other electrons being detected from the system during the same period are in coincidence with the photoelectron, and assumed to be a product of the same initial photoionisation event. The coincident electrons are then plotted in a \textit{coincidence map}, an example of which is given in Figure 7.2. The experimental setup is described in detail by Mucke \textit{et al.}\textsuperscript{134}
7.1.3 ArToF Spectrometer

The ArToF spectrometer is also a variation of a time-of-flight spectrometer, but instead of a field-free flight region it uses a complex electrostatic lens system to simultaneously obtain information about an electron’s kinetic energy and its angle of emission. This is achieved by every arrival point on the delay line detector corresponding to a defined flight path in the system. The arrival position and time on the detector can therefore fully characterise the electron kinetic energy and momentum.

7.2 Sample Delivery

7.2.1 Liquid Jet

For the study of volatile liquid samples a liquid jet\textsuperscript{136} setup is employed. The liquid jet (LJ) is generated by pushing the sample solution through a converging quartz capillary, referred to as the liquid jet nozzle, at a constant flow rate ($\sim 1$ ml/min). The diameter of the liquid jet is determined by the diameter of the nozzle ($d = 20-25 \, \mu m$) at the rip-off-point (i.e. when the liquid exits the nozzle into the vacuum of the chamber). The LJ is characterised by two distinct regions: After the rip-off the jet displays a laminar flow (for $\sim 10$ mm) which then degrades into turbulent flow and subsequent breakup into a diffuse droplet train. After the rip-off, the temperature of the LJ is lowered by evaporative cooling in the vacuum of the experimental chamber. This cooling rate

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7_2.png}
\caption{Coincidence map of water clusters with average size $\langle n \rangle = 65$. Each coincidence event is plotted as a function of the kinetic energy of the fast ($e_1$, x-axis) and slow ($e_2$, y-axis) electron. The ICD flank studied in Paper VI can be seen as the bump in intensity at 31 eV kinetic energy of $e_1$.}
\end{figure}
is not well determined for jets larger than 10 \( \mu \)m diameter due to a cut-off in the maximum radial ablation rate.\textsuperscript{53} This means that the effective temperature of the surface cannot be predicted easily. Using the (bulk) temperatures of a liquid water jet in vacuum, presented by Wilson et al.,\textsuperscript{53} we estimate the bulk cooling of the jet \( \Delta T \) to be on the order of 15 °C between rip off point and ionisation volume. The liquid jet is used in Papers I, II, III VII, and VIII.

### 7.2.2 Supersonic Expansion

When a gas stream of molecules is expanded into vacuum at a sufficiently high stagnation pressure, the supersonic expansion becomes supersaturated and the molecules can condense into small molecular aggregates or clusters held together by van-der-Waals interactions, and hydrogen bonds if possible. The sample can be co-expanded with a carrier gas (helium or nitrogen) which, as well as cooling the expansion nozzle, leads to more efficient condensation and a larger average cluster size. The cluster size created in an expansion can however not be determined in a straight forward manner, but scaling laws\textsuperscript{137} can be used as a first approximation of the average cluster size. This technique is used in Paper V and VI.

### 7.2.3 Aerodynamic Lens

For the study of particles larger than 10 nm a supersonic expansion can no longer be used. The particles are instead generated in an atomiser (impact
atomiser), transported by a gas stream, and introduced into the vacuum cham-
ber via an aerodynamic lens.\textsuperscript{138,139} The aerosol particles are focused by the 
oscillatory motion of the gas stream, as it is guided through a number of ori-
fices. This source is used in Paper II.

7.2.4 Vapour Deposition
To study condensed layers of volatile solvents, vapour is deposited onto a liq-
uid N\textsubscript{2} cooled substrate to create a thin layer of, in our case, amorphous solid 
water. To maintain the amorphous solid film on the substrate under vacuum 
conditions, the back of the substrate is maintained at a temperature well below 
the solvents freezing point (100 K in our studies). This technique is used in 
Paper IV.

7.3 Synchrotron Radiation
A synchrotron light source produces electromagnetic radiation by forcing elec-
trons of high energy on a curved path in a storage ring. When these elec-
trons are accelerated perpendicularly to their velocity (to maintain a somewhat 
spherical ring structure), the charged particles emit electromagnetic radiation. 
The frequency of this radiation can span the THz to the hard X-Ray regime 
and is commonly used for scientific purposes.
What makes synchrotrons so appealing is they produce tunable broad spectrum 
radiation with high flux, brilliance, and stability. Since the distribution of 
electrons in the storage ring into bunches can be varied, synchrotron radiation 
can either be produced in a semi-continuous manner (multi-bunch) or as a 
pulsed light source, when operated with a single-bunch fill pattern.
The radiation can be produced in bending magnets, or more sophisticated in-
sertion devices, such as wiggles and undulators. In an undulator, which is the 
radiation source used in this thesis, the electrons pass through a periodic array 
of dipole magnets, forcing them into an "oscillation", leading to the emis-
sion of radiation at each turn. Undulator radiation is very intense, several 
orders of magnitude higher than bending magnet radiation, and concentrated 
around narrow energy bands due to interference effects. The frequency of 
the bands can be tuned by changing the magnetic field inside the undulator. 
This is achieved be in- or decreasing the gap between the two arrays of mag-
nets in the undulator. The radiation is then passed through a beamline which 
monochromatises and shapes the radiation beam. It then arrives at the end-
station after passing through the exit slit of the beamline and, if needed, a 
differential pumping stage.
8. Acknowledgements

_Nothing is worth more than laughter._

_It is strength to laugh and to abandon yourself._

_to be light._

- Frida Kahlo

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References


81
36 “van der Waals forces,” in IUPAC Compendium of Chemical Terminology, Research Triagle Park, NC: IUPAC.


60 M.-M. Walz, J. Werner, V. Ekholm, N. L. Prisle, G. Öhrwall, and O. Björneholm,


D. Gao, “Acidities of Water and Methanol in Aqueous Solution and DMSO,”


Johann, ich gehe schlafen.
Machen Sie übermorgen Mittag
Wiederbelebungsversuche.
- Roda Roda
A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)