Free Neutral Clusters and Liquids Studied by Electron Spectroscopy and Lineshape Modeling

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Abstract

The electronic and geometrical structure of free neutral clusters and liquids have been studied using synchrotron-radiation based photoelectron and Auger electron spectroscopy in combination with lineshape modeling. A novel experimental setup has been developed for studies of liquids, based on the liquid microjet technique. Theoretical lineshapes have been computed using both classical (molecular dynamics) and quantum mechanical (mainly density functional theory) methods.

Clusters are finite ensembles of atoms or molecules, ranging in size from a few to several thousand atoms. Apart from being fundamentally interesting, clusters are also promising as building blocks for nano-technology. In this thesis results are presented for rare-gas and molecular clusters, ranging from weakly van-deer-Waals bonded to hydrogen bonded. It is shown that the combination of core-level photoelectron spectroscopy (XPS) and lineshape modeling can be used to estimate the sizes of clusters. A model for treating the effect of inter-molecular nuclear relaxation upon ionization is proposed. The structure of single-component molecular clusters are investigated by molecular dynamics simulations, validated against XPS data. Finally, the radial structure of a two-component molecular cluster is investigated by XPS.

Liquids have been studied for centuries, but still many questions remain regarding the microscopic properties. With the recent development of the liquid microjet technique, new insight into the atomic structure can be obtained. In this thesis we study aqueous solutions using photoelectron and Auger electron spectroscopy (AES). We investigate the structure of surface active molecules by XPS, study the Auger decay after core-level ionization in aqueous potassium chloride (KCl), and follow the changes in molecular structure of glycine as a function of pH.

Keywords: Clusters, Nano-particles, XPS, UPS, AES, Radial structure, Molecular dynamics, Density functional theory, Liquids, Liquid microjet, Solvation

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urn:nbn:se:uu:diva-8652 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-8652)
Wovon man nicht sprechen kann, darüber muß man schweigen.
Tractatus logico-philosophicus, proposition 7
Ludwig Wittgenstein
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals. Reprints were made with permission from the publishers.

I  Size of neutral argon clusters from core-level photoelectron spectroscopy
H. Bergersen, M. Abu-samha, J. Harnes, O. Björnholm, S. Svensson, L. J. Sæthre and K. J. Børve

II  First observation of vibrations in core-level photoelectron spectra of free neutral molecular clusters

III Lineshapes in carbon 1s photoelectron spectra of methanol clusters
M. Abu-samha, K. J. Børve, L. J. Sæthre, G. Öhrwall, H. Bergersen, T. Rander, O. Björnholm and M. Tchaplyguine

IV Two size regimes of methanol clusters produced by adiabatic expansion

V What Can C1s Photoelectron Spectroscopy Tell about Structure and Bonding in Clusters of Methanol and Methyl Chloride?
M. Abu-samha, K. J. Børve, J. Harnes, and H. Bergersen
VI  **Surface tension as driving force for radial structure in mixed molecular clusters**  
H. Bergersen, J. Harnes, M. Abu-samha, M. Winkler, A. Lindblad, L. J. Sæthre, K. J. Børve, and O. Björneholm  
In manuscript

VII  **A photoelectron spectroscopic study of aqueous tetrabutylammonium iodide**  
H. Bergersen, R. R. T. Marinho, W. Pokapanich, A. Lindblad, O. Björneholm, L. J. Sæthre and G. Öhrwall  

VIII  **Auger electron spectroscopy as a probe of the solution of aqueous ions**  
In manuscript

IX  **Photoelectron spectroscopy of aqueous glycine at different pH**  
H. Bergersen, N. Ottosson, K. J. Børve, L. J. Sæthre, O. Björneholm, M. Faubel, G. Öhrwall, and B. Winter  
In manuscript
The following is a list of papers to which I have contributed but that are not included in this Thesis.

**Self-assembled heterogeneous argon/neon core-shell clusters studied by photoelectron spectroscopy**

**Free nanoscale sodium clusters studied by core-level photoelectron spectroscopy**

**Direct observation of the non-supported metal nanoparticle electron density of states by X-ray photoelectron spectroscopy**

**The role of molecular polarity in cluster local structure studied by photoelectron spectroscopy**

**The far from equilibrium structure of argon clusters doped with krypton or xenon**

**Shell-dependent core-level chemical shifts observed in free xenon clusters**
Magnetron-based source of neutral metal vapors for photoelectron spectroscopy

Preferential site occupancy of krypton atoms on free argon-cluster surfaces

Preferential site occupancy observed in co-expanded argon/krypton clusters
M. Lundwall, H. Bergersen, A. Lindblad, G. Öhrwall, M. Tchaplyguine, S. Svensson, and O. Björneholm

Characterisation of weakly excited final states by shakedown spectroscopy of laser excited potassium

Fluorine as a $\pi$ donor. Carbon 1s photoelectron spectroscopy and proton affinities of fluorobenzenes
T. X. Carroll, T. D. Thomas, H. Bergersen, K. J. Børve, and L. J. Sæthre

Ioniclike energy structure of neutral core-excited states in free Kr clusters

Postcollision interaction in noble gas clusters; Observation of differences in surface and bulk line shapes
Final state selection in the 4p photoemission of Rb by combining laser spectroscopy with soft-x-ray photoionization

Femtosecond Interatomic Coulombic Decay in Free Neon Clusters: Large Lifetime Differences between Surface and Bulk
Comments on my own participation

Teamwork is the key to modern experimental science. Even more so in this work, since I have had the opportunity to work with the combination of theory and experiment. My contribution to the papers presented in this thesis has varied, and is generally indicated by my position in the list of authors. In paper I, II, and VII I was responsible for planning and performing the experiments, as well as analyzing data, performing calculations and preparing and finalizing the manuscripts. In paper IV and VI I was responsible for planning and performing the experiments, analyzing data and preparing and finalizing the manuscripts. In paper IX I was responsible for performing calculations and preparing and finalizing the manuscript.
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1. Populärvetenskaplig sammanfattning

Materia finns överallt omkring oss, och människor har säkert i alla tider fun-derat på varför världen ser ut och fungerar som den gör. Varför är träden gröna, och varför är stenar hårdare?


Vätskor är, till skillnad från kluster, ingen exotisk form av materia som måste produceras artificiellt, utan något som vi stöter på i vardagslivet hela tiden. Trots det är många frågor angående vätskors struktur och egenskaper ännu inte helt klarlagda.

Traditionellt har studier av materien fokuserat på egenskaper som man kan se eller känna, s. k. makroskopiska storheter. Under århundradena har mätmetoderna utvecklats så att man vid slutet av artonhundratalet tyckte sig ha en nästan komplet bild av världen. Det var bara det att ju längre in i materiens innersta man tittade, desto sämre stämde den bild man hade skapat sig baserat på makroskopiska storheter.

Problemets ser att i slutändan bestäms ett materials egenskaper av de ingående atomerna, hur de är fördelade i materialet, och framför allt vilken struktur deras elektroner har. Tyvärr är atomerna svåra att studera direkt, eftersom de är så väldigt små. Till viss del består problemet i att våra ögon inte är anpassade för att titta på små föremål (utan snarare för att hitta äpplen och undvika lejon t ex), men dessutom är vanligt ljus inte lämpat att undersöka så små saker. Eftersom synintryck uppstår genom att ljusvägor studsar mot det som skall
observeras, för att sedan detekteras av ögonen, så måste vågorna vara mindre än det föremål som skall observeras, för att ett eko skall uppstå. Jämför hur vattenvågor studeras mot en betongpir och mot ett vasstrå. Därför har elektornernas struktur inte kunnat studeras direkt, utan man har fått nöja sig med att studera de effekter som elektronstrukturen ger upphov till, t ex färgen eller hårdheten hos ett material.

Man kan studera elektronstrukturen direkt om man använder ljus som är tillräckligt kortvägigt, minst 100 ggr kortare våglängd än synligt ljus. Sådant ljus kallas röntgenljus. Röntgenljus finns inte naturligt på jorden, utan det måste skapas artificiellt. Det mest avancerade sättet att skapa röntgenljus är att använda sig av en synkrotron, i vilken elektroner cirklar runt i en ring nära ljushastigheten och sänder ut röntgenstrålning. I den här avhandlingen är de flesta resultaten producerade med hjälp av synkrotronljus från MAX-lab i Lund.


Med fotoelektronspektroskopi kan man undersöka vätskor på ett helt nytt sätt. Nyvunna insikter kan användas för att ge en atomärr förståelse för vätskans egenskaper, men också avslöja hittills okända egenskaper. I denna avhandling har vi studerat tetrabutylammoniumjodid, en molekyl som består av fyra kolkedjearmar, som sitter fast i en kväveatom i mitten. Molekylen är känd för att lägga sig på ytan i en vattenlösning, snarare än i det inre av vattnet. Vi konstaterar i våra experiment att det faktiskt förhåller sig så, men
också att de inte ligger platt på ytan, utan att kolkedjearmarna sticker ner i vattnet. Vi har också undersökt glycin, en molekyl som har väldigt olika struktur i vattenlösning och i gasfas. Strukturen ändras också när man ändrar pH. Vi undersöker förändringarna i struktur när molekyler löses i vatten, och vid förändring av pH, och konstaterar att de stämmer med våra beräkningar.

För kluster handlar det inte bara om att undersöka deras innersta struktur, utan om att alls observera dem, eftersom hela klustren är betydligt mindre än våglängden hos synligt ljus. Spektroskopiska mätningar ger oss information om t. ex. atomernas struktur, vilket är avgörande för att gå vidare och skapa kluster med skräddarsydda egenskaper, som kan bli användbara i olika sammanhang. Den här typen av funktionella nanostrukturer är dock komplicerade system, både att skapa och att undersöka. Trots att fotoelektronspektroskopi är mindre svår analysad än andra spektroskopier, är det, för dessa system, svårt att dra några säkra slutsatser enbart från experimentella data. Därför har vi utvecklat teoretiska modelleringsmetoder, som hjälper oss att tolka experimentella data. Modellering av såpass komplicerade system är dock långt ifrån enkelt, och därför har vi valt att bygga vår modellering stegvis, från enkla system till mer komplicerade. Vi började med ädelgaskluster, fortsatte med en-komponents molekylkluster, för att slutligen ta oss an blandade molekylkluster. Under vägen drog vi slutsatser, inte bara om hur modelleringen skall gå till, utan också om de olika systemen. Till exempel har vi upptäckt att man kan använda fotoelektronspektroskopi till att uppskatta storleken på kluster, och att storleken kan förändra sig drastiskt när man ändrar de experimentella betingelserna. Vi har dragit slutsatser om strukturen hos vätebundna kluster, och slutligen har vi lyckats skapa ett blandat molekylkluster med radiell struktur, ett viktigt delmål på vägen mot funktionella molekylkluster.
2. Introduction

The interaction between atoms and molecules is essential for properties of matter, and for most processes on earth. The difference between the properties of an atom or molecule in the gaseous phase and in the condensed phase is of utmost importance for the way we see the world. As an example, if it wasn’t for the anomalous behavior of water to have a higher density in the liquid phase than in the condensed phase, there would be no protecting ice layer covering the poles of the earth, and the ocean would surely be frozen solid. Still, our understanding of the properties of the interactions that governs the condensed phase is not complete.

On a thermodynamic level, the properties of atoms or molecules in the gas phase and in the solid phase are in many cases well characterized, but the properties of the intermediate phase, liquids, is largely unknown at a microscopic level. This owes in part to the higher complexity of the relatively disordered liquid phase, and in part to experimental limitations.

On a dimensional level, the properties of the single atoms or molecules and of the infinite solid are well characterized, but the intermediated sized systems, clusters, condensed matter consisting of a finite number of atoms or molecules, is often less so. Properties of these systems are often intermediate between single atoms and molecules and the infinite solid, but they can also have properties that differs from both single atoms and molecules and the infinite solid.

From a fundamental point of view, liquids and clusters comprise two frontiers of science where more insight is needed. But they are also complementary in providing a possibility to follow the evolution of the properties of matter, from single atoms or molecules, over the nano-scaled cluster to the liquid phase, which acts as an example of a macroscopic system.

2.1 Clusters

Clusters is an exotic form of matter which bridges the gap between the single atoms or molecules (monomers) and the infinite solid. Apart from being fundamentally interesting, low-dimensional systems are becoming increasingly important in technological applications. The unique properties of nano-objects, and the possibility to tune properties by changing their size, opens for a whole new class of materials, functionalized by nano-structure. One example is electronic devices, where an important way to improve performance
is to reduce the size. One aims eventually towards devices made up of a finite number of atoms, situated on a surface. However, to deposit atoms in the right structure on the surface is very difficult [1]. An alternative is instead to produce structures before they are deposited on the surface. This can be done using clusters as building blocks [2]. Using clusters of semi-conducting elements, atomic scale transistors can be produced [3].

In order to increase the capacity of storage media, there is a constant search for methods to increase the storage density. One approach in this respect is to produce nano-scaled islands with uniform magnetization. This can be achieved by depositing metallic clusters, for which the magnetization can be controlled, onto a surface [4]. However, it has proven difficult for these clusters to maintain the high-energy spin state at realistic temperatures.

As seen from the examples above, most technical applications of clusters use either metallic clusters, e.g. catalytically active metallic clusters deposited on a carrier, or covalently bonded semiconductor clusters, which form the basis for advanced materials with useful magnetic, optical, or electrical structure. Less attention has been paid to molecular clusters, maybe because of their lower stability. Nonetheless, molecular clusters are important in natural processes that involve nucleation and growth, and as a reaction medium, e.g. in atmospheric chemistry.

From an applied point of view, a main problem in constructing functionalized nano-sized materials is not only to construct stable clusters, but also to construct an array of deposited clusters forming a film. The main challenge in this respect is to balance the adhesion between the cluster and the surface and the cohesion of the cluster, and at the same time avoid coalescence. [5, 6, 7] Molecular clusters, as opposed to atomic clusters, provides a chemical tunability in the combination of intermolecular interactions, ranging from weak van-der-Waals forces to strong hydrogen bonds. The flexibility thus provided may be used to balance the adhesive and cohesive energies, and at the same time control coalescence. This approach is inspired by colloidal chemistry, where combinations of molecular species are used to create stable and even crystalline phases. While the micelles in colloidal chemistry are in the micro-meter size regimes, more than three orders of magnitude larger than the nano-sized clusters that we are aiming at, insight from from colloidal chemistry may be very useful to obtain a better understanding of nano-objects. It is especially interesting to observe how micelles obtain their stability through a radial structure, where different species are selected for their bulk and surface properties, respectively. If it would be possible to transfer knowledge from this area into the world of nano-scale clusters, this may give the possibility to produce molecular clusters with enhanced stability, that may be used as building blocks for materials design.

Complex nano-scaled clusters are thus interesting from both a fundamental and an applied point of view. However, these are complicated systems, and the experimental techniques available do not always provide data that are
easy to interpret. This means that it is important to build the analysis on a solid ground. This thesis is part of a larger work to develop computational and experimental techniques, starting from our understanding of single atoms and molecules and gradually developing into more complex systems. To this end we start with rare-gas clusters, continue with single-component molecular clusters and finally arrive at radially structured molecular clusters.

2.1.1 Rare-gas clusters

Of all the kinds of clusters that can be made from gases and liquids, rare-gas clusters are by far the most studied. The first reports on studies of rare-gas clusters were made in the 1970’s and the field is still very active. Rare-gas clusters are the hydrogen atoms of clusters. They do not have a lot of fancy applications, but they are easy to produce, chemically inert, and the bonding mechanism is simple. Developing theoretical models for rare-gas clusters is a first step towards understanding more complex clusters.

Neutral rare-gas clusters are held together by van-der-Waals forces. These forces have their origin in electron density fluctuations on one of the atoms, that give rise to an electric dipole. This dipole induces dipoles on the other atoms in the cluster, and this dipole-dipole interaction keeps the cluster together. For an ionized cluster there are also coulombic forces between the ion and the other atoms. The van-der-Waals forces holding neutral clusters together are typically very weak. This means that clusters have to be very cold, so that the thermal energy of the atoms does not dissociate the cluster.

2.1.2 Molecular clusters

Molecular clusters have in common that they are composed of molecules. In interaction strength they range from weakly van-der-Waals bonded clusters (e.g. methane) over dipole-dipole bonded (e.g. methyl chloride) to strong hydrogen bonded clusters (e.g. methanol), and there may even be covalent bonds between molecules in a clusters (e.g. within the NO₂ dimer). Van-der-Waals bonded molecular clusters show, in many aspects, properties similar to rare-gas clusters. For the more strongly bonded molecular clusters there is a directionality in the bonding. This means that both the electronic and the geometric structure of these clusters can be expected to be more complicated. As we will see later, this has implications on how to interpret experiments.

2.2 Liquids and solutions

Liquids are of immense importance for all aspects of life on earth. Despite this, many questions remain regarding the properties and structure of the liquid phase. Not even for the most studied compound on earth, water, has any
consensus been reached about the structure in the liquid phase. The textbook description of the structure states that each water molecule is hydrogen bonded to four other molecules, through two accepting and two donating hydrogen bonds. This view was challenged recently by Wernet et al. [8] who claimed that their results, from a combination of x-ray absorption and theory, suggested that over 80% of the molecules were engaged in only two hydrogen bonds. Later, using the same experimental technique, Smith. et al. obtained results in favor of tetrahedral coordination. [9] Obviously more work is needed here.

Another field of research where more insight is needed is the molecular description of the interplay between solvent and solute molecules. This can be illustrated with the case of alcohol-water solutions. These mixtures, despite their structural simplicity, do now show the thermodynamic properties that one expects from an ideal mixture of the two liquids. In the 1940’s a structure was proposed by Frank and Evans [10], in which a "iceberg-like" structure is formed around the hydrophobic entities. However, these results are not supported by modern studies. [11, 12, 13, 14, 15, 16] Recent molecular dynamics studies show that these molecules do not mix well, but rather form separate hydrogen bonded networks. [17, 18, 19, 20]

In this thesis a few examples are presented of how the elemental specificity in our experimental and theoretical methods can be utilized to obtain insight into liquids and solutions.
3. Experimental aspects

3.1 Electron spectroscopy

Electron spectroscopy is a powerful tool to investigate chemical properties of atoms and molecules, as well as of the condensed phase. Electron spectroscopy comes in different flavors, but in all of them the kinetic energy of electrons being emitted from the investigated sample is measured. The kinetic energy is then related to orbital energies in the sample, which are indicative of the electronic and geometric structure. Information can also be extracted from relative intensities, angular distributions and spin of the photoelectrons.

3.1.1 Photoelectron spectroscopy

Photoelectron spectroscopy is based on the photoelectric effect, which states that matter being irradiated with light may emit electrons. The photoelectric effect was discovered by Hertz in 1887, [21] and explained by Einstein in 1905. [22] The key concept of photoelectron spectroscopy is to ionize an atom or molecule using intense light of well-defined energy, and to measure the kinetic energy of the expelled electron. Then, knowing the energy of the photon and also the kinetic energy of the photoelectron, one can calculate the ionization energy [23]

\[ IE = h\nu - E_{\text{kin}}. \] (3.1)

where \( E_{\text{kin}} \) is the measured kinetic energy if the photoelectron, \( h\nu \) is the photon energy, and \( IE \) is the ionization energy, i.e. the smallest amount of energy required to remove that electron from the material. The principle expressed in the equation above is shown schematically in figure 3.1.

![Figure 3.1: Schematic figure of photoionization](image)

Figure 3.1: Schematic figure of photoionization. A photon with energy \( h\nu \) is used to ionize an atom. The difference between the photon energy and the binding energy of the electron is transferred to kinetic energy of the photoelectron. Figure modified from Ref. [24].
Photoelectron spectroscopy is often divided into ultra-violet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS).

In UPS, a photon is used to ionize a valence electron. Valence electrons are important since they are responsible for the chemical bonding between atoms in a molecule, and hence UPS is used extensively to characterize the bonding in molecules. However, since there may be many valence orbitals in a molecule with spectral overlap, and since ionization of these levels often leads to strong nuclear motion, UPS spectra are often far from trivial to interpret.

In XPS a photon of high energy is used to remove an electron from a core orbital. Core orbitals are, in most cases, localized and atomic-like.

To first order, the ionization energy of a core-level photoelectron depends on from which orbital the electron has been ejected. This can be used to obtain elemental information from XPS. On the next level, electrons emitted from the same type of orbital in different molecules, or from different positions in the same molecule, have different ionization energy. This is known as chemical shifts, since the ionization energy is dependent on the chemical surrounding of the ionized atom. Furthermore the ionization energy can be affected by coupling of spin and orbital momentum in the ionized state, resulting in spin-orbit splitting. The photoelectron peaks may exhibit broadening, which may be due to the probed system itself (e.g. vibrational fine structure and lifetime broadening) or be a result of finite experimental resolution. This will be thoroughly discussed in chapter 4.

XPS is a powerful tool for investigation of clusters since core-level binding energies are sensitive to the local surrounding of the atom being ionized. This means that XPS is, in principle, able to distinguish between atoms in different positions in clusters of different size. In practice however, the number of sites probed in experiments is vast, and the peaks are largely overlapping. However, knowing the structure of a cluster of a certain size makes it possible to construct a theoretical lineshape by calculating the ionization energy for each atom in the cluster. This lineshape can then be compared to experiments. This is an interesting possibility in many respects. For one, it gives a connection between theory and experiment, and confirms our understanding of the ionization process. If the cluster properties probed in experiments can be reproduced by the calculations, it gives credibility to calculated properties that can not readily be experimentally probed. Especially interesting is the possibility to calculate theoretical lineshapes for several cluster sizes, and compare these to experimental spectra to deduce the cluster size in experiments.

3.1.2 Auger electron spectroscopy

When a core electron is emitted from an atom, a highly unstable state is created. This state will decay rapidly, often within femtoseconds, into a more stable state. For shallow core levels the overwhelmingly dominating decay channel is Auger decay. In this process the core hole is filled by an electron
from an outer shell, and the excess energy is removed via emission of a second electron. The kinetic energy of the emitted electron is given by the energy difference of the core-ionized state and the doubly charged final state, and carries information of the orbitals involved in the decay and of their energy.

Often a core-hole can decay via Auger decay involving many different valence electrons, leading to a multitude of final states. These will show up in spectra as different peaks. Traditionally Auger decay has been regarded as a local decay process, meaning that only orbitals belonging to the core-ionized atom or molecule are involved in the decay. However, recently it was shown that also orbitals on neighboring atoms or molecules may be involved in the Auger decay, even for weakly bonded systems. [25, 26] Auger decay involving orbitals from neighboring atoms or molecules may be called non-local Auger decay, in contrast to the local Auger decay that involves orbitals from the same atom or molecule. This is shown schematically in Fig. 3.3. The presence of non-local Auger decay involving orbitals from different chemical species may be used to establish that these species are neighbors in the sample.

### 3.2 Beamline I411

The experimental data presented in this thesis has, with exception of the results of Paper IX, been recorded at beamline I411 at MAX-lab, Lund, Sweden. I411 is a multi-purpose gas phase and non-UHV beamline at the 1.5 GeV ring MAXII. I411 delivers photons in the range 60-1500 eV. However, the flux decreases rapidly with increasing photon energy, and for cluster measurements, where the sample is very dilute, using photon energies above 700 eV is very time consuming. The radiation is, to a very high degree, linearly polarized in the horizontal plane.

The beamline is equipped with an SX700 monochromator. The bandwidth of the radiation can be controlled with the exit slit. The beamline is equipped
Figure 3.3: The Auger decay. One electron fills the core vacancy, and one electron is expelled, carrying the excess energy. The two electrons may originate from the same atom or molecule (left) or neighboring atoms or molecules (right).

with a permanently mounted Scienta R-4000 electron analyzer (see Fig. 3.4). The electrons coming from the ionized sample are accelerated through the electron lens into the electric field from two hemispherical electrodes. The field makes the electrons bend differently depending on their kinetic energy, and by detecting the electron with a position sensitive detector the energy of the photoelectron can be found. By changing the amount of acceleration (or retardation) of the electrons in the electron lens, the resolution can be varied. To first order, the resolution is given by

\[ f_{\text{whm}} = E_p \cdot \frac{s}{2r} \]  

(3.2)

where \( f_{\text{whm}} \) is the full width at half maximum of the Gaussian energy distribution, \( s \) is the width of the entrance slit of the hemisphere, \( r \) is the radius of the center path of the hemisphere and \( E_p \) is the energy of the electrons after acceleration in the lens. \( E_p \) is called the pass energy. The electron analyzer can
be rotated around the direction of the light, to obtain angles between the polarization plane of the radiation and the analyzer from 0° to 90°. This enables recording of spectra in the so-called magic angle at 54.7°, where photoelectron anisotropic effects can be avoided.

The main experimental chamber has large flanges on both sides, perpendicular to both radiation and analyzer, to allow for maximum flexibility in mounting auxiliary equipment.

### 3.3 Cluster production

Clusters can be produced in a large number of ways, depending on the cluster constituents in question, and also on other requirements on the cluster beam, e.g. that the cluster beam should be mono-dispersed, or that a high cluster flux is needed. For the experiments presented in this thesis, clusters were produced by letting gas at high pressure through a narrow nozzle into vacuum. In that process the atoms lose most of their thermal energy and start condensing. The rapid temperature decrease is reached by a large pressure difference through the nozzle, and in some cases, liquid nitrogen cooling of the nozzle. It is also possible to mix the cluster constituent with a light element (usually helium) prior to the expansion. Helium will not condense under these conditions, but it will cool the growing clusters by collision. In this way the degree of condensation can be increased. A schematic illustration of the cluster source is displayed in Fig. 3.5. Gas of high pressure (1-5 bar) is let into the system and

![Figure 3.5: Schematic figure of the cluster source.](image-url)
through the small nozzle, which has a 150 \( \mu \text{m} \) opening. The nozzle is conical to increase the degree of condensation. In the expansion chamber the pressure is typically in the \( 10^{-3} \) mbar range. To reduce the background pressure a skimmer is placed after the nozzle. The skimmer also increases the cluster abundance in the ionization chamber by extracting the cluster rich part of the beam coming from the nozzle, while most of the background gas remains in the expansion chamber and is pumped out by large turbo pumps. The opening diameter of the skimmer is 0.3 mm. In the ionization chamber the cluster beam is hit by the synchrotron radiation and ionization takes place. The expelled electrons are analyzed by the electron analyzer. The pressure in the ionization chamber is typically in the \( 10^{-6} \) mbar range.

This setup can be used to make clusters out of gas phase atoms or molecules. If a heated container is placed upstream of the nozzle, samples can be evaporated, and subsequently expanded through the nozzle to condense into clusters. Hence it is also possible to make clusters out of samples that are liquid at room temperature.

This setup produces clusters with a distribution of sizes, centered around some average size, \( < N > \). By varying the pressure upstream from the nozzle as well as the temperature of the nozzle, clusters of different average size may be produced. With this experimental setup, clusters with average sizes between a few tens and several thousands of atoms can be produced in measurable amounts.

### 3.3.1 The size of clusters

It is far from trivial to measure the size of weakly bonded neutral clusters. A commonly used method is mass spectrometry. However, the reliability can be questioned, since extensive fragmentation may be expected upon ionization, making the measured distribution quite different from the one present in the neutral sample. [27] Often the potential energy surface of an ionized cluster is very different from that of the neutral cluster, which means that the cluster is ionized to high quantum numbers in the inter-atomic (inter-molecular) modes. This means that fragmentation will occur even when very little kinetic energy is transferred to the cluster in the ionization. [28]

Helium scattering is another method available for estimating the size distribution. [29] While applicable to neutral clusters, this method suffers from low resolution in the size range we are interested in. [29] Electron diffraction can be used to determine cluster mean sizes for neutral clusters. [30] This method is limited by the sensitivity of diffraction patterns to the size of the cluster. Rayleigh scattering can be used for absolute size determination of very large clusters. [31] This approach has also been used to determine the relative size of much smaller clusters. [32] Finally the mean size of neutral clusters in a jet can be estimated by leading the jet through a region of low gas pressure and measuring the retardation of the clusters. [33]
In a first approximation, the mean cluster size realized in an adiabatic expansion setup depends only on the stagnation conditions, i.e. the pressure and temperature of the gas prior to expansion, and the nozzle size and shape. After the expansion condensed phase (clusters) and uncondensed phase (atoms or molecules) are in coexistence. Gibb’s phase rule states that when two phases are in coexistence the number of degrees of freedom is reduced by one. In the case of expansion of a single chemical species this means that the pressure and temperature of the gas prior to expansion can be described by a single variable. For rare-gas clusters, Hagena introduced the condensation parameter $\Gamma^*$ to describe the cluster beam. $\Gamma^*$ can be calculated from the relation

$$\Gamma^* = \frac{k \cdot p \cdot d_{eq}^{0.85}}{T^{2.2875}}$$

where $k$ is a gas specific constant, $p$ is the expansion pressure (mbar), $d_{eq}$ is the equivalent nozzle diameter ($\mu$m), and $T$ is the nozzle temperature (K).

$\Gamma^*$ can be related empirically to the mean cluster size realized in experiment. There are several such scaling laws published. For small clusters the most reliable formula is based on helium scattering

$$<N> = 38.4 \cdot \left(\frac{\Gamma^*}{1000}\right)$$

This formula is valid in the range $350 \leq \Gamma^* \leq 1800$, which corresponds to $<N>\approx 6$ to $<N>\approx 90$.

For larger clusters there are several different scaling laws published. Ref. [34] is based on mass spectrometry, but uses a model to account for fragmentation. They give the formula

$$<N> = \exp[-12.83 + 3.51(ln \Gamma^*)^{0.8}]$$

This formula is frequently used among the cluster community, but it should be noted that using the scaling laws of other published works gives quite different cluster sizes (generally larger). It seems that it is difficult to derive reliable scaling laws. One reason for this may be that the condensation may be sensitive to imperfections in the nozzle and skimmer interference. Other reasons for this discrepancy could be limitations in the methods applied in each case, and difficulties in determining the nozzle temperature with accuracy.

It is very difficult to say something conclusive about the shape of the cluster size distribution. The reason for this is that very little is published on the subject. This may be due to that many experimental techniques are only sensitive to the mean of the distribution. However, the log-normal function has been found to describe the distribution of cluster sizes well for a wide range of nanoscale systems. [36, 37] This is also the typical shape of mass spectra of clusters. [34, 28] Published estimates of the width of the cluster size distribution are rare, but Ref. [29] estimates the size distribution of small argon clusters to have a full width at half maximum of $fwhm = <N>/2$. 

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For molecular clusters, a procedure for estimation of the cluster size based on stagnation conditions, similar to that of rare gases, has been proposed. [28] In this case Eq. 3.3 will be different, as well as the expressions relating $\Gamma^*$ and the mean size. Furthermore, unlike for rare-gas clusters, the expression relating $\Gamma^*$ and the mean size will be different for different molecular constituents of the clusters. An important improvement is that in this case, ionization is achieved by doping the cluster with a sodium atom, that is subsequently ionized. That way the ionization causes very little fragmentation.

### 3.4 The liquid jet setup

For several decades, X-ray photoelectron spectroscopy (XPS) has been used extensively to investigate the geometric and electronic structure of molecules, clusters and solids.[38, 39] However, the application of this method to liquids is non-trivial, since the high vapor pressure of many liquids prohibits the photoelectrons from reaching the spectrometer. Furthermore, it is difficult to handle a liquid volume exposed to vacuum, since evaporation tends to either freeze or deplete the sample.

One way of overcoming these problems is to combine a differentially pumped enclosure of the sample and a small, renewable, volume of liquid. In early experimental setups the latter was achieved either by a millimeter-sized jet [40] or by a rotating metal disc submerged in a cup of liquid. [41] As the disc rotates, the liquid will cover the metal surface, and the film can be ionized. Liquid flowing in a shallow groove has also been used. [42] Unfortunately, these methods only allowed studies of liquids with low vapor pressure. In the only published studies of liquid water, large amounts of salt were added, which allowed substantial cooling, to suppress the vapor pressure. [43, 44]

Important improvements were made by Faubel and coworkers, who used a liquid jet setup, where the size of the jet was reduced to the micrometer size range. [45] Such a small source enabled them to record the first photoelectron spectrum of pure liquid water. [46] However, using HeI radiation, only the outer valence region could be probed. This setup has been adapted to synchrotron radiation by Winter and coworkers. They have published several papers on the full valence region of liquid water and aqueous solutions. [47, 48, 49] A comprehensive overview of the field of photoemission from liquids can be found in Ref. [50].

We have developed an experimental setup similar to that of Winter and coworkers, intended for use with the permanent R-4000 spectrometer at beamline I411. The setup consists of a differentially pumped cylinder going through the permanent ionization chamber at I411. The jet is produced inside the cylinder, and there are openings for the synchrotron radiation to enter, and for the photoelectrons to reach the detector. This differential pumping stage separates
the high vacuum required by the spectrometer from the poor vacuum caused by evaporation from the jet. The setup is depicted in Fig. 3.6

Figure 3.6: The experimental setup. The enlargement shows the central part, where the ionization takes place.

Inside the differential pumping stage, the jet is produced by a micrometer-sized glass needle, where liquid of high pressure is pushed into vacuum. In early experiments the high pressure was obtained by pressurizing the liquid with a gas bottle, but the liquid is now pressurized by a high pressure pump. In this way, the liquid container can be kept at low pressure, which simplifies the sample handling.

In case of pressurizing the jet by a gas bottle, the backing pressure is kept constant. In that case, the velocity of the jet can be estimated by the Bernoulli equation:

\[ v = \sqrt{\frac{2P}{\rho}} \]  

(3.6)

where \( v \) is the flow velocity, \( P \) is the backing pressure and \( \rho \) is the density of the liquid. For water, a backing pressure of 50 bar yields a flow velocity of around 70 m/s. When using a pump, one instead operates in a constant flow mode. In that case, the flow velocity is given by mass conservation, such that a flow of 0.4mL/min and a 15 \( \mu \)m nozzle gives a flow velocity of around 37 m/s.

The jet breaks up into droplets at a distance \( L \) from the needle that can be estimated using the relation [51, 52]:

\[ L = 12v \left[ \sqrt{\frac{\rho d^3}{\sigma}} + \frac{3\eta d}{\sigma} \right] \]  

(3.7)
where $\sigma$ is the surface tension, $\eta$ is the viscosity, and $d$ is the diameter. For 50 bar backing pressure and a 10 $\mu$m nozzle diameter, this distance is 5 mm for water.

The jet is ionized shortly after leaving the needle by synchrotron radiation, that enters the differential pumping stage through a 1 mm hole. The position of the needle can be varied, to probe the jet at different times after jet formation. However, to avoid charging effects, it is important to ionize the jet before it breaks up into droplets. The sample must also be conducting. That is not a problem for the ionic systems investigated in this thesis though, since they all contain charge carriers. The emitted photoelectrons leave the differential pumping stage through an exchangeable skimmer, positioned at right angle with respect to both the jet and the synchrotron radiation. The distance from the jet to the skimmer is 2 mm. In the downstream end of the differential pumping stage, the jet is collected by a liquid nitrogen cold trap.

The differential pumping stage is pumped by two 1600 l/s turbomolecular pumps upstream of the ionization point, and a 300 l/s turbomolecular pump downstream of the ionization point. With this pumping capacity, the pressure inside the differential pumping stage, but far away from the jet, is in the $10^{-5}$ mbar range. Close to the jet, the pressure is equal to the vapor pressure of the sample. All pumps are equipped with liquid nitrogen cold traps between the turbo pumps and the fore vacuum pumps.
4. Lineshape modeling

Theoretical lineshape modeling is a very powerful tool to increase the amount of information that can be extracted from XPS spectra. A spectrum pertaining to a certain core-level of a certain element is often far from trivial to interpret, even for a small system. For the condensed phase the situation is even worse, due to the vast number of chemically inequivalent monomers in the system, which lead to a large number of partially overlapping spectral features. By constructing theoretical lineshapes it is possible to separate e.g. the contribution from the surface of a cluster from that of the bulk, or to distinguish chemically inequivalent atoms in a molecule. Generally the lineshape of a certain core-level of a system has many contributions. Below, some of the most important of these contributions are addressed.

4.1 Spin-orbit splitting

When removing one electron with angular momentum greater than zero from a closed shell, the electron with the same orbital momentum but opposite spin is left unpaired. This electron can have its spin and angular momentum either parallel or anti-parallel. These two possibilities will impose different total angular quantum numbers $J$ on the ionized state, and hence different final state energy. This is the case for argon for instance, where the ionization occurs in the $2p$ orbital. In this thesis, however, lineshape modeling will be performed within one spin-orbit component.

4.2 Chemical shift

The ionization energy of an electron in a certain orbital may vary depending on the chemical surrounding of that orbital. This is known as chemical shifts. When comparing ionization energies it is important to distinguish between vertical and adiabatic ionization energies. The vertical ionization energy is the the difference in energy between the ground state and that of the ion with the nuclei frozen in the position of the ground state, whereas the adiabatic energy is the difference in energy between the ground state and the lowest lying eigenstate. The two are connected through the nuclear relaxation upon ionization. For large systems, i.e. clusters and liquids, where the nuclear motion can be very complicated, vertical shifts are advantageous since this approach does
not require detailed knowledge of all nuclear motion involved. The vertical chemical shift, here denoted $\Delta I_{\text{vert}}$, can be divided into initial state effects and final state effects, which may be written [53]

$$\Delta I_{\text{vert}} = \Delta V - \Delta R$$ (4.1)

where initial state effects ($\Delta V$) are related to the electrostatic potential of the ground state. A more positive site of ionization leads to a higher ionization energy. This can be understood from the classical interaction between the outgoing photoelectron and the ion. Initial state effects are the reason why adding electronegative ligands increase the ionization energy of an atom, since these ligands withdraw electrons from the site of ionization, making it positively charged. The final state effects ($\Delta R$) are related to the relaxation of the system after ionization. Due to the short lifetime of the core-hole, only the electronic relaxation will effect the vertical ionization energy. The nuclear relaxation will be manifested in the difference between the vertical and adiabatic ionization energies.

The ionization energy of an atom in a system may be calculated from the total energy difference between the ground state and the core ionized state. Since ionization is a quantum mechanical (QM) process, the ionization energy must, in general, be calculated on a QM level. In practice this means solving the Schrödinger equation by expanding the electronic structure of a system in a basis of atomic-like orbitals.

A problem in QM calculations of shifts is the description of the core-ionized state. Due to the instability of the core-hole, any empty core orbital will quickly be filled in the SCF process. One way of overcoming this is to model the half empty core orbital using an effective core potential (ECP). This way filling of the core hole can be avoided by removal of the explicit treatment of the core hole. The drawback of this method is that no absolute ionization energy is obtained. Often this is a small limitation, since the relative ionization energy, e.g. between two atoms in a molecule, or between a molecule in the gas phase and in the condensed phase, is the essential information.

Even though ionization is a QM process, in certain cases chemical shifts can be calculated using classical methods. If the bonding between monomers in a system is purely electrostatic, i.e. there are no covalent contributions to the bonding, the chemical shift between the same molecule in two different environments is to first order dependent only on the difference in electrostatic environment of the two cases. This can be calculated using classical methods, provided that one uses an accurate description of both permanent and induced electrostatic moments of the molecules involved. The chemical shift is then given by the difference between the inter-molecular electrostatic energy of the core-ionized and neutral states. In practice, one calculates the total energy of both initial and final state, for e.g. a free monomer and a condensed molecule.
The chemical shift is then given by
\[ \Delta I^{\text{vert}} = E_i^c - E_f^c - (E_i^m - E_f^m) \] (4.2)

where \( E \) denotes total energy, \( c \) refer to condensed phase, \( m \) refer to monomer, and \( i \) and \( f \) denote initial and final state, respectively. Generally, the ionization energy of a condensed atom or molecule is lower than that of the free atom or molecule. This effect is caused mainly by final-state polarization screening, but in some cases also by the electrostatic potential from neighboring atoms or molecules. [54, 55, 56]

For rare-gas clusters, the interaction between atoms is governed by dispersion forces. This means that the initial state contribution can be neglected, and that the final state relaxation reduces to interaction between the ionized atom, and the rest of the atoms in the cluster. The latter can be modeled by calculating induced dipoles at all atoms in a cluster, based on an atomic polarizability. [57] Since the charge-induced dipole interaction decreases rapidly with distance, to first approximation, chemical shifts are dependent on the coordination of the ion. This is the cause of two features in the XPS spectrum, one at lower ionization energy, pertaining to ionization of bulk atoms, which have 12 nearest neighbors, and one an higher ionization energy, pertaining to ionization of surface atoms, with fewer nearest neighbors. Generally, such a clear separation can not be seen for molecular clusters, since the distribution of ionization energies within the surface or bulk is much broader.

### 4.2.1 Geometric structure

To be able to calculate ionization energies one needs to establish reliable geometric structures of the system under investigation. For free molecules, the potential energy surface usually exhibit one clear global minimum. If such a minimum exists, that structure can be used to calculate chemical shifts. Owing to the small size of these systems, the optimal structure can be calculated from electronic structure methods. The use of a single structure can be justified for large systems as well, if the sample is believed to be sufficiently ordered. We have used static structures to model spectra of rare-gas clusters (paper I). These atoms have simple, non-directional bonds, and the clusters form while hot, and are slowly cooled by evaporation, resulting in highly ordered cluster structures.

For large hydrogen bonded clusters, the potential energy surfaces are very complicated. In those cases, a global minimum may not only be difficult to find, but that structure alone may not be representative of the actual ensemble probed in the experiment. We have used molecular dynamics (MD) to obtain an ensemble of cluster structures. In practice, a model cluster is first equilibrated using an annealing procedure to remove instabilities. After that, the cluster is propagated for an extended time at constant temperature. At regular intervals, the cluster structure is extracted, and chemical shifts are calculated.
for all molecules in each snapshot. These chemical shifts are then collected in a histogram.

In the case of aqueous solutions, modeling of the solvent-solute can be done on many different levels. In the simplest model, the solvent is represented by a dielectric medium. This has been done in paper VII. This model does allow for final state polarization, but lacks any specific interaction between the solute and the solvent. Furthermore, it is known that using a continuum model, the contribution from the first coordination shell is overestimated. [57] To improve the accuracy, one may include the first solvation shell explicitly, and treat the rest of the solvent on a continuum basis. This has been done in paper IX. This allows for specific interaction between the solute and the solvent. However, these calculations have been based on a single geometric structure. The next level would mean invoking molecular dynamics, to probe the whole configuration space.

4.3 Vibrations

For many years, core-level ionization was believed not to give rise to vibrational excitations, since core orbitals are non-bonding. However, ionization may lead to large electronic relaxation, including contraction of valence orbitals at the ionized atom, transfer of electron density to the ionized atom to delocalize the positive charge, and also polarization of atoms and bonds. The resulting change in molecular geometry leads to vibrational excitations and is well described in terms of the Franck-Condon principle. [58] In core-level spectra of free molecules, vibrational structure was first observed in 1974 [59, 60], for the case for methane.

The vibrational contribution to a spectrum is calculated using the Franck-Condon principle, in which intensities are determined by the similarity between each final vibrational state and the ground vibrational state of the initial electronic state.

4.3.1 The Franck-Condon principle

The Franck-Condon principle states that an electronic transition occurs within a stationary nuclear framework. This means that when an atom in a molecule is ionized, the electrons readapt to the new situation while the nuclei remain in their original position. Next, once the electrons have settled in their new positions, the nuclei start vibrating about their new equilibrium positions.

The intensities of a transition between the initial vibrational state and a vibrational state for the final electronic state is given by the Golden rule of Fermi. [61]

\[ I \propto |\langle \Psi_f | \vec{\mu} | \Psi_i \rangle|^2 \]  

(4.3)
where the dipole operator is defined as

$$\bar{\mu} = -e \sum_i \vec{r}_i + e \sum_\alpha Z_\alpha \vec{R}_\alpha.$$  \hspace{1cm} (4.4)

Here $i$ are the electrons, and $\alpha$ are the nuclei.

According to the Born-Oppenheimer approximation, the electronic and vibrational wave functions can be separated, and that the electronic part depends parametrically on the positions of the nuclei, $\Psi \cong \Psi_e(\vec{r}, \vec{R}) \Psi_N(\vec{R})$.

Consider the transition dipole moments given by eq. 4.3. It can be expanded as

$$\langle \epsilon' \nu' | \bar{\mu} | \epsilon \nu \rangle =$$

$$\int \Psi^*_{\epsilon'} \Psi_{\nu'} (\bar{\mu}_e + \bar{\mu}_N) \Psi_{\epsilon} \Psi_{\nu} d\tau_e d\tau_N$$

$$= \int \Psi^*_{\nu'} \left\{ \int \Psi^*_{\epsilon'} \bar{\mu}_{\epsilon} \Psi_{\epsilon} d\tau_e \right\} \Psi_{\nu} d\tau_N$$

$$+ \int \Psi^*_{\nu'} \bar{\mu}_N \left\{ \int \Psi^*_{\epsilon'} \Psi_{\epsilon} d\tau_e \right\} \Psi_{\nu} d\tau_N$$

(4.5)

The last term of Eq. 4.5 is zero, because different electronic states are orthogonal. The remaining term is the electric dipole moment at position $\vec{R}$. To a first approximation this is independent of the position of the nuclei, and the integral can be replaced by a constant, that we call $\bar{\mu}_{\epsilon'\epsilon}$. In this case Eq. 4.5 simplifies to

$$\langle \epsilon' \nu' | \bar{\mu} | \epsilon \nu \rangle = \bar{\mu}_{\epsilon'\epsilon} \int \Psi^*_{\nu'} (\vec{R}) \Psi_{\nu} (\vec{R}) d\tau_N$$

$$= \bar{\mu}_{\epsilon'\epsilon} S(\nu', \nu)$$

(4.6)

where

$$S(\nu', \nu) = \int \Psi^*_{\nu'} (\vec{R}) \Psi_{\nu} (\vec{R}) d\tau_N$$

(4.7)

is the overlap between the initial and final vibrational states.

Often many transitions have non-vanishing intensity, and hence a vibrational progression can be seen in spectra. Since the transition dipole moments of Eq. 4.3 are squared, the relative intensities of these lines are given by $|S(\nu', \nu)|^2$. These are called Franck-Condon factors.

To simplify calculations for clusters, the vibrational envelope can be decomposed into independent contributions from nuclear dynamics within a monomer (intra-molecular modes) and nuclear dynamics between monomers (inter-molecular modes). The validity of this model is discussed in Paper II.
4.3.2 Intra-molecular vibrations

The nuclear Schrödinger equation for a molecule may be written

\[
\left[ \sum_A - \frac{\hbar^2}{2m_A} \nabla^2_A + V \right] \Psi_{\text{vib}} = E \Psi_{\text{vib}}. \tag{4.8}
\]

In general, \( V \) is a full matrix, but introducing new coordinates

\[
Q_j = \sum_{r=1}^{3N} L_{rj} M_r^\frac{1}{2} \Delta x_r \tag{4.9}
\]

where \( L \) is a unitary matrix, \( \Delta x_r \) is the cartesian displacement of the \( r \)th atom from equilibrium position, and \( M_r \) is its mass, diagonalizes \( V \), and Eq. 4.8 may be solved for each degree of freedom separately. The \( Q_j \) are called the normal modes of vibration. Furthermore, if the Taylor expansion of \( V \) around the equilibrium positions of the nuclei can be truncated above the second order, the solutions to Eq. 4.8 can be written

\[
\tilde{\Psi}_{\text{vib}}(y_j) = N_{y_j} H_{y_j}(y_j) e^{-\frac{1}{2}y_j^2}, \quad y_j = \left( \frac{\omega_j}{\hbar} \right)^{1/2} Q_j \tag{4.10}
\]

where \( N_{y_j} \) is a constant, \( H_{y_j} \) are the Hermite polynomials, \( \hbar \) is Planck’s constant, and \( \omega_j \) is the vibrational frequency of mode \( j \).

The initial and final state normal coordinates are related by the Duschinsky relation:

\[
\vec{Q}_f = \vec{J} \vec{Q}_i + \vec{K} \tag{4.11}
\]

If the off-diagonal elements of \( \vec{J} \) can be neglected, the problem is greatly simplified. In that case the intensity for transition to a specific final state is given by a product of one dimensional Franck-Condon factors [62].

4.3.3 Inter-molecular vibrations

In clusters, the effect of vibrations on XPS spectra may conceivably become very complicated, due to the large number of vibrational degrees of freedom. However, the force constants of intra-molecular modes are, for the systems we study, typically much larger than those of inter-molecular modes. This can be used to decompose the vibrational spectrum into contributions from intra- and intermolecular modes, respectively. The intra-molecular modes are assumed to be similar to that of a free monomer, while the inter-molecular part can be treated in the Gaussian limit of the linear coupling approximation. In this model vibrations are assumed to give rise to a Gaussian distribution, with a full width at half maximum (fwhm) given by:

\[
\Gamma = 2\ln(2) \sqrt{\sum_i \left( \frac{\partial E}{\partial Q_i} \right)^2 \gamma_i^{-1}} \tag{4.12}
\]
where $E$ is the final state energy, $Q_i$ are the normal coordinates of the ground state, and $\gamma_i$ are given by $\gamma_i = \frac{\omega_i}{\hbar}$, where $\omega_i$ is the vibrational frequency of normal mode $i$. [54]

### 4.4 Inelastic scattering

Not all electrons emitted from the interior of a condensed medium reach the surface unperturbed. Some electrons collide with atoms and lose energy. The signal loss due to inelastic scattering as electrons travel through the medium is often modeled by an exponential decay, $e^{-x/\lambda}$, where $x$ is the distance from the emitting atom to the surface and $\lambda$ is known as the electron attenuation length. $\lambda$ is dependent on the kinetic energy of the outgoing electron, and material specific, although it has proven similar for many materials. At high kinetic energy (hundreds of eV) $\lambda$ is relatively long, and increasing with kinetic energy. At low energy (a few eV) $\lambda$ is long, but varies strongly and irregularly with energy. Somewhere between 20-100 eV $\lambda$ has a minimum.

The inelastic scattering can be used to obtain depth profiles of a sample. By recording XPS spectra using two different photon energies, the photoelectrons will have different kinetic energy, and hence different surface sensitivity. Often one spectra is recorded with kinetic energies close to the minimum in $\lambda$, and one is recorded at higher energy. In that case the bulk will be enhanced in the latter spectrum, compared to the former.

The inelastic scattering is also a complication in constructing theoretical lineshapes in XPS. In this thesis we include the effect of inelastic scattering in the lineshape modeling of rare-gas clusters by assuming an exponential signal attenuation and averaging over all emission angles. Since $\lambda$ is not known for rare-gases, we use several different values of lambda, and compare the calculated lineshapes to experiments.

### 4.5 Line broadening

#### 4.5.1 Lifetime broadening

When an atom is core ionized, i.e. one electron is removed from an inner shell, a very unstable system is produced. As discussed in section 3.1.2, the core hole has a very short lifetime, typically in the order of a few femtoseconds. This short lifetime of the state results in an energy uncertainty. If the average lifetime of the core-hole is $\tau$, the energy uncertainty is [23]

$$\Delta E = \frac{\hbar}{\tau}. \quad (4.13)$$

This uncertainty introduces a broadening to core-level spectra. The form of the broadening is known as a Lorentzian lineshape. For atoms with a core hole
lifetime in the femtosecond region, the lifetime broadening is tens to hundreds of meV.

### 4.5.2 Post-Collision Interaction

When an atom or molecule is core-ionized, a photoelectron is emitted. This electron will travel in the electric field of the $+e$ charge of the ion. After some time the core-hole will decay by emitting a second (Auger) electron. If the energy of the photoelectron is lower than that of the Auger electron, the Auger electron will overtake the photoelectron at some point. This means that the photoelectron will suddenly find itself in the electric field of the doubly charged ion, and will be retarded. The lower the kinetic energy of the photoelectron the earlier the photoelectron will be overtaken by the Auger electron, on average. This interaction results in an asymmetry of the photoelectron lines towards higher binding energy (lower kinetic energy). For atoms and free molecules, Post-Collision interaction (PCI) is well accounted for using the formalism of Ref. [63]. Recent studies of rare-gas clusters show that cluster lines may be less affected by PCI than free monomers, due to the electrostatic screening of the ionized states. [64]

### 4.5.3 Experimental broadening

The experimental broadening arises from the finite precision in the experiment. The main contributions to the experimental broadening comes from the uncertainties in the photon energy and in the kinetic energy of the photoelectron.

The energy bandwidth of the photons is controlled by the monochromator. It is placed before the experimental chamber, and allows only photons of certain wavelengths to pass on to the experimental chamber. Since the recorded binding energy is the difference between the photon energy and the measured kinetic energy, it is very important to have a small bandwidth in photon energy. On the other hand, since photons from the undulator have a rather broad distribution, the intensity drops rapidly with increasing resolution.

In the spectrometer the resolution can be controlled by changing the pass energy and the width of the entrance slit. Also in this case, a better resolution results in a lower intensity.

In most cases the experimental broadening gives rise to a *Gaussian distribution*. Usually one chooses the broadening to be in the same order of magnitude as the lifetime broadening.
5. Results

The results will be discussed in two steps. First we will present the results for clusters (paper I-VI), and after that the results for liquids (paper VII-IX).

5.1 Clusters

5.1.1 Rare-gas clusters

Rare-gas clusters are the simplest of all clusters. The bonding is non-directional, the structures are well known, and the monomer is well characterized. This make rare-gas clusters a good starting point when developing theoretical methods.

As stated in Chapter 3.3.1, measuring the size of neutral rare-gas clusters is far from trivial. Several methods have been employed, all with different problems. This has motivated us to develop yet another approach: By constructing theoretical lineshapes for clusters of different size, and comparing them to experiments, it should be possible to estimate the size distribution realized in experiments.

To be able to construct a lineshape for a cluster of a certain size, one must first obtain a reliable cluster structure. Rare-gas clusters have weak, non-directional bonds. When creating clusters by adiabatic expansion, the clusters form while quite hot (close to the boiling point), and slowly cool by evaporation until they reach the point where the remaining kinetic energy of the cluster don’t allow further evaporation. This leads to well ordered cluster structures, and justifies the use of crystalline structures from literature. In this size regime clusters are believed to be icosahedral. Unfortunately, the icosahedral structure only tells us the structure for cluster sizes that corresponds to closed geometric shells. For open shell structures we expect some distribution of single atoms or groups of atoms, islands, on an icosahedral core. Finding the actual distribution of the surface atoms is non-trivial. Limiting cases are all atoms collected in one island, favored by energy considerations, or all atoms evenly spread, favored by entropy. To estimate the importance of different surface distributions we have used equilibrium thermodynamics. By assigning an energy and a degeneracy to each distribution of a certain number of surface atoms on an icosahedral core, we calculate the contribution of that specific surface distribution to the ensemble observed in experiments. The results show that for typical cluster temperatures ($\sim 40K$) the distribution corresponding to
all surface atoms in a single island is strongly dominating. Below, only these structures are considered.

The lineshape of a cluster of a certain size is constructed by calculating chemical shifts for ionization of all atoms in the cluster, relative to the free atom. These chemical shifts are collected in a histogram. Inelastic scattering is included by assuming an exponential signal attenuation as the photoelectron travels through the cluster. As the attenuation length $\lambda$ is largely unknown, we have tried several different values of $\lambda$. Our results for Ar clusters show that $\lambda$ needs to be larger than 10 Å to afford a good fit to experiments. The lineshape was subsequently convoluted by a lineshape function that accounts for the natural linewidth (118 meV for Ar 2p) and post-collision interaction (PCI) between the photoelectron and the Auger electron emitted in the deexcitation of the core-hole state. Finally this was convoluted by a Gaussian distribution, to account for finite experimental resolution, as well as vibrational broadening. The latter was calculated using the Gaussian limit of the linear coupling approximation. The vibrational broadening is found to be small in all cases, and more important for the surface than the bulk. Lineshapes corresponding to all relevant cluster sizes has been constructed according to the recipe above, and compared to experimental data. The model spectra have been fitted to the experiments using a least-squares technique. To model the size distribution, we have used a log-normal distribution, as well as a normal distribution and a Poisson distribution. The results show that our calculated lineshapes reproduce the main features of the experimental data. Furthermore, the results show that clusters are larger than expected from stagnation conditions. The resulting fits are not strongly dependent on the choice of size distribution function. Figure 5.1 shows an example of a fit of calculated lineshapes to experiments.

Figure 5.1: Experimental Ar2p3/2 photoelectron spectrum where stagnation conditions corresponds to $N(\Gamma^\ast) = 60$ fitted with calculated lineshapes, assuming $\lambda = 15$ Å and log-normal-distributed sizes. The best fit is obtained at $<N> = 200$. The binding energy is given relative to that of the atom.

to all relevant cluster sizes has been constructed according to the recipe above, and compared to experimental data. The model spectra have been fitted to the experiments using a least-squares technique. To model the size distribution, we have used a log-normal distribution, as well as a normal distribution and a Poisson distribution. The results show that our calculated lineshapes reproduce the main features of the experimental data. Furthermore, the results show that clusters are larger than expected from stagnation conditions. The resulting fits are not strongly dependent on the choice of size distribution function. Figure 5.1 shows an example of a fit of calculated lineshapes to experiments.
5.1.2 From atomic to molecular monomers

When going from atomic to molecular cluster an additional complication has to be considered: the possibility of exciting strong intra-molecular vibration upon ionization. For free molecules the vibrational fine structure is well described within the Franck-Condon principle (section 4.3.1). For clusters, the vibrational structure can conceivably become very complicated, due to the large number of vibrational degrees of freedom, and also due to the presence of both intra-molecular and inter-molecular modes. While presenting a potential complication in calculations, it also raises the question of to what extent the vibrational structure of a molecule is quenched in a cluster surrounding. However, the force constants of intra-molecular modes are typically much larger than those of inter-molecular modes. This has been used to decompose the vibrational structure into independent contributions from intra- and inter-molecular modes, respectively. The intra-molecular part is assumed to be identical to that of the free monomer, while the inter-molecular is simplified to line broadening, according to the Gaussian limit of the linear coupling approximation. This approach can be justified from theoretical considerations, but due to the large widths of many molecular cluster XPS spectra, which in turn can be explained by the broad distribution of ionization potentials within the cluster, it has been difficult to prove experimentally.

In Paper II, the vibrational fine structure of methane ($CH_4$) clusters has been investigated. Methane is a favorable case when searching for vibrations in cluster XPS, due to the large vibrational excitations in the monomer, and also the weak bonding between the monomers in the clusters. Methane is a highly symmetric molecule, the highest non-vanishing electric moment is a small octopole. This means that the molecule is essentially van-der-Waals bonded. From this one expects narrow cluster linewidths.

Figure 5.2 shows the C 1s XPS of methane clusters. The spectra were fitted by theoretical lineshape models based on the Franck-Condon envelope calculated for the free monomer, adopted from Ref. [65]. Three identical Franck-Condon envelopes were used, one to represent uncondensed gas, and two to represent monomers in a cluster, corresponding to ionization at the surface and in the bulk of the cluster, respectively. The latter two were fitted using a free Gaussian width, to include a distribution of ionization potentials as well as the effect of inter-molecular vibrations.

Figure 5.2 clearly shows, that using the monomer lineshape with an increased Gaussian width affords an excellent fit to the experimental spectra, including the shoulder due to vibrationally excited molecules at the surface. From this we conclude that the vibrational spectrum can be well described by performing a full Franck-Condon analysis of the monomer and treating all intermolecular vibrations within the Gaussian limit of the linear-coupling approximation. [66, 67]
Figure 5.2: Experimental C 1s photoelectron spectra of cluster beams of methane, corresponding to two different values of backing pressure. The spectra were recorded at a photon energy of 350 eV. The upper spectrum corresponds to higher pressure (2.5 bar) and presumably larger clusters than does the lower spectrum (1.2 bar). In both cases, experimental data points are shown as circles and lines are used to represent fitting models. The thin solid line at higher ionization energy represents uncondensed methane molecules; the dotted line represents methane molecules in the surface layer of a cluster; the dashed line represents methane molecules in the bulk (interior) of a cluster; and a thicker solid line shows the full model spectrum.

5.1.3 Hydrogen bonded clusters

Hydrogen bonded systems differ from van-der-Waals bonded systems in the bonding pattern. Hydrogen bonds are not only stronger than dispersion forces, but they also exhibit a strong directionality in the bonding. This is clearly manifested in core-level spectra. Figure 5.3 shows the C 1s spectra of methane and methanol ($CH_3OH$), respectively. As stated above, the spectrum pertaining to methane clusters exhibits resolved surface and bulk features, as well as a shoulder pertaining to vibrationally excited molecules at the surface. Methanol clusters on the other hand, displays a single, broad, and featureless peak. In methane, much information could be extracted from very simple analysis. In methanol, additional information is clearly needed to draw conclusions about the clusters, providing yet another reason for developing theoretical modeling.

We have used a modeling approach based on the methods used for argon clusters. Chemical shifts are calculated based on differences in the electro-
static environment of a free monomer and a monomer in a cluster. However, since in methanol the electrostatic potential varies also within a neutral cluster, initial state contributions to the chemical shift must be included. Furthermore, unlike van-der-Waals bonded clusters, the structure of hydrogen bonded clusters may conceivably be very complicated and vary both in time and between clusters of the same size. To obtain cluster structures we have used molecular dynamics (MD), to propagate clusters in time. At regular time intervals, the ionization energies of all molecules in the cluster are calculated, relative to that of a free monomer. These ionization energies are collected into a histogram. This histogram is then convoluted with the Franck-Condon envelope of the monomer as well as a Gaussian broadening to account for the intermolecular broadening. Finally, the finite lifetime of the core-hole, the effect of Post-collision interaction and the finite experimental resolution are accounted for, as described above for rare-gas clusters.

In Paper III, calculations are presented for clusters containing 101 and 204 methanol molecules, as well as small methanol oligomers (N<6). For the larger clusters, a geometric criterion can be used to divide calculated ionization energies into two parts, corresponding to ionization of molecules in the bulk and surface of the cluster, respectively. Within these components, the calculated lineshape varies only slowly with size, although the ratio between
them increases as cluster size grows, due to the increased abundance of bulk molecules. By varying the relative intensity of the surface and bulk features, lineshapes for clusters with sizes different from 101 or 204 can be constructed. By treating the surface to bulk intensity as a free parameter, a good agreement between calculated lineshapes and experimental data can be obtained. Moreover, by using the obtained surface to bulk ratio, the actual cluster size in experiments can be estimated. Figure 5.4 shows the methanol spectrum of

![Figure 5.4: Experimental C 1s photoelectron spectrum of a cluster beam of methanol (circles) together with calculated lineshapes for the free molecule (solid line), surface (dotted line) and bulk (dashed line). The thick solid line denotes the sum of the lineshapes. Energies are given relative to the free monomer.](image)

gure 5.3 again, but this time together with calculated lineshapes for surface and bulk. The relative intensity of these, obtained from least-squares fitting, corresponds to a cluster size of 280 molecules. This number should be considered as a lower bound though, since inelastic scattering was not included.

Regarding the geometric structure of the clusters, visual inspection reveals that the interior of the clusters are composed mainly by long hydrogen bonded chains, whereas the surface layer displays mainly cyclic structures.

As stated above, core-level spectra are sensitive to the size of clusters. As the size increases, the chemical shifts increase as more monomers contribute to the electrostatic screening. Furthermore, as the cluster size increase, the abundance of bulk monomers (with larger shifts) increase, as discussed above. For many compounds this leads to a slow increase of cluster–to–monomer shift with increasing cluster size. For methanol, the effect of changing stagnation conditions is very dramatic. This has been investigated in Paper IV, by recording spectra corresponding to different stagnation pressures, presumably corresponding to different cluster sizes. Figure 5.5 shows C1s spectra of
methanol recorded under two different stagnation pressures. It can be noted immediately that the spectra are very different. The two spectra in figure 5.5 show extreme cases. For intermediate stagnation pressures, spectra can be best described as a superposition of the cases A and B. To understand the spectra in figure 5.5 we compare them to the calculations described above. Doing this we find that spectrum B is very similar to the spectrum of figure 5.4 above, i.e. consisting of a few hundred molecules. Spectrum A on the other hand displays much smaller shifts. However, these shifts correspond well to the ionization energies calculated for small oligomers. Figure 5.6 shows spectrum A together with calculated ionization energies for oligomers, both linear and cyclic. From Figure 5.6 we note first of all that the calculated energies agree well with the experimental intensity. From this we conclude that the cluster peak is due to ionization of oligomers. Furthermore we note that the difference in ionization energy within one linear oligomer is larger than the width of the experimental spectrum. The distribution of ionization energies is due to the different chemical environments of the molecules in a chain, which either act as H-bond donor or acceptor. Since the contribution from all monomers in a chain should be equal, the large width of calculated shifts leads to the conclusion that the contribution from linear oligomers must be small. Cyclic oligomers, on the other hand, seem to be in better agreement with the experimental feature. Since all monomers in a ring acts both as hydrogen bond acceptor and donator, the intra-oligomer shifts are small, and can easily be accommodated within the experimental peak. That cyclic oligomers
are more stable than linear ones has been suggested earlier, and can easily be understood by noting that cyclic oligomers offer one additional hydrogen bond, compared to a linear oligomer of the same size.

As discussed above, XPS spectra of molecular clusters are often broad and featureless. This raises the question of to which extent the intermolecular bonding is manifested in XPS. To investigate this, we have, in Paper V, compared clusters composed of two molecules: methanol and methyl chloride ($\text{CH}_3\text{Cl}$). These molecules show many similarities. They are isoelectronic and have similar dipole moments: 1.70 D for methanol and 1.87 D for methyl chloride. The main discrepancy is that while both molecules engage in dipole-dipole interactions, only methanol is capable of forming hydrogen bonds. Their C 1s XPS spectra are shown in figure 5.7. At a first glance the spectra of figure 5.7 are very similar. The gas phase peaks at high ionization energy both show a similar vibrational progression due to excitation of the C-H stretching mode. The peaks corresponding to ionization of molecules in the clusters are broad and featureless. The cluster–to–monomer shifts are similar: 1.10 eV for methanol and 1.08 eV for methyl chloride. However, the cluster peak pertaining to methanol is considerably broader than that of methyl chloride (1.25 eV and 0.84 eV respectively). In our analysis we will concentrate on two questions: why is the cluster peak of methanol broader than that of methyl chloride, and why are the cluster-to-monomer shifts almost the same, despite the polarizability of methyl chloride being more than 35% larger than that of methanol,
and the density of liquid methyl chloride being almost 30% higher than that of methanol. *A priori* it cannot be ruled out that the spectral observations are caused by differences in size distribution between the two species. To avoid that, we start by discussing the results of the theoretical modeling, where the sizes can be precisely controlled.

We have performed simulations of both methanol and methyl chloride clusters containing around 200 molecules each, using the methods described above. The calculated chemical shifts are displayed in the upper part of figure 5.8. Theory predicts, in agreement with experiments, that the cluster peak of methanol is significantly broader than that of methyl chloride. Regarding the chemical shift, the modeling predicts the shift in methyl chloride to be 0.11 eV smaller than what is observed experimentally. This can be explained by the density of liquid methyl chloride in the simulations being somewhat underestimated. Correcting for that, the calculated shift is in agreement (within estimated error bars) to the experiments. Having established an agreement between theory and experiments, we move on to discuss the molecular origin of the observed spectra.

It is useful to decompose the chemical shifts into contributions from permanent multipole ($\Delta M$) and polarization ($\Delta P$) interactions. This has been done for both species in the lower part of figure 5.8. Starting with methyl chlo-
ride, we find that the contribution from permanent multipoles is small, and hence the chemical shift is dominated by polarization. The polarization shows the bulk-surface resolution seen for rare-gases (where final state polarization is the only contribution), but the distribution of permanent multipoles masks this resolution. Turning to methanol, we find that the polarization contribution to the shifts is smaller than for methyl chloride, as we would expect from the lower polarizability and density. On the other hand, the permanent multipole interaction gives a larger net contribution. This is the reason why the observed shifts are so similar. Furthermore, the permanent multipoles is also the source of the larger width in methanol. The larger contribution from permanent multipoles can be understood by recognizing that in the condensed phase, methanol forms shorter and stronger bonds than does methyl chloride. Hence, in summary, both chemical shifts and widths carry information on the different bonding mechanisms of the two systems, hydrogen bonding and dipole-dipole interaction.

5.1.4 Mixed molecular clusters

Having thoroughly investigated several one-component clusters we are now ready to take on mixed clusters. As discussed in section 2.1, radially structured mixed molecular clusters are promising in the construction of nano-structured materials. In Paper VI, we have produced clusters by expanding a mixture of chloroform and methanol into vacuum. The recorded C 1s photoelectron spectrum is shown in figure 5.9 (center), together with the spectra recorded after expansion of pure chloroform or methanol (top and bottom).

The first step in the analysis is to ensure that the clusters are indeed mixed. This is done by comparing the cluster-to-monomer shift for methanol in figure 5.8: Distributions of chemical shifts for methyl chloride and methanol, and their contribution from permanent multipoles ($\Delta M$) and polarization ($\Delta P$), respectively.
Figure 5.9: Experimental C 1s photoelectron spectra of clusters produced from (a) pure chloroform, (b) a mixture of chloroform and methanol, and (c) pure methanol. Vertical bars indicate the center of gravity of the monomer (M) and cluster (C) features, and the numbers denote the monomer-to-cluster shifts.

5.9 b to the spectra in figure 5.5. In Paper IV it was found that methanol cluster spectra can be characterized into three categories: spectra similar to case A of 5.5, similar to case B of 5.5, or a superposition of the two. The shift observed in figure 5.9 b correspond to the latter case, but without the bimodal distribution that we expect from a pure cluster. From that we conclude that clusters are indeed mixed.

Having established that clusters are mixed, we move on to discuss the radial structure of the clusters. This is investigated by means of depth profiling. Spectra were recorded for two photon energies: 330 eV and 440 eV, allowing around 35 eV or 145 eV kinetic energy of the photoelectrons. The results show that in the latter case, the intensity of the chloroform feature is enhanced relative to that of methanol. Since a higher kinetic energy allows us to probe deeper into the bulk, we conclude that chloroform is enriched in the bulk, and methanol is enriched at the surface.

For rare-gases it is known, that mixed clusters produced by co-expansion are formed with the species with higher cohesive energy enriched in the bulk. In the present case, the heat of vaporization is larger for methanol than for chloroform, which would suggest methanol to be enriched in the bulk, contrary to what is observed. However, the free energy of a cluster may be decomposed into bulk and surface contributions. In the case of rare-gases, both terms are minimized by having the most polarizable component in the bulk. For methanol-chloroform clusters, the bulk contribution is favored by having
methanol in the bulk. However, since the surface tension of methanol is lower than that of chloroform, the surface contribution is favored by having chloroform in the bulk. The results from the depth profiling suggest that the surface term is dominating the free energy in this size regime.

The lower surface tension of methanol compared to chloroform can be explained by the different bonding patterns of the two components. The surface tension is a measure of the loss of binding energy of a molecule at the surface compared to the bulk. For chloroform, dominated by dipole-dipole interaction, the binding energy is proportional to the coordination. For methanol on the other hand, it is known that molecules at the surface retain a high degree of hydrogen bonding by orienting their hydroxyl groups inwards, thereby maintaining a larger fraction of their bulk binding energy.

5.2 Liquids

As stated in the introduction, the use of core-level electron spectroscopy to obtain atomic insight into liquid systems, in particular water and aqueous solutions, has recently been enabled by experimental breakthroughs. In this thesis a few examples of such insight are presented.

5.2.1 Surface activity

Surface active molecules, also known as surfactants, are molecules that tend to the surface when dissolved in water. In Paper VII, we have studied aqueous tetrabutylammonium iodide (TBAI), a classical example of a surface active molecule, where the surface activity is due to hydrophobic interaction between the butyl groups and the surrounding water.

Figure 5.10 shows the C1s photoelectron spectrum of 0.04 m TBAI in water. The spectrum exhibits a peak at around 290 eV and a shoulder at higher

![Figure 5.10: (Color online) The C 1s photoelectron spectrum of aqueous TBAI obtained with 330 eV photon energy.](image-url)
ionization energy. Intuitively one would expect the carbon bonded to nitrogen to have higher ionization energy than the other carbons. From that we would expect peak 1 to be due to ionization of that carbon and peak 2 to be due to ionization of the alkane-like carbons. Consistently peak 2 is larger than peak 1. However, the relative intensity of the two peaks do not correspond to the stoichiometric ratio of three to one. To investigate whether this is a scattering effect, we have recorded spectra using higher photon energies. Indeed, as the kinetic energy of the photoelectrons increase, the relative intensities approaches the stoichiometric value, albeit slowly. We record ratios of 1.66, 2.06, and 2.22 for 40, 65, and 150 eV kinetic energy. Since the intensity of the alkane-like carbons is in all cases lower than what we would expect, we conclude that the molecule is oriented at the surface with the butyl arms sticking into the liquid. This may sound counterintuitive since the butyl arms are hydrophobic, but the tendency of arms sticking into the liquid has been found also in molecular dynamics simulations of aqueous TBAI, reported in Ref. [49]. It was also found that the tendency of arms sticking into the liquid decreases with decreasing TBAI concentration. To investigate this, we have recorded a spectrum of a 0.02 m TBAI solution, and find that the peak ratio indeed increase with decreasing concentration, consistent with a decrease in the tendency of sticking into the liquid (peak ratios 2.38 and 2.06, respectively).

5.2.2 Auger electron spectroscopy as a probe of aqueous solutions

Auger electron spectroscopy (AES) is a powerful tool for investigation of properties of the condensed phase. In Paper VIII this method is applied to a liquid system, aqueous potassium chloride (KCl). KCl is an ionic salt, where both ions have the closed shell electronic configuration of argon. KCl has been previously studied in the gas phase, and it was found that after 2p ionization, both potassium and chloride decay into localized $3p^{-2}$ states, split into several multiplets. For potassium, there is also a weaker feature at higher kinetic energy. No corresponding feature was found after Cl 2p ionization.

The K and Cl 2p AES spectra of aqueous KCl are shown in figure 5.11. Starting with K 2p AES (to the left in figure 5.11), we find that the spectrum is similar to that of solid KCl, but not as well resolved as that of gas phase KCl. For a free ion, we expect the lowest lying states to have two holes in the $3p$ shell, giving rise to $1S$, $1D$, and $3P$ states. Assuming the same states for an aqueous ion, we obtain a good fit to the experimental data. Furthermore, at 15-20 eV higher kinetic energy, relative to the main peak, we find additional intensity. Higher kinetic energy means lower final state energy, and we suspect this intensity to be due to delocalized final states, as these typically have lower final state energy due to smaller Coulomb repulsion between the final state vacancies. In gas phase KCl a similar high energy feature was found, at
around 20-25 eV above the main peak, and was assigned to K 3p\(^{-1}\) Cl 3p\(^{-1}\) delocalized final states.

To investigate this, calculations have been performed of the KCl molecule and of KCl(H\(_2\)O\(_{1-3}\) clusters. For the K\(^+\) Auger spectrum, the calculations show that the assignment of the main peak above is essentially correct. Furthermore, the calculations reproduce the delocalized final states reported for gas phase KCl. It can also be seen, that when water is added to the system, the delocalized states involving K and Cl start decreasing, and new features, somewhat closer to the main line, appear. These states correspond to final states with vacancies on K and water, respectively. These features fit well to the experimentally observed delocalized features. From this we conclude that the delocalized final states are indeed caused by final states delocalized over K and the surrounding water molecules.

Turning to Cl 2p AES (to the right in figure 5.11), we note that the spectrum is less resolved than the corresponding solid phase spectrum. This is partly due to the greater variation in chemical surrounding of atoms in the liquid. However, a simple estimate of where delocalized final states involving Cl and water would end up suggests that these states would spectrally overlap with the main peak. The reason for this is that there is no Coulomb repulsion between the vacancies in either localized or delocalized final states, since the initial state is negatively charged. Turning to the calculations, there are a number of states, both localized and delocalized, spectrally overlapping, and there is also considerable mixing between these. For that reason we restrain from curve fitting in the Cl case.
5.2.3 Monitoring structural changes as a function of pH

Some molecules have very different structure in the aqueous phase depending on pH. One example of this is glycine. An XPS study of aqueous glycine is presented in Paper IX. Glycine is the smallest amino acid, and consists of an amine group and a carboxylic group linked by a methylene group. When dissolved in neutral water (pH=7) a proton is transferred from the carboxylic group to the amine group. We have recorded N 1s and C 1s XPS spectra of aqueous glycine at neutral pH. The spectra are displayed in the middle of figure 5.12. The N 1s spectrum shows a single peak, corresponding to the (protonated) ammonium nitrogen. The C 1s spectrum shows two peaks, one at higher ionization energy, corresponding to ionization of the (deprotonated) carboxylate group, and one at lower energy, corresponding to ionization of the methylene group. Increasing pH to 13 results in a large chemical shift of the N 1s peak towards lower ionization energy. This shift is consistent with the molecules being in the anionic form at high pH. The large shift is a manifestation of the transfer from the charged ammonium group to the neutral amine group. In the carbon spectrum, the shifts are in the same direction but smaller than for N 1s, and smaller for the carboxylate than for the methylene carbon, corresponding to increasing distance to the site of deprotonation. If pH is instead decreased to 1, the N 1s peak shift to somewhat higher ion-

\begin{figure}
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\includegraphics[width=\textwidth]{figure5.12.png}
\caption{N1s (left) and C 1s (right) photoelectron spectra of aqueous glycine, recorded for three different pH, pH 1 (top), pH 7 (middle) and pH 13 (bottom). Circles represent experimental data points, and the solid lines represent the fit. Shifts are given relative to the zwitterionic form.}
\end{figure}
ization energy relative to the zwitterionic form. This shift is consistent with the molecules being in the cationic form, where both end are protonated. The observed shift is due to the protonation of the carboxylate group. Naturally, in this case the carbon atoms show larger shifts. The shift at the carboxylic carbon is smaller than the shift in N 1s ionization energy upon protonation of the amine group, and we explain this by the larger spatial distribution of the carboxylate charge, compared to the ammonium charge. The shift in the methylene carbon is similar to that upon protonation of the amine group.

To support the conclusions, first-principle calculations have been performed for gas phase and aqueous zwitterionic glycine. In order to obtain accurate ionization energies, a combination of methods have been used. By performing several calculations and sum the results, we manage to calculate ionization energies that take into account electron correlation, explicit core-hole treatment and non-equilibrium pcm.

For the zwitterionic structure dissolved in a continuum, we find that the calculated ionization energies are too high by 0.8 eV for the ammonium end, and too low by 0.7 eV for the carboxylate end. The different signs of the errors leads to the conclusion that these are connected to the specific hydrogen bonding to the solvent, since these ends are exclusively H-bond donating and accepting, respectively. From this we conclude that to improve the accuracy, it is important to include the first solvation shell explicitly.

We have used a model where 7 water molecules are explicitly included, 3 accepting hydrogen bonds from the ammonium group, and 4 donating hydrogen bonds to the carboxylate group. Using this structure, the calculated ionization energies are too low by 0.47 eV, 0.46 eV and 0.58 eV for the nitrogen, carboxylate and methylene carbon, respectively. Apparently, including the first solvation shell explicitly improves the calculation considerably. Still, and error of around 0.5 eV remains for all of the core-levels. It has been reported previously that using continuum models overestimate the final state polarization. [57] However, since the sites of ionization are so differently screened by explicit waters, it is unlikely that such an effect would render errors so uniform. One explanation would be that there is a systematic error in the experiments, either in the gas phase or aqueous case. Finally, it is possible that the errors originates in the use of not fully representative solvation structures. To improve on that, one would need to calculate shifts for many structures, generated e.g. by Molecular Dynamics.
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